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Variational localized-site cluster expansions. IX. Many-body valence-bond theory

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A cluster-expansion approach to constructing valence-bond wave functions is described, such that calculations even on many-body systems are possible. In addition, the valence-bond idea of electron pairing is extended to site pairing, or site coupling, even though the sites may involve many electrons and be of a higher spin multiplicity.

I. INTRODUCTION

Valence-bond (VB) theory for molecular electronic structure was developed in the first decade of quantum mechanics by Heitler, London, Rumer, Slater, Van Vleck, Pauling, and many others. The theory was immediately noted to be physically and intuitively appealing because of its explicit treatment of electron correlation in a manner closely related[1] to classical chemical concepts, and particularly those of Lewis involving electron pairs. For computational purposes linearly independent VB bases were identified[2] and matrix-element evaluation schemes were developed.[3-5] Still VB calculations have largely been confined to smaller systems, with fewer than a couple dozen electrons. Despite this lack of a general many-body VB theory, it is known[6] that VB wave functions differ qualitatively from and are sometimes much superior to those of molecular-orbital or band theory. Indeed, VB theory explicitly includes local correlations and spin pairings between electrons (or sites). As such VB theory should be preferable in application to the narrow-band organic semiconductors of recent interest and in general to molecular crystals of paramagnetic species.

Here, in Sec. II, we present a VB approach for singlet spin states, which may even be of the many-body variety. It is based upon a recent[7,8] localized-site cluster expansion for electronic wave functions. This new cluster VB approach is related to other[9,10] recent spin-symmetry adapted cluster expansions, but there are differences in that the present approach employs: (i) localized *sites*, which may be molecules in a larger aggregate or solid; component atoms in a molecule or solid, or localized electron pairs (or groups or shells) in an atom or molecule; (ii) a molecular graph, connecting more strongly "bonded" sites, to aid in introducing and characterizing VB structures; and (iii) matrix-element evaluation techniques introduced in earlier work[7,8] for more conventional localized-site cluster-expanded wave functions.

Further differences appear in Sec. III where we consider VB wave functions constructed from "covalent" structures only. There the overall system singlets are expressed in terms of *spin-pairing* schemes, i.e., schemes in which different pairs of sites are coupled to singlets. When dealing with certain site spin multiplicities "island counting" methods become of utility in the matrix-element evaluation. Theorems extending previous spin-pairing and island-counting techniques are proven in the Appendixes A and B. Calculations on some model (infinite) systems are illustrated in the following paper; these calculations we believe to be the first many-body VB calculations.

II. SINGLET VB CLUSTER ANSATZ

We consider a system of localized sites, and with each site i we associate *site states* r_i, each of a pure spin multiplicity. One site state g_i is termed the site "ground state," and our cluster VB wave function will be constructed from a (antisymmetrized) product

$$|\Phi\rangle \equiv |1g_1 \times 2g_2 \times 3g_3 \times \cdots \times Ng_N\rangle. \tag{2.1}$$

When the total of the site-ground-state spins is an integer (i.e., when the total electron number is even), the overall system ground state is frequently a singlet, at least for the common nonrelativistic spin-independent Hamiltonians. Indeed for systems of weakly interacting sites with the physically favored[11] antiferromagnetically signed exchange coupling there are[12] some theorems to the effect. Hence, we shall here deal with an overall singlet ground state. Further we shall refer to an overall system *molecular graph* Γ with sites identified as vertices of Γ and near-neighbor (bonded) pairs of sites identified as edges of Γ; we presume Γ is a connected graph.

Our cluster VB *ansatz* now is

$$\begin{gathered} |\Psi_\Gamma\rangle \equiv \mathcal{U}_s(e^{T^+})|\Phi\rangle, \\ T^+ \equiv \sum_{\gamma}^{\Gamma(\mathrm{con})} T^+_\gamma . \end{gathered} \tag{2.2}$$

Here the γ sum is over connected subgraphs of Γ, and the excitation operators T_γ^+ (which are further elaborated upon in a later paragraph) are required to couple the sites in γ to a singlet. The script $\mathcal{U}$ indicates only the *unlinked* portion of e^{T^+} is to be retained, i.e., any term in the Taylor-series expansion of $\exp\sum_\gamma T_\gamma^+$ involving two (or more) excitation operations, T_γ^+ and $T_{\gamma'}^+$ say, with γ and γ' having one (or more) sites in common is to be discarded. Further the subscript s on the script $\mathcal{U}$ indicates excitation of a site is required if the corresponding site ground state is not a singlet, i.e., all terms involving a site in a nonsinglet ground state are to be deleted. Clearly the *ansatz* $|\Psi_\Gamma\rangle$ is a linear combination of products of singlets and hence is overall a (pure) singlet.

For a system with no singlet sites, $|\Psi_\Gamma\rangle$ would involve "excitations" on every site. As a simple example, which also illustrates some of our notation, let us consider four doublet sites in a cycle, with the graph Γ such that $1\sim 2\sim 3\sim 4\sim 1$, where "$\sim$" indicates "bonding" between a pair of sites: restricting the T^+ expansion to just two-site terms, we have

$$T^+ = T_{12}^+ + T_{23}^+ + T_{34}^+ + T_{41}^+, \tag{2.3}$$

the unlinked portion of e^{T^+} is

$$\mathcal{U}(e^{T^+}) = 1 + T_{12}^+ + T_{23}^+ + T_{34}^+ + T_{41}^+ + T_{12}^+T_{34}^+ + T_{23}^+T_{14}^+, \tag{2.4}$$

and

$$\mathcal{U}_S(e^{T^+}) = T_{12}^+T_{34}^+ + T_{23}^+T_{14}^+. \tag{2.5}$$

The two surviving terms of (2.5) suggest a correspondence to the two classical Kekulé structures. In fact the two-site *ansatz* for a $s=\frac{1}{2}$ Heisenberg model does involve (exactly) all the Kekulé structures on Γ. Typically our truncated cluster *ansatz* of (2.2) can be described as a VB wave function because spin-couplings (and correlations) occur only between near-neighbor localized sites. If T^+ is not truncated it can still be described as a VB *ansatz*, because the spin couplings would still be so organized that the terms with near-neighbor spin couplings would appear separately (at an "earlier" point in the expansion).

We can express the excitation operators T_γ^+ in a formal way if we introduce[7,8] site-creation operators: $A_{i\rho_i s_i m_i}^+$ (from the site vacuum) creates on site i the site state $\rho_i s_i m_i$ with spin multiplicity $2s_i+1$ and z component of spin m_i. Complementary to these site-state creation operators we also introduce annihilation operators $\tilde{A}_{i\rho_i s_i m_i}$ annihilating the corresponding site states from the biorthogonal[8] set of site states. Then T_γ^+ can be written in the form

$$T_\gamma^+ = \sum_{s(\gamma)} \sum_{\rho(\gamma)} x_{\rho(\gamma)s(\gamma)c} \sum_{m(\gamma)} (s(\gamma)m(\gamma)\,|\,cs(\gamma);00) \times \prod_i^{\in\gamma} A_{i\rho_i s_i m_i}^+ \prod_j^{\in\gamma} \tilde{A}_{jg_i}, \tag{2.6}$$

where $s(\gamma)$, $\rho(\gamma)$, and $m(\gamma)$ denote (ordered) sets of s_i, ρ_i, and m_i for the sites in γ. Here the $(s(\gamma)m(\gamma)\,|\,cs(\gamma);SM)$ denote Clebsch-Gordan (or vector coupling) coefficients for coupling together spins $s(\gamma)$ to an overall spin S with z component M; c labels the particular coupling scheme chosen. These Clebsch-Gordan coefficients can be expressed in a diagrammatic form[13] and used[10,14] in evaluating few-site-linked matrix elements which arise in the overall matrix-element analysis. In Sec. III here, however, we follow a different approach, which further emphasizes the relation to classical VB theory.

The most general (untruncated) form of (2.2) constrains the form of the wave function only in that it be a (pure) singlet. Hence any singlet can be so expressed. In practice, however, T^+ will generally be truncated, with only rather small connected subgraphs γ included and only a restricted space of site-states employed; hence $|\Psi_\Gamma\rangle$ will in practice be constrained, but in a physically reasonable manner.[7,15] Further because of the cluster form of our *ansatz*, previously described[7,8] methods of matrix-element evaluation apply.

III. COVALENT STRUCTURES ONLY

In this section we consider the case when for each site there are just $2s_i+1$ site states, all $2s_i+1$ belonging to a single-spin multiplet. Thus each site state is identified just by its z component m_i of spin. Further, we note that

$$|\Psi_\Gamma\rangle = \mathcal{U}_s(e^{T^+})\,|\Phi\rangle = \mathcal{A}[\,|\Phi^{SF}\rangle \otimes \mathcal{U}_s(e^{\hat{T}^+})\,|\Phi^\sigma\rangle], \tag{3.1}$$

where $\mathcal{A}$ is an antisymmetrizer, $|\Phi^{SF}\rangle$ is the ordinary product of the spin-free site states, $\hat{T}^+$ acts only on spin space, and $|\Phi^\sigma\rangle$ is a product of spin kets. We choose

$$|\Phi^\sigma\rangle \equiv \prod_i^{\in\Gamma} \varphi_i^{s_i\bar{s}_i}, \tag{3.2}$$

where $\varphi_i^{s_i m_i}$ is a standard (normalized) spin ket for site i with z component m_i. Then, in order to obtain $\hat{T}^+$ from T^+, each term $A_{im_i}^+\tilde{A}_{ig_i}$ of T^+ may simply be replaced by $\mu(s_i,m_i)(s_i^+)^{s_i+m_i}$, where s_i^+ is the usual spin-raising operator for site i and

$$\begin{aligned}\varphi_i^{s_i m_i} &= \mu(s_i,m_i)(s_i^+)^{s_i+m_i}\varphi_i^{s_i\bar{s}_i}, \\ \mu(s_i,m_i) &\equiv [(s_i-m_i)!/(2s_i)!\,(s_i+m_i)!\,]^{1/2}.\end{aligned} \tag{3.3}$$

Matrix elements over an operator, say H, can be

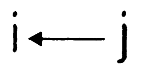

FIG. 1. Diagram representing the two-site singlet spin pairing operator $\hat{T}^{+}_{ij}$ for $s=\frac{1}{2}$ sites.

obtained entirely in spin space if one uses

$$|\Psi^{\sigma}_{\Gamma}\rangle \equiv \mathcal{U}_{s}(e^{\hat{T}^{+}})\,|\Phi^{\sigma}\rangle, \tag{3.4}$$

and the apppropriate effective spin-space Hamiltonian and overlap operators $\mathcal{H}$ and $\mathcal{S}$,

$$\begin{aligned} \mathcal{H} &\equiv \langle \Phi^{\mathrm{SF}}|H\mathcal{a}^{2}|\Phi^{\mathrm{SF}}\rangle^{\mathrm{SF}}, \\ \mathcal{S} &\equiv \langle \Phi^{\mathrm{SF}}|\mathcal{a}^{2}|\Phi^{\mathrm{SF}}\rangle^{\mathrm{ST}}, \end{aligned} \tag{3.5}$$

where the integrations here in (3.5) are just over spin-free coordinates. Because H is spin free and $\mathcal{a}$ (and $\mathcal{a}^2$ also) is a linear combination of permutations $P^{\mathrm{SF}} \otimes P^{\sigma}$, with P^{SF} and P^{σ} acting on spin-free and spin spaces, the spin-space operators of (3.5) are seen to be linear combinations of permutations in spin space. Hence a critical aspect of working with the VB *ansatz* is the evaluation of spin-space matrix elements

$$\langle \Psi^{\sigma}_{\Gamma}|P^{\sigma}|\Psi^{\sigma}_{\Gamma}\rangle / \langle \Psi^{\sigma}_{\Gamma}|\Psi^{\sigma}_{\Gamma}\rangle. \tag{3.6}$$

The cluster wave functions Ψ^{σ}_{Γ} can be expanded as described in earlier work[7,8] to express these system matrix elements in terms of residual overlap ratios and linked few-site matrix elements.

For the site-spin-$\frac{1}{2}$ case, i.e., where all sites are doublets, we can employ the Rumer basis in constructing $\hat{T}^{+}$ and the $\hat{T}^{+}_{\gamma}$. The excitation operators $\hat{T}^{+}_{\gamma}$ must involve an even number of sites, and the two and four-site ones are of the form

$$\begin{aligned} \hat{T}^{+}_{ij} &= x_{ij}(s^{+}_{i} - s^{+}_{j}), \\ \hat{T}^{+}_{ij\cdot kl} &= x_{ij\cdot kl}(s^{+}_{i} - s^{+}_{j})(s^{+}_{k} - s^{+}_{l}) \\ &\quad + x_{il\cdot jk}(x^{+}_{i} - s^{+}_{l})(s^{+}_{k} - s^{+}_{j}), \end{aligned} \tag{3.7}$$

where sites i,j,k,l form a connected subgraph of Γ. The conventional[2] diagrammatic representation of the singlet spin-paired wave functions which result from applying this T^{+}_{γ} of (3.7), to $|\Phi^{\sigma}\rangle$ are given in Figs. 1 and 2. In general a linearly independent set of singlet spin-pairing diagrams are[2] those without crossing bonds when the sites are located as points around the periphery of a circle.

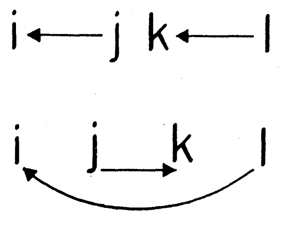

FIG. 2. Two diagrams representing the two linearly independent spin pairings for $s=\frac{1}{2}$ sites. These two diagrams are represented in $\hat{T}^{+}_{ij\cdot kl}$.

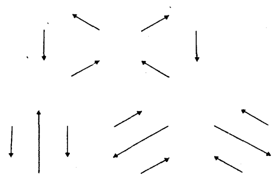

FIG. 3. Five diagrams without crossing bonds. They represent five linearly independent six-site pairings for $s=\frac{1}{2}$ sites.

Thus, for 6 sites the five diagrams of Fig. 3 result.

For the site-spin-1 case, i.e., when all sites are triplets, a very similar type of VB basis can be used if the number of sites is even. The critical point, shown in Appendix A, is that any possible singlet for $2n$ sites is obtainable as a linear combination of singlet spin-pairing schemes (including those with crossing bonds). Thus only excitation operators involving an even number of sites need be considered. The two- and four-site excitation operators may then be expressed as

$$\begin{aligned} \hat{T}^{+}_{ij} &= x_{ij}\Lambda_{ij}, \\ \hat{T}^{+}_{ijkl} &= x_{ij\cdot kl}\Lambda_{ij}\Lambda_{kl} \\ &\quad + x_{ik\circ jl}\Lambda_{ik}\Lambda_{jl} + x_{il\circ jk}\Lambda_{il}\Lambda_{jk}, \end{aligned} \tag{3.8}$$

where Λ_{ij} pairs sites i and j to a singlet

$$\Lambda_{ij} \equiv \tfrac{1}{2}\left[(s^{+}_{i})^{2} - s^{+}_{i}s^{+}_{j} + (s^{+}_{j})^{2}\right]. \tag{3.9}$$

Further, we may associate the diagrams of Figs. 4 and 5 with the spin functions obtained on applying these excitation operators to $|\Phi^{\sigma}\rangle$.

For higher site spins such singlet pairing schemes generally do *not* exhaust all possible overall singlet couplings. This is readily noted since for four sites, each of spin s, the number of singlet couplings is $2s+1$ while the number of singlet pairing schemes is simply 3. Of course, even if a system consists of spin s sites, with $s \geqslant \frac{3}{2}$, one could still construct constrained VB cluster *ansätze* incorporating only the singlet-pairing schemes.

When using these singlet-pairing schemes a diagrammatic approach to evaluating (linked) few-site matrix elements is available. In this approach a matrix element $\langle A|B\rangle$ between two spin pairing structures A and B is represented by the *superposition* diagram obtained by superposing the two Rumer-type diagrams for A and B. For $\langle A|\vec{s}_{i}\cdot\vec{s}_{j}|B\rangle$ we also add a squiggly line between sites i and j. Here we shall choose the spin pairings between sites i and j to be effected by

FIG. 4. Diagram representing the singlet spin pairing for two $s=1$ sites.

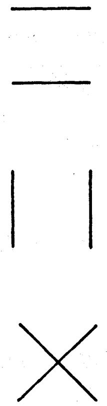

FIG. 5. Three diagrams representing three linearly independent spin pairings for four $s=1$ sites.

$$\sum_{m=-s}^{+s}(-1)^{s-m}\varphi_i^{sm}\varphi_j^{s\bar{m}}\,, \tag{3.10}$$

a function normalized to $2s+1$. Then, as shown in Appendix B,

$$\langle A\,|B\rangle=(-1)^{2sn_{AB}}(2s+1)^{I_{AB}}, \tag{3.11}$$

where I_{AB} is the number of *islands*, i.e., connected pieces, in the superposition diagram, and n_{AB} is the number of arrow reversals required so that every site in the diagram has either two incoming arrows or two exiting arrows. Also, we have

$$\langle A\,|\vec{s}_i\cdot\vec{s}_j\,|B\rangle=f_{ij}^{AB}\langle A\,|B\rangle, \tag{3.12}$$

where the *deletion* factor f_{ij}^{AB} is, as shown in Appendix B,

$$f_{ij}^{AB}=\begin{cases}0, & i \text{ and } j \text{ in different islands}\\ \pm s(s+1), & i \text{ and } j \text{ in the same island.}\end{cases}$$

When i and j occur in the same island, the sign of the deletion factor is (+) or (−) as the number of "bonds" traversed in going from i to j is even or odd. The three simplest types of diagrams applying to the three cases of (3.13) are shown in Fig. 6. On specializing to $s=\frac{1}{2}$ all these overlap and matrix element formulas are already well known.[3]

Finally, keeping track of phases (associated with the arrows in the diagram) is often very simple. As seen from (3.11) the phases are always +1 if s is an integer, and arrows may be deleted from the diagrams. For $s=\frac{1}{2}$, the phases in (3.11) can still be eliminated if Γ is bipartite, i.e., composed of α and β sites with no bonds between like sites; for if we choose the arrow directions in our basic vectors to always be from α to β, then n_{AB} in (3.11) is always zero.

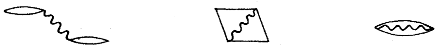

FIG. 6. Three simple superposition diagrams with an interaction line, the first connecting sites in two different islands, the second connecting two sites in the same island an even number of bonds apart, and the third connecting two sites in the same island on odd number of bonds apart.

Hence, for covalent structures conventional spin-pairing schemes are easily extended beyond the usual $s=\frac{1}{2}$ case, and the "classical" superposition diagram techniques are easily utilized in the evaluation[7,8] of matrix elements for the present VB cluster *ansatz*. Further if ionic structures are included in spin-pairing functions as suggested by Choi and Thorson,[6] then much of this section is still directly applicable.

IV. DISCUSSION

In describing intersite interactions, Slater[16] has emphasized that if the orbitals on different sites are orthogonalized, then ionic structures as well as covalent ones are of critical importance, even for qualitatively correct descriptions. Hence, if site states composed from such orthogonalized orbitals are used, then ionic structures should be included in Ψ_Γ and the T_γ^+; whereas, using nonorthogonal orbitals the earlier matrix-element evaluation techniques need to be supplemented by a cluster expansion of the antisymmetrizer. A second solution is to use Heisenberg spin Hamiltonians, where the site states appear (at least formally) to be strongly orthogonal; in this case Slater's criticism is[11,17] bypassed through the use of a "renormalized" exchange interaction.

For large systems another criticism is sometimes voiced concerning the use of covalent structures only (or similarly of Kekulé structures only). This criticism notes that as one increases the number of sites the weight of all ionic structures should be very much greater than the weight of purely covalent structures; this is readily seen, for if the probability of a single site being ionic is $\sim p$, then the probability of no sites being ionic, i.e., the probability of a purely covalent structure, is $\sim(1-p)^N$. Such arguments are, of course, true of virtually all approximate wave functions for large systems. In fact, it is a well-known characteristic of cluster wave functions, such as proposed here, that at least for (extensive) bulk properties the relative error should typically be similar to that for a smaller system.

In conclusion we have proposed a VB cluster *ansatz* which should make possible many-body VB calculations, as illustrated in the following paper. The physical appeal of VB descriptions, especially for localized systems, and their qualitative distinction from conventional molecular orbital and

Green's function descriptions suggests[6] a wide utility of such VB *ansätze*.

APPENDIX A: PAIRING FOR $s = 1$ SITES

To establish our spin-pairing results for spin $s = 1$ sites we view each site as composed of two spin-$\frac{1}{2}$ particles coupled together to form a site triplet. A singlet coupled pair of particles a and b is denoted by

$$[a,b] \equiv \alpha(a)\beta(b) - \beta(a)\alpha(b), \tag{A1}$$

a (unnormalized) triplet projector is denoted by

$$\tau_{ab} \equiv 1 + (ab), \tag{A2}$$

and a spin-paired pair of singlet coupled sites $\bar{a}$ and $\bar{b}$ is, in this Appendix, denoted by

$$\begin{aligned}\{\bar{a},\bar{b}\} = {} & \alpha(a)\alpha(-a) \otimes \beta(b)\beta(-b) \\ & -\tfrac{1}{2}(\tau_{a-a} \otimes \tau_{b-b})\alpha(a)\beta(-a) \otimes \alpha(b)\beta(-b) \\ & + \beta(a)\beta(-a) \otimes \alpha(b)\alpha(-b),\end{aligned} \tag{A3}$$

where a and $-a$ are the particle indices to be associated with site $\bar{a}$. We will make use of the simple results

$$[a,b][c,d] - [a,c][b,d] + [a,d][b,c] = 0, \tag{A4}$$

and

$$\tau_{1\,-1}\tau_{2\,-2}[1,-2][-1,2] = 4\{\bar{1},\bar{2}\}. \tag{A5}$$

Further, we define

$$|\bar{p},\bar{p}+\bar{1},\ldots,\bar{M}\rangle \equiv \left(\prod_{m=p}^{M} \tau_{m\,-m}\right)\left([p,-M]\prod_{l=p}^{M-1}[-l,l+1]\right), M \geqslant p+1\,. \tag{A6}$$

All this notation is useful in our main theorem and in an initial lemma.

Lemma: For a system of N sites

$$|\bar{1},\bar{2},\ldots,\bar{N}\rangle = (-1)^{n+1}2^{n+1} \sum_{P}{}' (-1)^P \bar{P} \prod_{l=1}^{n} \{\bar{2}\bar{l}-\bar{1},\bar{2}\bar{l}\},$$

where $\bar{P}$ is a permutation on the site indices and the sum is over all permutations $P \in \mathcal{S}_N$ such that

$$P(2i-1) < P(2i), \quad i = 1 \text{ to } n,$$

$$P(2i-1) < P(2j+1), \quad 1 \leqslant i < j \leqslant n.$$

Proof: from (A5) we see that the lemma is true for the $n = 1$ case. We now proceed by induction, presuming that the lemma is true for all $n < \frac{1}{2}N$. We first use (A4),

$$\begin{aligned}|\bar{1},\bar{2},\ldots\bar{N}\rangle &= \left(\prod_{m=1}^{N}\tau_{m\,-m}\right)([1,-N][-2,3])[-1,2]\prod_{l=4}^{N}[-(l-1),l] \\ &= \left(\prod_{m=1}^{N}\tau_{m\,-m}\right)\left(([1,-2][-1,2])[-N,3]\prod_{l=4}^{N}[-(l-1),l] - ([1,3][-1,2][-N,2])\prod_{l=4}^{N}[-(l-1),l]\right).\end{aligned}$$

Now, using the definition of (A3) and the fact that $\tau_{a\,-a}\omega_{a\,-a} = \tau_{a\,-a}\omega_{-aa}$ for any ket ω_{a-a} involving indices a and $-a$, we have

$$\begin{aligned}|\bar{1},\bar{2},\ldots,\bar{N}\rangle = {} & -4\{\bar{1},\bar{2}\}|\bar{3},\ldots,\bar{N}\rangle \\ & -(\bar{2},\bar{3},\ldots,\bar{N})|\bar{1},\bar{2},\ldots,\bar{N}\rangle,\end{aligned}$$

where $(\bar{2},\bar{3},\ldots,\bar{N})$ is the site permutation carrying $\bar{2}$ to $\bar{3}$, $\bar{3}$ to $\bar{4},\ldots,$ and $\bar{N}$ to $\bar{2}$. Iteration then yields

$$\begin{aligned}|\bar{1},\bar{2},\ldots,\bar{N}\rangle &= -4\sum_{i=0}^{N-2}(-1)^i(\bar{2},\bar{3},\ldots,\bar{N})^i\{\bar{1},\bar{2}\}|\bar{3},\bar{4},\ldots,\bar{N}\rangle \\ &\quad + (-1)^{N-1}(\bar{2},\bar{3},\ldots,\bar{N})^{N-1}|\bar{1},\bar{2},\ldots,\bar{N}\rangle,\end{aligned}$$

so that, for N even,

$$|\bar{1},\bar{2},\ldots,\bar{N}\rangle = -2\sum_{i=0}^{N-2}(-1)^i(\bar{2},\bar{3},\ldots,\bar{N})^i\{\bar{1},\bar{2}\}|\bar{3},\bar{4},\ldots,\bar{N}\rangle\,.$$

Use of the induction hypothesis then leads directly to the lemma.

Each permutation P in the P sum of this lemma is called a *pairing*; the corresponding term in the P sum, or the corresponding diagram, is called a pairing too. Hence, the P sum of this lemma is over all possible pairings. Next, we give the key theorem of this Appendix.

Theorem: The set of all possible pairings of $2n = N$ triplets spans the space of overall singlet symmetry obtained from the coupling of these $2n$ triplets.

Proof: Still assigning two spin-$\frac{1}{2}$ particles to each site, we see that the $s = \frac{1}{2}$ Rumer theorem implies an overall singlet ket is a linear combination over N-fold products of spin pairings as in (A1). But since the pair of particles on a given site are to be coupled to a site triplet, we see that our overall singlets are in fact linear combinations over terms of the form

$$\prod_{m=1}^{N} \tau_{m-m} \; P[-N,1][-1,2][-2,3]\cdots[-(N-1),N]. \tag{A7}$$

Now, (A7) can be expressed as a product of linked[18] kets, of the form

$$(-1)^{Q}\overline{Q}\left(\prod_{j=1}^{m} \tau_{j-j}\right)[1,-m][-1,2] \times[-2,3]\cdots[-(m-1),m], \tag{A8}$$

where $\overline{Q}$ similarly permutes each member of a particle pair for a site. Now, if m is even, then (A8) is of the form considered in the lemma, so that (A8) is a linear combination of pairings for $s=1$ sites. If m is odd, then there must be some other linked m'-site ket of similar form with m' odd, also. In this case let $\overline{a}$ and $\overline{b}$ be two directly linked sites in the m-site ket and $\overline{a}'$ and $\overline{b}'$ in the m'-site ket, so that the product of these linked m- and m'-site kets involves $[a,b][a',b']$. Then, using (A4), we may replace this product by $[a,a'][b,b']-[a,b'][b,a']$, so that the product of the m- and m'-site kets is expressed as the difference of two $(m+m')$ site kets, each of which is evidently linked. Since all odd cycles may be so paired off yielding just even cycles, the lemma again applies, and (A7) is seen to be a linear combination of site pairing schemes. Hence, the theorem is established.

Finally, we note that the spanning set of this theorem is in fact a basis for $n=1$, 2, and 3 as is seen on computing the dimensions of the relevant singlet spaces and comparing to the number of possible pairing schemes.

APPENDIX B: MATRIX-ELEMENT EVALUATION

In this Appendix we represent the pair functions of (3.10) by $[i,j]$. First we wish to obtain the overlap matrix element formula of (3.11). Since both A and B are assumed to correspond to single (singlet) VB pairing structures, any one of which is composed from a single product of (disjoint) pair functions, we see that $\langle A|B\rangle$ will be a product of (linked) terms each of which is associated with a single island. Thus, we consider the overlap for a single island, such as,

$$\begin{aligned}
&\langle[1,2][3,4]\cdots[L-1,L]\,|\,[2,3]\cdots[L-2,L-1][L,1]\rangle \\
&= \sum_{m_1,\ldots,m_l}\;\sum_{m'_1,\ldots,m'_l} (-1)^{s-m_1+\cdots+s-m_l}(-1)^{s-m'_1+\cdots+s-m'_l}\left\langle \prod_{i=1}^{l} \varphi_{2i-1}^{sm_i}\varphi_{2i}^{s-m_i}\,\middle|\,\prod_{j=1}^{l}\varphi_{2j}^{sm'_j}\varphi_{2j+1}^{s-m'_j}\right\rangle \\
&= \sum_{m_1,\ldots,m_l}\;\sum_{m'_1,\ldots,m'_l} (-1)^{2sl-m_1-m'_1-\cdots-m_l-m'_l}\prod_{i=1}^{l}\left(\langle\varphi_{2i-1}^{sm_i}\,|\,\varphi_{2i-1}^{s-m'_{i-1}}\rangle\langle\varphi_{2i}^{s-m_i}\,|\,\varphi_{2i}^{sm'_i}\rangle\right)=(-1)^{2sl}(2s+1),\quad L=2l\,,
\end{aligned} \tag{B1}$$

and (3.11) follows:

Now, to establish the deletion factor results of (3.12) and (3.13) we first consider the first case of equation (3.13), whence i and j occur in different islands of the superposition diagram for A and B. We choose $i=1$, as we can do upon correctly renumbering the sites, and consider the island involving this site. The matrix elements associated with this island then are the form

$$\langle[1,2][2,3]\cdots[L-1,L]\,|\,s_1^{\mu}\,|\,[2,3]\cdots[L-2,L-1][L,1]\rangle, \tag{B2}$$

where $\mu=+,0,-$. But noting that both the bra and the ket in (B2) are singlets we see that the Wigner-Eckart theorem implies that (B2) must be zero. Then, since $\langle A|\vec{s}_i\cdot\vec{s}_j|B\rangle$ is a linear combination over three products of such matrix elements, the first case of (3.13) is established.

Next, we consider the (−) sign case of (3.12), whence we obtain a single island matrix element of the form

$$\begin{aligned}
&\langle [1,2][3,4]\cdots[L-1,L]|\vec{s}_1\cdot\vec{s}_{2k}|[2,3]\cdots[L-2,L-1][L,1]\rangle \\
&\quad=\sum_{m_1,\ldots,m_l}\ \sum_{m_1',\ldots,m_l'}(-1)^{2sl-m_1-m_1'-\cdots-m_l-m_l'}\prod_i^{\neq 1}\delta_{m_i,-m_{i-1}'}\prod_j^{\neq k}\delta_{m_j,m_j'}\langle\varphi_1^{sm_1}|\vec{s}_1|\varphi_1^{s-m'n}\rangle\cdot\langle\varphi_{2k}^{s-m_k}|\vec{s}_{2k}|\varphi_{2k}^{sm_k'}\rangle \\
&\quad=\sum_{m_1,m_{k+1}}(-1)^{2sl-m_1+m_{k+1}}\langle\varphi_1^{sm_1}|\vec{s}_1|\varphi_1^{sm_{k+1}}\rangle\cdot\langle\varphi_{2k}^{s-m_1}|\vec{s}_{2k}|\varphi_{2k}^{s-m_{k+1}}\rangle \qquad \text{(B3)}\\
&\quad=\langle[1,2k]|\vec{s}_1\cdot\vec{s}_{2k}|[1,2k]\rangle(-1)^{2sl} \\
&\quad=\tfrac{1}{2}\langle[1,2k]|[(\vec{s}_1+\vec{s}_{2k})^2-\vec{s}_1^{\,2}-\vec{s}_{2k}^{\,2}]|[1,2k]\rangle(-1)^{2sl} \\
&\quad=-s(s+1)\langle[1,2k]|[1,2k]\rangle(-1)^{2sl},
\end{aligned}$$

where sites have been appropriately renumbered and $1<k\leqslant l\equiv L/2$.

In a rather similar manner for the (+)sign case of (3.12) we consider

$$\begin{aligned}
&\langle [1,2][3,4]\cdots[L-1,L]|\vec{s}_1\cdot\vec{s}_{2k-1}|[2,3]\cdots[L-2,L-1][L,1]\rangle \\
&\quad=\sum_{m_1,\ldots m_l}\ \sum_{m_1',\ldots,m_l'}(-1)^{2sl-m_1-m_1'-\cdots-m_l-m_l'}\prod_i^{\neq 1,k}\delta_{m_i,-m_{i-1}'}\prod_j\delta_{-m_j,m_j}\ \langle\varphi_1^{s_1m_1}|\vec{s}_1|\varphi_1^{s-m_l'}\rangle\cdot\langle\varphi_{2k-1}^{sm_k}|\vec{s}_{2k-1}|\varphi_{2k-1}^{s-m_k'-1}\rangle \\
&\quad=\sum_{m_1,m_k}(-1)^{2sl}\langle\varphi_1^{sm_1}|\vec{s}_1|\varphi_1^{sm_k}\rangle\cdot\langle\varphi_{2k-1}^{sm_k}|\vec{s}_{2k-1}|\varphi_{2k-1}^{sm_1}\rangle=\sum_{m_1}(-1)^{2sl}\langle\varphi_1^{sm_1}|\vec{s}_1\cdot\vec{s}_1|\varphi_1^{sm_1}\rangle \\
&\quad=+(-1)^{2sl}s(s+1)(2s+1), \qquad \text{(B4)}
\end{aligned}$$

where there is renumbering and $1\leqslant k\leqslant l\equiv\frac{1}{2}L$.

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[18] We term such a ket *linked* if so also is the graph constructed with particle indices as vertices and edges between pairs of particles, say a and b, which are either coupled to a triplet by τ_{ab} or to a singlet in $[a,b]$.