Variational localized-site cluster expansions. II. Trees and near trees

D. J. Klein and M. A. Garcia-Bach

Department of Physics, University of Texas, Austin, Texas 78712
(Received 15 May 1975)

Cluster expanded wavefunctions involving localized-site states and only pair excitations between nearest neighbor sites are considered. In the case that the bonds connecting these nearest neighbor sites form a tree graph (without rings), exact matrix element formulas are obtained in terms of the inverse of a modified type of topological matrix associated with this tree graph. The treatment of some near-tree cases, without any touching rings, is also discussed.

I. INTRODUCTION

In this paper we continue[1] considering the utility of localized sites in cluster expanded wavefunctions. Here we shall explore some of the computationally practicable simplifications that arise on constraining our wavefunction *ansatz* to include only excitations among near neighbor sites. It is, of course, just these excitations which are expected to be most important for the case of weakly interacting localized sites. Even cases which are not extremely localized and/or weakly interacting can sometimes be rather well treated with this approach. In particular, we note that such *ansätze* often bear a relation to classical chemical concepts which also involve electrons typically localized about a single atom (or site) or within a bond between two atoms.

In Sec. II we shall consider localized-site cluster expansions of the form

$$|\Psi\rangle \equiv e^{S^+}|\Phi\rangle$$

$$S^+ \equiv \sum_{i\sim j} S_{ij}^+ \,. \tag{1.1}$$

Here $|\Phi\rangle$ is an antisymmetrized product of site kets, the $i\sim j$ summation is restricted to nearest neighbor pairs of sites, and S_{ij}^+ creates[1] excitations on both sites i and j. If the ground state site kets are chosen optimally, single-site excitations will not mix directly with the "zero-order" configuration $|\Phi\rangle$; hence (just as in the usual case[2] where the sites are taken as spin orbitals) these single excitations might reasonably be neglected, at least in a first approximation. We consider $|\Psi\rangle$ to be in correspondence with a *graph*[3] with vertices and edges corresponding to sites and (nonzero) pair excitations, respectively.

The case when the graph of $|\Psi\rangle$ forms a *tree* (i.e., a graph with no cycles) is found to be especially amenable to treatment. First in Sec. II a set of exact recurrence relations to evaluate matrix elements is obtained. In Secs. III and IV these recurrence relations are related to some simple matrix inversions. Finally, in Sec. V these techniques are generalized to near-tree structures, which include graphs with no "touching rings."

II. MATRIX ELEMENTS FOR TREES

In this section we consider a cluster expanded wavefunction involving only pair excitations in such a manner as to form a tree graph. We wish to apply the formulas of Sec. IV of the preceding article, first to treat the residual overlap ratios

$$f_{i(m)(j(n))} \equiv \frac{\langle\Psi|\Psi\rangle_{(j(n))}}{\langle\Psi|\Psi\rangle_{(i(m)j(n))}} \qquad \{i(m)\}\cap\{j(n)\}=0\,. \tag{2.1}$$

Here we recall a subscripted set of site labels enclosed in parentheses indicates that excitations on these subscripted sites are to be deleted from the quantity to which the subscript is appended; thus, for instance, $\langle\Psi|\Psi\rangle_{(j(n))}$ indicates a (residual) overlap matrix element where no excitations are allowed on sites $j(n)\equiv j_1 j_2\cdots j_n$.

According to formula (4.4) of Paper I,

$$f_{i(m)(i_{m+1}\cdots i_n)} = \langle\Psi|\Psi\rangle_{i(m)} \sum_{\{i(q)\}}^{\supset\{i(n)\}} \mathcal{L}_{i(m)i_{n+1}\cdots i_q}(1_{i(m)}) \frac{1}{f_{i_{n+1}\cdots i_q(i(n))}}\,. \tag{2.2}$$

Here $\mathcal{L}_{i(m)i_{n+1}\cdots i_q}(1_{i(m)})$ is a sum over all linked few-site overlap matrix elements involving sites $i(m)i_{n+1}\cdots i_q$. Since a pair excitation S_{ij}^+ yields excitations on sites i and j both of which are orthogonal to the ground states for these sites, it follows that all the sites $j(m)$ involved in $\mathcal{L}_{j(m)}(1_{j1})$ must be excited on both the bra and ket sides of the few site overlaps. Such linked few-site overlaps might generally be $\langle\Phi|S_{ij}S_{ij}^+|\Phi\rangle$ or $\langle\Phi|S_{ij}S_{kl}S_{ik}^+S_{jl}^+|\Phi\rangle$; however, this second example cannot occur in the present case with a tree structure, because of the cyclic excitation pattern involved. Therefore we see that the only linked overlaps which may presently arise are those involving exactly two sites, and

$$f_{i(m)(i_{m+1}\cdots i_n)} = \langle\Psi|\Psi\rangle_{i(m)} + \sum_{p=1}^{m}\sum_{j_p}^{\sim i_p}{}' \frac{\langle\Phi|S_{i_p j_p}S_{i_p j_p}^+|\Phi\rangle}{f_{j_p(i(n))}} \langle\Psi|\Psi\rangle_{i(m)-i_p}\,. \tag{2.3}$$

Here j_p is to be a nearest neighbor site to i_p (denoted $i_p\sim j_p$), and the prime on the j_p-sum reminds us that it is to be taken only over sites not already deleted (i.e., $j_p\notin\{i(n)\}$).

Once the residual overlaps are obtained, either by direct use of the recurrence relations (2.3) or by one of the methods of Secs. III, IV, or V, the various matrix elements are simply given. For a one-site oper-

ator X_i,

$$\frac{\langle\Psi|X_i|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle\Phi|X_i|\Phi\rangle \frac{1}{f_i} + \sum_k^{\sim i} \langle\Phi|S_{ik}X_iS_{ik}^\dagger|\Phi\rangle \frac{1}{f_{ik}} . \quad (2.4)$$

We have again noted that, in order for the excitations on all sites (except possibly site i) to balance out on the bra- and ket sides, terms with $S_{ij}X_iS_{jk}$, $j\neq k$, give zero because of our noncyclic tree structure. For a two-site operator X_{ij} with i and j nearest neighbor sites, $i\sim j$, we similarly find

$$\frac{\langle\Psi|X_{ij}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \langle\Phi|(1+S_{ij})X_{ij}(1+S_{ij}^\dagger)|\Phi\rangle \frac{1}{f_{ij}} + \sum_k^{\sim i} \langle\Phi|S_{ik}X_{ij}S_{ik}^\dagger|\Phi\rangle \frac{1}{f_{ijk}} + \sum_l^{\sim j} \langle\Phi|S_{jl}X_{ij}S_{jl}^\dagger|\Phi\rangle \frac{1}{f_{ijl}} + \sum_k^{\sim i}\sum_l^{\sim j} \langle\Phi|S_{ik}S_{jl}X_{ij}S_{ik}^\dagger S_{jl}^\dagger|\Phi\rangle \frac{1}{f_{ijkl}} , \quad (2.5)$$

In other cases, such as for two-site interactions between nonneighboring sites or for three-site interactions, tions, the matrix element formulas are also readily given. However, we wish to emphasize that, because of the assumed localized nature of the system Hamiltonian, the most important interactions are already accounted for in (2.4) and (2.5). Further, we wish to note that residual overlap ratios which involve more subscripts, such as f_{ijkl} in (2.5), occur in conjunction with greater numbers of excitations, and hence approximations in the evaluation of such overlap will have relatively negligible effects on over-all matrix elements.

III. TREES AND CONTINUED FRACTIONS

Now recurrence relations for the residual overlaps such as in (2.3) may in general become rather involved if directly used when there are a great number (say > 20) of sites. Thus, in this section and the next we will attempt to cast these recurrence relations into a more tractable form. Actually it is sufficient to study just the set

$$f_{j_n(j(n-1))} = 1 + \sum_k^{\sim j_n}{}' \langle\Phi|S_{j_nk}S_{j_nk}^\dagger|\Phi\rangle \frac{1}{f_{k(j(n))}} \quad (3.1)$$

of recurrence relations, in as much as all other residual overlap ratios are simply obtained from these.

Now Eqs. (3.1) appear to generate some sort of continued fractions, and we seek to treat this system in a manner similar to the matrix approach expounded by Wall.[4] [Although Wall treats a less general class of continued fractions, with the sums in (3.1) restricted to a single term, his approach directly generalizes to our case.] The matrix equation

$$\mathbf{A}\mathbf{x} = \mathbf{y} \quad (3.2)$$

is equivalent to the set of equations

$$\begin{aligned} &a_{j_1j_1}x_{j_1} + \sum_{j_2}^{\neq j_1} a_{j_1j_2}x_{j_2} = y_{j_1} , \\ &a_{j_2j_2}x_{j_2} + a_{j_2j_1}x_{j_1} + \sum_{j_3}^{\neq j_1j_2} a_{j_2j_3}x_{j_3} = y_{j_2} , \\ &a_{j_3j_3}x_{j_3} + a_{j_3j_2}x_{j_2} + \sum_{j_4}^{\neq j_2j_3} a_{j_3j_4}x_{j_4} = y_{j_3} . \\ &\quad\vdots \end{aligned} \quad (3.3)$$

Now, choosing

$$a_{ii} \equiv 1 \text{ and } y_i \equiv \delta_{ij_1} \quad (3.4)$$

we see that the set of equations (3.3) may be transformed to

$$\begin{aligned} &\frac{1}{x_{j_1}} = 1 + \sum_{j_2}^{\neq j_1} (a_{j_1j_2}x_{j_2}/x_{j_1}) , \\ &(a_{j_1j_2}x_{j_2}/x_{j_1}) = -a_{j_2j_1}\Big\{1 + \sum_{j_3}^{\neq j_1j_2} (a_{j_2j_3}x_{j_3}/x_{j_2})\Big\}^{-1} a_{j_1j_2} \\ &(a_{j_2j_3}x_{j_3}/x_{j_2}) = -a_{j_3j_2}\Big\{1 + \sum_{j_4}^{\neq j_2j_3} (a_{j_3j_4}x_{j_4}/x_{j_3})\Big\}^{-1} a_{j_2j_3} \\ &\quad\vdots \end{aligned} \quad (3.5)$$

Further choosing

$$\begin{aligned} a_{ij} &\equiv +\langle\Phi|S_{ij}S_{ij}^\dagger|\Phi\rangle^{1/2} \quad i<j \\ &\equiv -\langle\Phi|S_{ij}S_{ij}^\dagger|\Phi\rangle^{1/2} \quad i>j , \end{aligned} \quad (3.6)$$

we see that the set of Eqs. (3.5) duplicates the set

$$\begin{aligned} &f_{j_1} = 1 + \sum_{j_2}^{\sim j_1}{}' \langle\Phi|S_{j_1j_2}S_{j_1j_2}|\Phi\rangle \frac{1}{f_{j_2(j_1)}} , \\ &\frac{\langle\Phi|S_{j_1j_2}S_{j_1j_2}^\dagger|\Phi\rangle}{f_{j_2(j(1))}} = \langle\Phi|S_{j_1j_2}S_{j_1j_2}|\Phi\rangle \Big\{1 + \sum_{j_3}^{\sim j_2}{}' \frac{\langle\Phi|S_{j_2j_3}S_{j_2j_3}^\dagger|\Phi\rangle}{f_{j_3(j(2))}}\Big\}^{-1} , \\ &\frac{\langle\Phi|S_{j_2j_3}S_{j_2j_3}^\dagger|\Phi\rangle}{f_{j_3(j(2))}} = \langle\Phi|S_{j_2j_3}S_{j_2j_3}^\dagger|\Phi\rangle \Big\{1 + \sum_{j_4}^{\sim j_3}{}' \frac{\langle\Phi|S_{j_3j_4}S_{j_3j_4}^\dagger|\Phi\rangle}{f_{j_4(j(3))}}\Big\}, \\ &\quad\vdots \end{aligned} \quad (3.7)$$

which is obtained from (3.1). Thus

$$f_{j_1} = \frac{1}{x_{j_1}} = \frac{1}{[\mathbf{A}^{-1}\mathbf{y}]_{j_1}} = \frac{1}{[\mathbf{A}^{-1}]_{j_1j_1}} \quad (3.8)$$

and to obtain these "one-site" residual overlap ratios all we need do is compute the diagonal elements of the inverse of $\mathbf{A}$, with matrix elements given by (3.4) and (3.6). In the Appendix, the existence of $\mathbf{A}^{-1}$ is proven

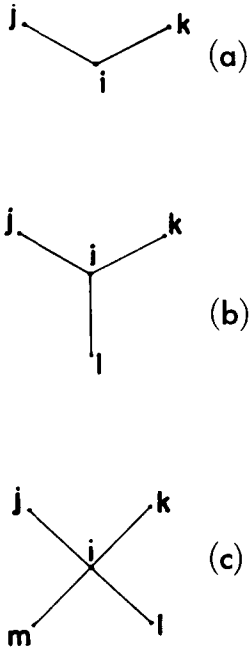

FIG. 1. Portion of the $|\Psi\rangle$ graph illustrating the connections to site i in cases (a), (b), and (c) of the text.

and suggestions made for its computation.

IV. MORE RESIDUAL OVERLAP RATIOS

Having obtained in (3.8) a simple formula for the residual overlap ratios f_j, we next wish to consider other overlap ratios, involving deletions of two or more sites. Clearly, the method of the previous section is applicable to an arbitrary residual overlap $f_{j(i(m))}$, where all one need do is imagine that sites $i(m)$ are not present. Thus, letting $\mathbf{A}_{(i(m))}$ be the matrix obtained from $\mathbf{A}$ by deleting rows and columns $i(m)$, it follows that

$$f_{j(i(m))} = 1/[\mathbf{A}^{-1}_{(i(m))}]_{jj} \,. \tag{4.1}$$

This, of course, follows since a subgraph of a tree is either a tree or a forest[3] of trees. The direct use of (4.1) involves inverting different matrices for each possible set of sites deleted. Thus, in the remaining portion of this section we investigate more economical approaches.

In computing matrix elements the most important residual overlap ratios (i.e., those which occur the latest in the recurrence relations) involve just a few deleted sites, typically close to one another. Hence, we first consider the $f_{i(j)}$ with $i \sim j$, using the equations

$$f_j = 1 + \sum_i^{\sim j} \langle \Phi | S_{ij} S^\dagger_{ij} | \Phi \rangle \frac{1}{f_{i(j)}} \,. \tag{4.2}$$

But these can be recast in terms of $f_{ij} = f_{i(j)} f_j$, which are symmetric in their indices,

$$1 - \frac{1}{f_j} = \sum_i^{\sim j} \langle \Phi | S_{ij} S^\dagger_{ij} | \Phi \rangle \frac{1}{f_{ij}} \,. \tag{4.3}$$

Now we define a *bond* matrix $\mathbf{B}$, with N rows labelled by sites and $N-1$ columns labelled by bonds,

$$\mathbf{B}_{j, i\sim k} \equiv \delta_{ji} + \delta_{jk} \,, \tag{4.4}$$

where $i \sim k$ labels the bond between bonded sites i and k. (There are $N-1$ bonds in a connected tree, as is seen by induction: it is true for $N=1$ and 2, and assuming it is true for $N=M$ we add a single site to the graph introducing a new single bond if we are still to have a connected tree; hence it is true for $N=M+1$ also). Thus,

$$1 - \frac{1}{f_j} = \sum_{i\sim k} \mathbf{B}_{j, i\sim k} \langle \Phi | S_{ik} S^\dagger_{ik} | \Phi \rangle \frac{1}{f_{ik}} \tag{4.5}$$

and

$$f_{ik} = \langle \Phi | S_{ik} S^\dagger_{ik} | \Phi \rangle \left\{ \sum_j [\mathbf{B}^{-1}]_{i\sim k, j} \left(1 - \frac{1}{f_j}\right) \right\}^{-1} \,. \tag{4.6}$$

We note that $\mathbf{B}$ does indeed have an inverse, since the set of Eqs. (4.3) could also be solved for the f_{ik} iteratively starting from the ends of the tree branches. Hence, in order to obtain two-site residual overlap ratios involving nearest neighbor sites, all one need do is invert a universal matrix $\mathbf{B}$ characterized only by the tree structure.

The general manner of deriving (4.6) was to use the residual overlap recurrence relations in the reverse direction to which they were originally intended. In some, but not all, additional cases this idea may be successfully pursued. We thus next consider three-site residual overlaps for three nearest neighbor sites, say i, $j \sim i$ and $k \sim i$, with $j \neq k$. First, if no other site is bonded to the central site i, as in Fig. 1(a), then

$$f_{i(j)} = 1 + \langle \Phi | S_{ik} S^\dagger_{ik} | \Phi \rangle \frac{1}{f_{k(ij)}} \tag{4.7}$$

and this is easily inverted to give $f_{k(ij)}$ (or $f_{ijk} = f_{k(ij)} f_{ij}$ or $f_{j(ik)} = f_{ijk}/f_{ik}$; also $f_{i(jk)} = f_{ijk}/f_{jk} = 1$). Second, if exactly one other site l is bonded to site i, as in Fig. 1(b), then

$$\begin{aligned}
1/f_j &= 1/f_{ij} + \langle \Phi | S_{ik} S^\dagger_{ik} | \Phi \rangle / f_{jik} + \langle \Phi | S_{il} S^\dagger_{il} | \Phi \rangle / f_{jil} \,, \\
1/f_k &= 1/f_{ik} + \langle \Phi | S_{il} S^\dagger_{il} | \Phi \rangle / f_{kil} + \langle \Phi | S_{ij} S^\dagger_{ij} | \Phi \rangle / f_{kij} \,, \\
1/f_l &= 1/f_{il} + \langle \Phi | S_{ij} S^\dagger_{ij} | \Phi \rangle / f_{lij} + \langle \Phi | S_{ik} S^\dagger_{ik} | \Phi \rangle / f_{lik} \,,
\end{aligned} \tag{4.8}$$

and these three equations are easily solved simultaneously for f_{ijk}, f_{ikl}, and f_{ilj}. In a third case, if two other sites are bonded to site i, as in Fig. 1(c), then four such equations are obtained although there are six unknown three-site residual overlap ratios; hence, this case cannot be inverted. Finally, we note that four-site overlap ratios f_{ijkl} may be obtained by inversion of the relevant equations in cases (a) and (b) of Fig. 2, although not so in case (c).

In conclusion, we see that exact results are available for the most important residual overlap ratios. Since the requisite matrix inversions are for an $N \times N$ matrix $\mathbf{A}$, with N the number of sites, this portion of the matrix element calculation would not severely limit the size of the system to which the method could be applied. Any residual overlap ratios that might be needed but are not given by (3.8), (4.6), (4.7), (4.8), etc., should be of only marginal importance in energy evaluation and hence well approximated by a method such as discussed in Sec. V of Paper I.

V. AGGREGATES OF SITES AND NEAR-TREES

Let us group a number of adjacent sites, say $i(m)$, together into an aggregate, say A. Then Eqs. (2.3) for

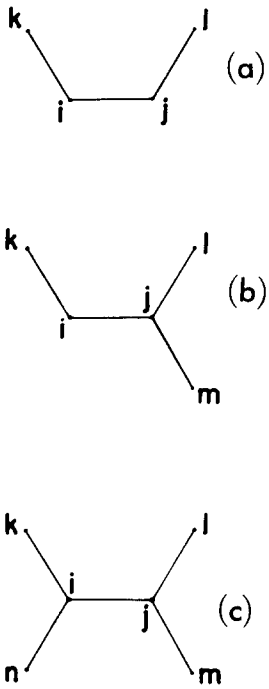

FIG. 2. Portion of the $|\Psi\rangle$ graph illustrating the connections to sites i and j in cases (a), (b), and (c) for the evaluation of the residual overlap ratios, as f_{ijkl}.

a tree imply

$$f_A = \langle\Psi|\Psi\rangle_A + \sum_j^{\sim A} \langle\Psi|\Psi\rangle_{Aj}/f_{j(A)} \tag{5.1}$$

[where the meaning of the symbols is readily understood on replacing A by $i(m)$]. Similarly,

$$f_i = 1 + \sum_J^{\sim i} \frac{\langle\Psi|\Psi\rangle_J}{f_{J(i)}} + \sum_J^{\sim i} \sum_k^{\sim J\prime} \frac{\mathcal{L}_{iJk}(1_J)}{f_{J(i)} f_{k(Ji)}} , \tag{5.2}$$

where J may be either a single site or the aggregate A. Here a "three-site" term $\mathcal{L}_{iAk}(1_A)$ may arise because of the composite structure of A; for instance, if $A = \{j_1, j_2\}$ with $i \sim j_1 \sim j_2 \sim k$, then

$$\mathcal{L}_{iAk}(1_A) = \langle\Phi| S_{ij_1} S_{j_2k} S^\dagger_{ij_1} S^\dagger_{j_2k} |\Phi\rangle \tag{5.3}$$

is generally nonzero. Now, in fact, if we introduce a number of aggregates, but in such a manner that any aggregate of more than one site has only single-site aggregates neighboring it, then we obtain a general set of recurrence relations in terms of aggregates

$$f_{J_n(J(n-1))} = \langle\Psi|\Psi\rangle_{J_n} + \sum_{J_{n+1}}^{\sim J_n\prime} \mathcal{L}_{J_nJ_{n+1}}(1_{J_n})/f_{J_{n+1}(J(n))}$$
$$+ \sum_{J_{n+1}}^{\sim J_n\prime} \sum_{J_{n+2}}^{\sim J_{n+1}\prime} \mathcal{L}_{J_nJ_{n+1}J_{n+2}}(1_{J_{n+1}})/f_{J_{n+1}(J(n))} f_{J_{n+2}(J(n+1))} . \tag{5.4}$$

Here we have a recurrence relation for residual overlaps in terms of few-aggregate (rather than few-site) matrix elements, such as $\langle\Psi|\Psi\rangle_{J_nJ_{n+1}}$.

Now a point of interest is that Eqs. (5.4) still apply even if we allow the many-site aggregates to have rings of sites within an aggregate. That is, regardless of the internal aggregate structure, Eqs. (5.4) still follow for a tree of aggregates, just as Eqs. (3.1) followed for a tree of sites. The restriction that any many-site aggregate have only one-site aggregates adjacent to it just limits the linked terms in (5.4) to involve no more than three aggregates. Thus, if we are able to evaluate the requisite few-aggregate matrix elements (involving not too many sites), even if an aggregate involves a cyclic ring (or path), then over-all systems more general than a tree of sites are amenable to treatment. If we restrict each aggregate to involve no more than a single ring of sites, then the over-all site structures which are allowed include all those with no rings touching one another (i.e., with no common sites).

Since the aggregates still form a tree, the techniques of the previous sections are applicable in only a slightly modified form. For instance, in analogy to the **A** matrix of Sec. III we now define a matrix $\mathbf{A}^{agg}$

$$[\mathbf{A}^{agg}]_{JJ} = \langle\Psi|\Psi\rangle_J ,$$
$$[\mathbf{A}^{agg}]_{IJ} = \pm \left\{ \mathcal{L}_{IJ}(1_I) + \sum_K^{\sim J\prime} \mathcal{L}_{IJK}(1_J)/f_{K(IJ)} \right\} . \tag{5.5}$$

Again the diagonal elements of $\mathbf{A}^{agg}$ identify residual overlap ratios

$$f_J = [(\mathbf{A}^{agg})^{-1}]_{JJ} . \tag{5.6}$$

The only hitch is that to compute the off-diagonal elements of $\mathbf{A}^{agg}$ equation (5.5) can require residual overlaps $f_{K(IJ)}$, which themselves are to be computed from the f_J by methods similar to those described in Sec. IV. A self-consistent procedure suggests itself; further, it should be rapidly convergent since we already believe that we have good approximation schemes for an initial estimate of $f_{K(IJ)}$, and since $\mathcal{L}_{IJK}(1_J)$, which multiplies $1/f_{K(IJ)}$ in $[\mathbf{A}^{agg}]_{JJ}$, involves at least two pair excitations and hence is rather small.

VI. CONCLUSION

We thus see that practical and simple techniques can be found for exactly evaluating matrix elements over localized-site cluster expansions, at least when $|\Psi\rangle$ involves only nearest neighbor pair excitations such that the associated $|\Psi\rangle$ graph forms a tree. The utility of our present techniques is, however, not restricted to trees. These techniques should provide very good approximations for other graphs with low connectivity and only large cycles. Further, the present approach might be generalized. Indeed, we have seen, in Sec. V, how these techniques can be extended to include graphs without fused rings if we are willing to evaluate matrix elements over single rings (typically with rather few sites) through direct use of the recurrence relations of Paper I.

It is of interest to point out that the chemical bond structures of molecules do not usually have an extremely high connectivity, if very many sites (atoms in this case) are involved. Indeed, these structures have bonds restricted to near neighbors, just as in our $|\Psi\rangle$ graph, and often the graphs are planar. Another indication of low connectivity is the "saturation effect" wherein total (and correlation) energies proceed as N for large N, even though the total number of all possible pairs proceeds as N^2. Finally we note that our matrix **A**, or **A** -1, is rather similar in structure to the topological matrix,[5] as is used in Hückel or free-electron theories.

Evidently we might expect our localized-site cluster functions to be related to various chemical concepts, when applied to particular cases.

APPENDIX: PROPERTIES OF A AND $\mathbf{A}^{-1}$

Because of the utility of the matrix **A** we briefly consider some of its properties. The matrix $\mathbf{A}-\mathbf{1}$ is seen to be skew symmetric, real, and of order $N\times N$, with N the number of sites. Thus $\mathbf{A}-\mathbf{1}$ has N orthonormal eigenvectors with pure imaginary eigenvalues, and **A** has N eigenvalues all of which are nonzero, since their real component is 1. Thus, **A** has an inverse.

Now the optimization of the parameters appearing in the S_{ij}^{+} operators is a nonlinear problem, which is generally expected to only be solved by an iterative search procedure. Thus, we may wish to invert a number of slightly differing **A** matrices. Some of these inversions can be avoided if we consider a uniform scale variation of all the parameters, i.e., we consider variations such that each S_{ij}^{+} changes to xS_{ij}^{+} with x independent of i, j. Under this scale change **A** changes to $\mathbf{1}+x(\mathbf{A}-\mathbf{1})$. Now we let **P** be the easily determined[6] lower right triangular finite product of elementary matrices which brings $\mathbf{A}-\mathbf{1}$ to upper right triangular form

$$\mathbf{P}(\mathbf{A}-\mathbf{1})=\mathbf{R}\ . \tag{A1}$$

Then $\mathbf{P}^{-1}$ is upper right triangular, as well as

$$\mathbf{P}(\mathbf{A}-\mathbf{1})\mathbf{P}^{-1}=\mathbf{R}\mathbf{P}^{-1}\ . \tag{A2}$$

(We note $\mathbf{P}^{-1}$ is easily generated at the same time as **P**, since the elementary matrices from which **P** is composed all have trivially found inverses.) Because the inverse of an upper triangular matrix, such as $\mathbf{1}+x\mathbf{R}\mathbf{P}^{-1}$, is easily found by a straightforward Gaussian elimination process, we obtain the computationally useful result

$$\{\mathbf{1}+x(\mathbf{A}-\mathbf{1})\}^{-1}=\mathbf{P}\{\mathbf{1}+x\mathbf{R}\mathbf{P}^{-1}\}^{-1}\mathbf{P}\ . \tag{A3}$$

Of course, the same **P** and **R** are used for all values of x. In carrying out other types of variations in S_{ij}^{+} many general cases may lend themselves to bond-order identifications which, if known, would determine the parameters; thus, a self-correcting iterative procedure for the bond orders and parameters may be of use.

[1]Paper I: D. J. Klein, J. Chem. Phys. **63**, XXX (1975).
[2]See, for instance, (a) O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); (b) H. Primas, in *Modern Quantum Chemistry*, edited by O. Sinanoğlu (Academic, New York, 1965), Vol. II, p. 45; (c) J. W. Clark and P. Westhaus, J. Math. Phys. **9**, 131 (1968).
[3]See, for instance, F. Harary, *Graph Theory* (Addison-Wesley, Reading, MA, 1972).
[4]H. S. Wall, *Continued Fractions* (Chelsea, New York, 1967), Chap. XII.
[5]See, for instance, (a) M. J. S. Dewar and H. C. Longuet-Higgins, Proc. R. Soc. A **214**, 482 (1952); (b) E. Heilbronner, Helv. Chim. Acta **36**, 170 (1953); **45**, 1722 (1962); (c) N. S. Ham and K. Rudenberg, J. Chem. Phys. **29**, 1199, 1229 (1958); (d) H. Hosoya, Bull. Chem. Soc. Japan **44**, 2332 (1971); (e) W. C. Herndon, J. Chem. Ed. **51**, 10 (1974); (f) D. Cvetkovic, I. Gutman, and N. Trinajstic, J. Chem. Phys. **61**, 2700 (1974).
[6]J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Oxford U. P., London, 1965), Sec. 4.17.