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# Arrow diagram approach to nonorthogonal electron group functions in extended systems

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## Abstract

For nonorthogonal electron group functions, the arrow diagram (AD) method (Kantorovich and Zapol 1992 *J. Chem. Phys.* **96** 8420; 1992 *J. Chem. Phys.* **96** 8427) provides a convenient procedure for calculating matrix elements  $\langle \Psi | \hat{O} | \Psi \rangle$  of arbitrary symmetrical operators  $\hat{O}$ . The total wavefunction of the system  $\Psi = \hat{A} \prod_I \Phi_I$  is represented as an antisymmetrized product of nonorthogonal many-electron group functions  $\Phi_I$  of each group  $I$  in the system. For extended (e.g. infinite) systems the calculation of the mean value of an operator is ill defined, however, as it requires that each term of the diagram expansion be divided by the normalization integral  $S = \langle \Psi | \Psi \rangle$  which is given by an AD expansion as well. In this work, we cast the mean value of a symmetrical operator in a form of an AD expansion which is a linear combination of linked ADs. By analysing an exactly solvable one-dimensional Hartree–Fock problem, we find that pre-factors, attached to every linked AD in the linear combination, can be expanded in a power series with respect to overlap. A general method of calculating these pre-factors in a form of a power series expansion with respect to overlap is suggested. This advance makes the AD theory applicable to extended systems, and allows one to calculate the mean value of an arbitrary symmetrical operator correct up to the desired order of overlap within the group function theory. In particular, we derive the effective Hamiltonian of a quantum cluster surrounded by overlapping group functions (e.g. bonds) in the environment region which is correct up to the second order with respect to overlap (an embedding problem).

## 1. Introduction

For a wide range of quantum-mechanical problems, the entire electronic system can conveniently be split into a set of electron groups (EGs) such as core and valence electrons in molecules or crystals, electrons on atoms or ions in atomic or ionic solids, and core and bond

electrons in strongly covalent materials [1–3]. Similar partitioning ideas can also be applied to separate electrons in a cluster and environment regions to derive a particular embedding potential for the quantum cluster [3–5]. Provided that the partition scheme applied to the given system is physically (or chemically) appropriate, one can assume that electrons fixed to the given group spend most of their time at this group. Therefore, to a good approximation, the wavefunction of the whole system consisting of electronic groups  $I$  can be represented as an antisymmetrized product of wavefunctions  $\Phi_I(X_I)$  of every individual group:

$$\Psi(X_1, \dots, X_M) = \widehat{A} \prod_{I=1}^M \Phi_I(X_I) \quad (1)$$

where  $M$  is the total number of EGs. Here the  $I$ th group is associated with  $N_I$  electrons whose coordinates are collected into a set  $X_I = (x_1, \dots, x_{N_I})$ . Note that the single electron coordinates  $x$  include the spin coordinate as well. The antisymmetrization operator is defined via

$$\widehat{A} = \frac{1}{N!} \sum_{P \in S_N} \epsilon_P \widehat{P} \quad (2)$$

where the sum runs over all  $N!$  permutations  $\widehat{P}$  of the complete group of permutations  $S_N$ , the total number of electrons in the whole system being  $N = N_1 + N_2 + \dots + N_M$  and the factor  $\epsilon_P = \pm 1$  according to the parity of the permutation  $\widehat{P}$ . It is assumed here that the group functions  $\Phi_I(X_I)$  are already individually antisymmetric.

By applying expression (2) for the operator  $\widehat{A}$  in equation (1), one obtains an expansion of the wavefunction via various function-products. When used in calculating matrix elements  $\langle \Psi | \widehat{O} | \Psi \rangle$  of symmetrical (with respect to permutations of electronic coordinates) operators  $\widehat{O} \equiv \widehat{O}(x_1, \dots, x_N)$  (e.g. an external field or electron–electron interaction), a corresponding expansion of matrix elements between various function-products is obtained. Earlier attempts (see, e.g. [6–12]) to simplify the expansion and associate each term with a transparent diagram have been generalized in [13, 14] where the arrow diagram (AD) theory was developed. First, by exploiting a double-coset decomposition of the group  $S_N$ , many terms in the expansion were found to be identical and the corresponding rules to number all distinct terms were worked out in a general case. Second, each distinct term in the expansion was given by a well-defined picture (arrow diagram) which allowed one to construct simple rules to associate an analytical expression with any of the ADs. The theory was formulated in a very general way for arbitrary number of electron groups and explicit AD expansions were constructed for reduced density matrices (RDMs) [1, 2] of orders one and two (RDM-1 and RDM-2). These enable one to calculate matrix elements of arbitrary symmetrical one- and two-particle operators and are thus sufficient in most cases relevant to quantum chemistry of molecules and solids (generalization to higher-order RDMs is cumbersome but straightforward).

In general, the success of this technique depends crucially on the value of the overlap between different group functions  $\Phi_I(X_I)$  and thus their localization in certain *regions* of space (also known as *structure elements* [3]). This is because greater localization of the group functions results in better convergence of the AD expansion, i.e. smaller number of terms in the expansion are to be retained. That is why the choice of electronic groups and appropriate regions of their localization [15, 16] is so important for this method to work.

Although the AD theory formulated in [13, 14] is applicable to any system consisting of arbitrary numbers of overlapping electron groups, one cannot directly use it to describe an extended (in particular, infinite) system. Indeed, to calculate an observable

$$\overline{O} = \frac{\langle \Psi | \widehat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (3)$$

of the operator  $\widehat{O}$ , in the case of an extended system one has to calculate the ratio of two AD expansions, one arising from the matrix element  $\langle \Psi | \widehat{O} | \Psi \rangle$  and the other from the normalization integral  $S = \langle \Psi | \Psi \rangle$ . Both expansions contain very many terms; in fact, the number of terms is infinite in the case of an infinite system (e.g. a solid).

It was suggested in [17] that the mean value of a symmetrical operator (3) may be cast in a form of a linear combination of all linked ADs with the pre-factors equal to unity. However, a more critical look at the theory made in this paper demonstrates that this result is approximate and only works if the overlap between different group functions is relatively small.

Our main objective of this paper is to develop a general method of calculating these pre-factors, so that the AD theory can be applied to extended systems. We were fortunate to discover a simple model of a one-dimensional Hartree–Fock ring which consists of an infinite number of *one*-electron groups (to be referred to as a *toy model* hereafter). We find that the RDM of the toy model can be obtained analytically. In particular, this allows us to investigate the pre-factors of the linear combination of linked ADs for the RDM of the toy model. The heuristic analysis of the toy model provides a way towards the general method of calculating the pre-factors.

The paper is organized as follows. In the next section we shall briefly review the arrow diagram theory for the reader's convenience. In section 3, we analyse in detail the toy model and obtain an exact expression for RDM-1 in the limit of an infinite ring size. This result will enable us to conclude that the conjecture [17] that the pre-factors are equal to unity is only approximate. In section 4, we develop a general method for calculating the pre-factors in a form of a power series expansion with respect to overlap. In section 5, we generally discuss the linked-AD expansion of RDM-1 and RDM-2 as well as the energy functional. An effective Hamiltonian of a quantum cluster embedded in an environment consisting of an arbitrary large number of overlapping EGs is then derived, correct up to the second-order overlap between the cluster and the environment.

## 2. The arrow diagram theory

First we consider a symmetric group  $S_{N_i}$ . Its elements permute electronic coordinates belonging only to the  $i$ th group. Joining together all such groups we obtain a subgroup  $S_0 = S_{N_1} \cup S_{N_2} \cup \dots \cup S_{N_M}$  of  $S_N$ . Any element of  $S_0$  only interchanges electronic coordinates within the groups, i.e. performs only intra-group permutations. The algebraic foundation of the AD theory is based on the *double coset* (DC) decomposition of the complete symmetric group  $S_N$  with respect to  $S_0$ , which enables one to single out all inequivalent *intergroup* permutations  $\widehat{P}_{qT}$  [13]:

$$S_N = \frac{1}{N_0} \sum_{qT} \mu_{qT} (S_0 \widehat{P}_{qT} S_0). \quad (4)$$

Here the sum runs over all distinct types,  $q$ , of operations for intergroup permutations as well as all distinct ways,  $T$ , of labelling actual groups (EGs) involved in it, and  $N_0 = N_1! N_2! \dots N_M!$  is a numerical factor.  $\widehat{P}_{qT}$  is a DC generator, which involves only intergroup permutations and, in general, can be constructed as a product of some *primitive* cycles each involving no more than one electron from each group.

Each such cycle is represented as a directed closed loop connecting all groups involved in it. Thus, in general, each permutation  $\widehat{P}_{qT}$  can be drawn as an arrow diagram containing a collection of closed directed loops. These loops may pass through the given group several times (depending on the number of electrons of the group which are involved in the permutation  $\widehat{P}_{qT}$ ). If the groups involved in the diagram cannot be separated without destroying the directed

loops, the AD is called *linked* or *connected*. If, however, this separation is possible then the diagram is called *non-linked* or *disconnected* and it can be represented as a collection of linked parts. The decomposition coefficients  $\mu_{qT}$  can be calculated merely by counting the arrows entering and leaving each group in the AD.

By writing the antisymmetrizer  $\hat{A}$  of equation (2) using the DC generators, it is possible to obtain the diagram expansion of the normalization integral [14]:

$$S = \langle \hat{A}\Phi | \hat{A}\Phi \rangle = \Lambda \sum_{qT} \epsilon_q \mu_{qT} \langle \Phi | \hat{P}_{qT} | \Phi \rangle \quad (5)$$

where  $\Lambda = N_0/N!$  and  $\Phi = \prod_I \Phi_I(X_I)$  is a product of all group functions. Equation (5) gives an expansion of  $S$  in terms of diagrams identical to those for the permutation group  $S_N$  of equation (4). The matrix elements  $\langle \Phi | \hat{P}_{qT} | \Phi \rangle$  are represented as a product of RDMs of electron groups involved in the permutation  $\hat{P}_{qT}$  integrated over corresponding electronic coordinates. If each of the group functions  $\Phi_I$  is given as a sum of Slater determinants with molecular orbitals expanded via some atomic orbitals (AOs) basis set, then the matrix elements  $\langle \Phi | \hat{P}_{qT} | \Phi \rangle$  are eventually expressed as a sum of products of simple overlap integrals between the AOs of different electron groups (see, e.g. [17]). It is important to note here that a total contribution of a non-linked AD is exactly equal to the product of contributions associated with each of its linked parts [14].

For the following, it is convenient to sort out all the terms in the diagrammatic expansion by the number of groups involved in the ADs. Getting rid of the common factor  $\Lambda$ , we can write

$$\tilde{S} = \frac{S}{\Lambda} = 1 + \sum_{K=2}^M \sum_{A_1 < \dots < A_K} S_K(A_1, A_2, \dots, A_K) \quad (6)$$

where  $S_K(A_1, A_2, \dots, A_K)$  is the contribution of *all* ADs that correspond to intergroup permutations among  $K$  different groups with the particular labelling  $A_1, A_2, \dots, A_K$ . The unity in the equation above corresponds to the trivial permutation.

For convenience, the expansion in equation (6) will be referred to as the normalization-integral expansion. In principle, in this expansion all groups of the entire system participate. It is also found convenient to introduce a derivative object,  $\tilde{S}(T)$ , which is obtained from the above expansion by retaining all the ADs which are associated only with the groups from a finite manifold  $T = \{A_1, \dots, A_K\}$  (i.e. containing groups with labels  $A_1, \dots, A_K$ ). If  $T$  comprises the whole system, we arrive at  $\tilde{S}$  of equation (6). We shall also introduce a manifold  $[T]$ , i.e. an artificial system which is obtained by ‘removing’ from the entire system all groups comprising the set  $T$ . Then,  $\tilde{S}([T])$  (we shall also use a simpler notation  $\tilde{S}[T]$  when convenient) is obtained from equation (6) by retaining only ADs in which *none* of the groups belonging to  $T$  are present; in other words,  $\tilde{S}([T])$  is obtained from  $\tilde{S}$  by assuming that in any of the ADs all the overlap integrals involving groups from the manifold  $T$  are equal to zero. Obviously,  $\tilde{S}$  can be considered as a particular case of  $\tilde{S}[T]$  when the manifold  $T$  is empty. We shall occasionally also use the notation  $\tilde{S}[A_1, \dots, A_K]$  for  $\tilde{S}[T]$ , where  $T = \{A_1, \dots, A_K\}$ , if we want to indicate explicitly which particular groups are excluded.

The *unnormalized* RDM-1 of the whole system,

$$\bar{\rho}(x; x') = N \int \Psi(x, x_2, \dots, x_N) \Psi^*(x', x_2, \dots, x_N) dx_2 \dots dx_N \quad (7)$$

can also be written as a matrix element of a certain symmetrical one-particle operator [1, 2, 14]. Therefore, as in the case of the normalization integral, by inserting the AD expansion for the operator  $\hat{A}$ , one obtains the corresponding AD expansion for the RDM-1 [14]. It can be constructed by considering the AD expansion of  $S$  and then modifying each diagram by placing

a small open circle, representing the variables  $(x, x')$ , in either of the three following ways: (i) on a group not involved in the diagram; (ii) on a group involved in the diagram; and, finally, (iii) on an arrow. Thus, each AD in the  $S$  expansion serves as a reference in building up the AD expansion for the RDM-1. Since the contribution of any non-linked diagram is equal to the product of contributions corresponding to each of its linked parts, it can be shown [17] that, in general, the AD expansion of the RDM-1 can be represented as

$$\tilde{\rho}(x; x') = \frac{\bar{\rho}(x; x')}{\Lambda} = \sum_{K=1}^M \sum_{A_1 < \dots < A_K} \tilde{S}[A_1, \dots, A_K] \sum_t \rho_K^t(A_1, \dots, A_K \parallel x; x') \quad (8)$$

where  $\rho_K^t(A_1, \dots, A_K \parallel x; x')$  is the sum of contributions of all ADs with an open circle which are constructed using the particular group labelling  $A_1, A_2, \dots, A_K$ . The sum over  $t$  takes account of the two possible positions of the open circle on the reference AD: on an arrow and on a group. Note that each AD with the open circle is necessarily a linked (connected) AD. One can see from the above equation that each AD with an open circle, constructed from groups  $T = \{A_1, \dots, A_K\}$ , is multiplied by the sum of all possible normalization-integral ADs (i.e. ADs without the circle),  $\tilde{S}[A_1, \dots, A_K] = \tilde{S}[T]$ , constructed using the rest of the system [17].

The RDM-1 introduced by equation (7) is not normalized to the total number of electrons in the system since the wavefunction  $\Psi$  constructed using group functions,  $\Phi_I$ , is, in general, not normalized to unity:  $S = \langle \Psi | \Psi \rangle \neq 1$ . Therefore, the *true* RDM-1 should be calculated according to equation (3) as [17]

$$\rho(x; x') = \frac{\bar{\rho}(x; x')}{\langle \Psi | \Psi \rangle} = \sum_{K=1}^M \sum_{A_1 < \dots < A_K} f_{[T]} \sum_t \rho_K^t(A_1, \dots, A_K \parallel x; x') \quad (9)$$

where

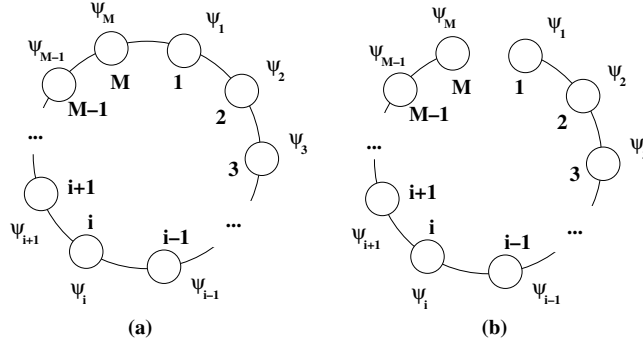
$$f_{[T]} = f_{[A_1, \dots, A_K]} = \frac{\tilde{S}[A_1, \dots, A_K]}{\tilde{S}} \quad (10)$$

are numerical pre-factors. These depend only on the chosen set of groups  $T$ . Since the normalization integral  $\tilde{S}$  is represented via an AD expansion, equation (6), one can see that the pre-factors are given as a ratio of two AD expansions, each containing a very large (infinite) number of terms for a large (infinite) system. Thus, it follows from the last passage in equation (9), that the *true* RDM-1 is represented as a sum of all linked ADs with the open circle,  $\rho_K^t(A_1, \dots, A_K \parallel x; x')$ , multiplied by numerical pre-factors,  $f_{[A_1, \dots, A_K]}$ . The calculation of the pre-factors poses the main problem in applying the AD theory to infinite or even large system (for small systems all ADs can be accounted for explicitly and thus  $\rho(x; x')$  can easily be calculated, at least in principle).

In [17] it was suggested that the pre-factors can be set to unity. We shall show, however, in the forthcoming section that this conjecture is not strictly valid, although it is a good approximation in the cases of small overlap between the group functions.

### 3. 1D toy model: a Hartree–Fock ring

Let us consider a ring of  $M$  equally spaced one-electron groups (hence  $M = N$ ) as shown in figure 1(a). Each group is described by a single real s-type normalized wavefunction  $\psi_i(x)$  ( $i = 1, 2, \dots, M$ ) localized around the group centre. Spin is ignored here, since we only wish to set up an exactly solvable model and utilize it to investigate the pre-factors. The general case will then be considered in section 4.2.



**Figure 1.** The 1D toy model: (a) a Hartree–Fock ring consisting of equidistant one-electron orbitals  $\psi_1, \psi_2, \dots, \psi_M$  and (b) the corresponding chain model in which there is no overlap between the first and the last orbitals in the ring.

All groups are identical, i.e. every localized function  $\psi_i(x)$  can be obtained by a spatial translation of other functions. Within the Hartree–Fock theory, the total wavefunction of the ring is represented by a single Slater determinant  $\Psi \propto \det |\psi_1(x_1) \cdots \psi_M(x_M)|$ . We assume that the wavefunctions  $\psi_i(x)$  spatially *spread* only over their nearest neighbours, so that only the product of two nearest neighbour wavefunctions is nonzero. Due to the symmetry of the model, only one parameter, i.e. the overlap integral  $\sigma = \int \psi_i(x) \psi_j(x) dx$  between any neighbouring group pairs, is required to characterize the system. Thus, the actual form of  $\psi_i(x)$  is not needed.

For the convenience of the following calculation, we also introduce a similar *chain* system, shown in figure 1(b), in which the overlap between the groups 1 and  $M$  is equal to zero.

We shall show that the RDM-1 of the ring can be analytically calculated when the number of electron groups tends to infinity. As a result, the exact expression for the RDM-1 obtained this way would enable us to analyse the pre-factors attached to each AD in it.

### 3.1. Finite ring

We first consider the normalization integral  $\tilde{S} \equiv G_N^{\text{Ring}}$  of the ring. Since all groups contain a single electron and only nearest groups have nonzero overlap, the AD expansion contains essentially only bubble-like ADs between two adjacent groups (including all non-linked ADs constructed out of them) and two ADs connecting *all* groups (an  $N$ -vertex polygon) with the opposite direction of arrows:

$$G_N^{\text{Ring}} = 1 + \left[ \text{bubble diagrams} \right] + \dots + \left[ \text{polygon diagrams} \right]. \quad (11)$$

An AD expansion for the normalization integral  $G_N^{\text{Chain}}$  of the chain looks similarly. There are two differences: (i) bubble ADs containing the groups 1 and  $N$  are missing, and (ii) it does not contain the two polygon diagrams. Recall that there is no ‘connection’ between the groups 1 and  $N$  in the chain.

An AD expansion for the diagonal elements of the ring electron density,  $\tilde{\rho}(x) \equiv \tilde{\rho}(x; x)$ , equation (8), can also be written explicitly as follows:

$$\tilde{\rho}(x) = \circ \left[ 1 + \left[ \text{bubble diagrams} \right] \right] + \left[ \text{chain diagram} \right] + \left[ \text{polygon diagrams} \right]. \quad (12)$$

It contains three terms. The first term is associated with an open circle AD, associated with, say, group  $i$ , multiplied by all bubble ADs (shown in the square brackets) which are constructed out of the remaining  $N - 1$  groups  $1, \dots, i - 1, i + 1, \dots, N$ . The contribution of the open circle  $\rho_i^{(\circ)}(x) = |\psi_i(x)|^2$ , while the bubble ADs in the square brackets all amount to  $G_{N-1}^{\text{Chain}}$  (and are the same for any  $i$ ), since they represent all ADs for a chain with  $N - 1$  groups. Finally, one has to sum over all values of  $i$  (all positions of the open circle). Hence, the first term contributes  $G_{N-1}^{\text{Chain}} \sum_{i=1}^N \rho_i^{(\circ)}(x)$  to the density  $\tilde{\rho}(x)$ .

The second term in equation (12) contains a bubble diagram with an open circle on an arrow, multiplied by all possible bubble ADs constructed out of the remaining  $N - 2$  groups. Assuming that the bubble AD is taken between the groups  $i$  and  $i + 1$ , we obtain the contribution  $\rho_{i,i+1}^{(\text{bubble})}(x) = -\sigma \psi_i(x) \psi_{i+1}(x)$  for it. Since the contribution of all groups  $1, \dots, i - 1, i + 2, \dots, N$  in the square brackets in the second term is equal to  $G_{N-2}^{\text{Chain}}$  (which is the same for any pair  $i, i + 1$ ), the final contribution of the second term in equation (12) becomes  $2G_{N-2}^{\text{Chain}} \sum_{i=1}^N \rho_{i,i+1}^{(\text{bubble})}(x)$ , where we have also summed over all pairs, i.e. all possible positions of the open circle on the bubble ADs (recall, that the bubble ADs can be taken only between nearest neighbours in our model).

Finally, the last two terms in equation (12) are represented by polygons with an open circle. Each such diagram contributes  $\rho_{i,i+1}^{(\text{poly})} = (-\sigma)^{N-1} \psi_i(x) \psi_{i+1}(x)$  if the open circle is positioned on the arrow connecting groups  $i$  and  $i + 1$ . The total contribution of the polygons is obtained by summing over all possible positions of the circle and multiplying by a factor of two since each AD accepts two directions of the arrows.

Summing all three contributions, we arrive at the following expression for the unnormalized electron density:

$$\tilde{\rho}(x) = G_{N-1}^{\text{Chain}} \sum_{i=1}^N \rho_i^{(\circ)}(x) + 2G_{N-2}^{\text{Chain}} \sum_{i=1}^N \rho_{i,i+1}^{(\text{bubble})}(x) + 2 \sum_{i=1}^N \rho_{i,i+1}^{(\text{poly})}(x). \quad (13)$$

Dividing this expression by  $G_N^{\text{Ring}}$ , one obtains the normalized electron density

$$\begin{aligned} \rho(x) = & \left( \frac{G_{N-1}^{\text{Chain}}}{G_N^{\text{Ring}}} \right) \sum_{i=1}^N |\psi_i(x)|^2 - 2\sigma \left( \frac{G_{N-2}^{\text{Chain}}}{G_N^{\text{Ring}}} \right) \sum_{i=1}^N \psi_i(x) \psi_{i+1}(x) \\ & - \frac{2}{\sigma} \left( \frac{(-\sigma)^N}{G_N^{\text{Ring}}} \right) \sum_{i=1}^N \psi_i(x) \psi_{i+1}(x). \end{aligned} \quad (14)$$

Note that this result can also be obtained by a completely independent calculation based on matrix algebra (see the appendix).

### 3.2. Infinite ring

To investigate the limiting behaviour of pre-factors in the round brackets of equation (14), it is useful to introduce two recurrence relations for  $G_N^{\text{Chain}}$  and  $G_N^{\text{Ring}}$ .

Consider first the AD expansion for  $G_N^{\text{Chain}}$  which contains only zero, one, two, etc, bubble diagrams (see the bubble-containing terms in equation (11)). Recall that the chain is broken between groups 1 and  $N$ . Let us ‘fix’ group 1. Then,  $G_N^{\text{Chain}}$  can be written as the sum of two contributions: (i) due to all diagrams involving group 1, and (ii) due to the rest of them which do not involve it. The first contribution is simply a single bubble AD between groups 1 and 2, equal to  $-\sigma^2$ , times all the bubble ADs made of all the other groups, i.e. the whole contribution is  $(-\sigma^2) G_{N-2}^{\text{Chain}}$ . The contribution of all ADs which do not involve group 1 is simply equal to  $G_{N-1}^{\text{Chain}}$ . Thus, we have the recurrence relation

$$G_N^{\text{Chain}} = G_{N-1}^{\text{Chain}} - \sigma^2 G_{N-2}^{\text{Chain}}. \quad (15)$$



Similarly, a recurrence relation for  $G_N^{\text{Ring}}$  can be obtained. We first ‘fix’ group 1. Then, the sum of all ADs in equation (11) is equal to the sum of three contributions: (i)  $G_{N-1}^{\text{Chain}}$  due to all ADs which do not involve group 1; (ii) all the bubble ADs involving it, given by  $2(-\sigma^2)G_{N-2}^{\text{Chain}}$  analogously to the case of the chain discussed above (the factor of two arises due to the fact that one can construct two bubble ADs with group 1, namely those involving group pairs 1,  $N$  and 1, 2); (iii) the contribution  $-2(-\sigma)^N$  of the two polygon ADs. Summing all three terms, we obtain

$$G_N^{\text{Ring}} = G_{N-1}^{\text{Chain}} - 2\sigma^2 G_{N-2}^{\text{Chain}} + 2(-1)^{N+1} \sigma^N. \quad (16)$$

It is useful to introduce the quantity  $P_N = \sigma^2 G_{N-1}^{\text{Chain}} / G_N^{\text{Chain}}$ . From the explicit expressions  $G_2^{\text{Chain}} = 1 - \sigma^2$  and  $G_1^{\text{Chain}} = 1$ , we get  $P_2 = \sigma^2 / (1 - \sigma^2)$ . Using the recurrence relation (15) for  $G_N^{\text{Chain}}$ , a very simple recurrence relation for  $P_N$  can also be derived:  $P_N = \sigma^2 / (1 - P_{N-1})$ . Hence, the limit  $N \rightarrow \infty$  for  $P_N \rightarrow P_\infty$  can be attained by solving the quadratic equation  $P_\infty(1 - P_\infty) = \sigma^2$ . Only the negative root of this equation,  $P_\infty = \frac{1}{2}(1 - \sqrt{1 - 4\sigma^2})$ , is accepted as it gives the correct limit for the case of zero overlap, i.e.  $P_N = 0$  for any  $N$  when  $\sigma = 0$ . Note that the  $P_N \rightarrow P_\infty$  limit exists only for  $\sigma < \frac{1}{2}$  which corresponds to a not overly large overlap. This restriction is a consequence of the nearest-neighbour approximation adopted in our toy model. We also note in passing that  $P_N > 0$  for any  $N$ .

Using recurrence relations (15) and (16), the first two pre-factors in equation (14) can be directly expressed in terms of the quantities  $P_N$ :

$$\frac{G_{N-1}^{\text{Chain}}}{G_N^{\text{Ring}}} = \frac{1}{1 - 2P_{N-1} + 2\sigma\chi_{N-1}} \quad (17)$$

$$\frac{G_{N-2}^{\text{Chain}}}{G_N^{\text{Ring}}} = \frac{\sigma^{-2} P_{N-1}}{1 - 2P_{N-1} + 2\sigma\chi_{N-1}} \quad (18)$$

where  $\chi_N = (-\sigma)^N / G_N^{\text{Chain}}$ .

Now, we consider the limiting behaviour of the ratios  $\chi_N$  and

$$\xi_N = \frac{(-\sigma)^N}{G_N^{\text{Ring}}} = \frac{-\sigma\chi_{N-1}}{1 - 2P_{N-1} + 2\sigma\chi_{N-1}} \quad (19)$$

which enter equations (17), (18) and (14), respectively. To calculate  $\chi_\infty = \lim_{N \rightarrow \infty} \chi_N$ , we use the definition of  $P_N$  and write

$$G_{N-1}^{\text{Chain}} = \frac{(\sigma^2)^{N-3}}{P_{N-1} P_{N-2} \cdots P_3} G_2^{\text{Chain}} > \left( \frac{\sigma^2}{P_\infty} \right)^{N-3} \cdot G_2^{\text{Chain}}$$

since  $P_N < P_\infty$  for any finite value of  $N$  and any  $0 \leq \sigma < \frac{1}{2}$ . Since  $G_2^{\text{Chain}} = 1 - \sigma^2 > 0$  and all of the quantities  $P_N$  are positive, one can write

$$0 < \frac{\sigma^N}{G_{N-1}^{\text{Chain}}} < \frac{\sigma^3}{G_2^{\text{Chain}}} \left( \frac{P_\infty}{\sigma} \right)^{N-3}.$$

Because  $P_\infty/\sigma < 1$  for any  $0 \leq \sigma < \frac{1}{2}$ , we obtain that both  $(P_\infty/\sigma)^{N-3}$  and  $\sigma^N / G_{N-1}^{\text{Chain}}$  tend to zero when  $N \rightarrow \infty$ . Hence,  $\chi_N$  has a zero limit and disappears in the ratios (17) and (18). Consequently,  $\xi_N \rightarrow 0$  too (see equation (19)), so that the third term in the right-hand side of equation (14) also does not contribute when the limit of an infinite ring is taken.

Finally, combining the above results, we obtain the *exact* electron density for the infinite ring:

$$\rho(x) = \sum_i f_{[i]} \rho_i^{(\circ)}(x) + 2 \sum_i f_{[i,i+1]} \rho_{i,i+1}^{(\text{bubble})}(x) \quad (20)$$

where the corresponding expressions for the two pre-factors are

$$f_{[i]} = \frac{1}{\sqrt{1-4\sigma^2}} \quad (21)$$

$$f_{[i,i+1]} = \frac{1}{2\sigma^2} \left( \frac{1}{\sqrt{1-4\sigma^2}} - 1 \right). \quad (22)$$

It is now instructive to make the following Taylor expansion for the two pre-factors:

$$f_{[i]} = 1 + \sum_{n=1}^{\infty} \frac{(2n-1)!!}{n!} (2\sigma^2)^n \quad (23)$$

$$f_{[i,i+1]} = \sum_{n=1}^{\infty} \frac{(2n-1)!!}{n!} (2\sigma^2)^{n-1}. \quad (24)$$

It is easy to check that both series are convergent when  $\sigma \leq 0.5$ .

It follows from the above consideration of the exactly solvable toy model (the infinite ring) that in a general case the pre-factors may be expanded in a power series with respect to overlap. In addition, one may see that different pre-factors may be related to each other. For instance, using equations (21) and (22), one gets  $2\sigma^2 f_{[i,i+1]} = f_{[i]} - 1$ .

#### 4. Method of power series expansion

We shall generalize the above ideas to arbitrary many-electron group systems. Then the method of power series expansion will be developed for calculating the pre-factors. In order to illustrate the general method, it is instructive first to recalculate the two pre-factors for the toy model, starting from the above ideas.

##### 4.1. Series expansion for the 1D toy model

Let us consider the 1D toy model (the infinite ring) for which the exact solution is known. Fix group 1. Then, the normalization integral for the whole ring,  $\tilde{S}$ , can be constructed as a sum of three terms: (i) all ADs of the rest of the system,  $\tilde{S}[1]$ , where  $T = [1]$  corresponds to the ring with group 1 'removed', i.e. this group does not have any overlap with its neighbours; (ii) a bubble AD between groups 1 and 2 (contributing  $-\sigma^2$ ) multiplied by all possible bubble ADs due to all other groups,  $\tilde{S}[1, 2]$  (as usual,  $T = [1, 2]$  denotes the system in which groups 1 and 2 are removed); and, similarly, (iii) a bubble AD between group 1 and the last group in the ring (the other neighbour of group 1) times all the bubble ADs of the rest of the system. The last two contributions are identical. Note that we do not consider the polygon here as we know that in the limit of an infinite ring its contribution vanishes. Thus, one can write  $\tilde{S} = \tilde{S}[1] - 2\sigma^2 \tilde{S}[1, 2]$ . Dividing both sides of this equation by  $\tilde{S}$ , we obtain an equation relating two first pre-factors:  $1 = f_{[1]} - 2\sigma^2 f_{[1,2]}$ .

Repeating the above procedure for the system  $T = [1]$  and fixing group 2, we similarly obtain  $\tilde{S}[1] = \tilde{S}[1, 2] - \sigma^2 \tilde{S}[1, 2, 3]$ , where  $T = [1, 2, 3]$  denotes a system in which groups 1, 2 and 3 are removed. In fact, the above equation also follows from the recurrence relation (15). Dividing the last equation by  $\tilde{S}$ , we obtain another relationship between pre-factors:  $f_{[1]} = f_{[1,2]} - \sigma^2 f_{[1,2,3]}$ . Continuing this procedure, one can write an infinite series of relationships in which every time a new pre-factor appears, for instance,  $f_{[1,2]} = f_{[1,2,3]} - \sigma^2 f_{[1,2,3,4]}$  and  $f_{[1,2,3]} = f_{[1,2,3,4]} - \sigma^2 f_{[1,2,3,4,5]}$ .

Next, we assume that the pre-factors are well-defined functions of the overlap,  $\sigma$ . Hence, they all can be expanded in a power series:

$$f_{[T]} = 1 + \sum_{n=1}^{\infty} a_n^{[T]} \sigma^n \quad (25)$$

where  $T$  is either 1 or 1, 2 or 1, 2, 3, and so on. Note that the expansion starts from unity for any  $[T]$  since  $f_{[T]} = 1$  for zero overlap ( $\sigma = 0$ ). Substituting the series expansions for the pre-factors into the identities given above, that relate various pre-factors to each other, one can recursively recover the expansion coefficients up to a certain order by comparing terms of the same power of  $\sigma$ . This way one obtains the first several terms in the expansion of the two pre-factors that are required for the 1D toy model:

$$f_{[1]} = 1 + 2\sigma^2 + 6\sigma^4 + 20\sigma^6 + 70\sigma^8 + \dots \quad (26)$$

$$f_{[1,2]} = 1 + 3\sigma^2 + 10\sigma^4 + 35\sigma^6 + \dots \quad (27)$$

Indeed, the above expansions are identical to those given by equations (23) and (24) term by term. To obtain more terms in the expansion using this method, one has to consider more pre-factors  $f_{[T]}$  with increasing number of groups 'removed'.

#### 4.2. General method

The idea of the series expansion method illustrated in the previous subsection can actually be generalized for an arbitrary system containing groups with any numbers of electrons, i.e. for the most general wavefunction of equation (1). Indeed, what is needed is a way to connect the pre-factor  $f_{[T]} = \tilde{S}[T]/\tilde{S}$  associated with some set  $T = \{A_1, A_2, \dots, A_K\}$  of groups (not necessarily nearest neighbours) with the pre-factor  $f_{[T']} = \tilde{S}[T']/\tilde{S}$  associated with a *smaller* set  $[T'] = [T \cup \Delta T] = [T + \Delta T]$ . The set  $T'$  contains  $L$  additional groups forming a set  $\Delta T = \{B_1, B_2, \dots, B_L\}$ .

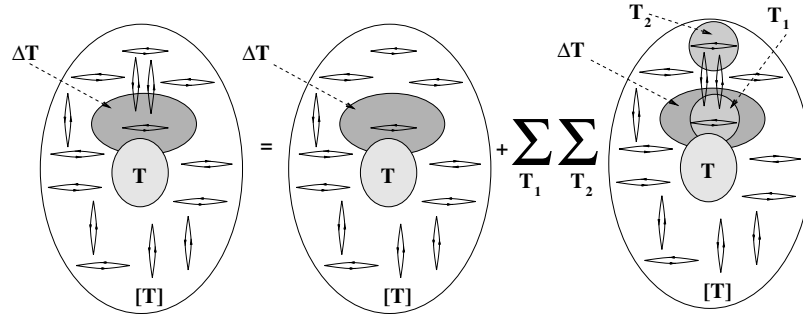
The corresponding relationship between the pre-factors can be obtained as follows. Consider the sum of all possible ADs which make up the entire normalization integral  $\tilde{S}[T]$  for the subsystem  $[T]$ . From all of them we separate out those which are related to the set  $[T + \Delta T]$ :

$$\tilde{S}[T] = \tilde{S}(\Delta T)\tilde{S}[T + \Delta T] + \sum_{T_1 \subset \Delta T} \sum_{T_2 \subset [T + \Delta T]} \tilde{D}(T_1 T_2) \tilde{S}(\Delta T - T_1) \tilde{S}[T + \Delta T + T_2]. \quad (28)$$

The first term in the right-hand side contains all the ADs that can be constructed out of the groups of the set  $\Delta T$ , given by  $\tilde{S}(\Delta T)$ . These should be multiplied by all ADs constructed out of the rest of the groups, i.e. by all groups from the manifold  $[T + \Delta T]$ . The second term contains all the ADs which are formed by the groups belonging to *both* sets  $\Delta T$  and  $[T + \Delta T]$ . Indeed, the double sum picks up subsets  $T_1$  and  $T_2$  from the manifolds of groups  $\Delta T$  and  $[T + \Delta T]$ , respectively. The sum of all possible ADs constructed using *every* group from  $T_1$  and  $T_2$  is denoted by  $\tilde{D}(T_1 T_2)$ . Note that ADs in  $\tilde{D}(T_1 T_2)$  may contain non-linked diagrams as well; however, in this case *each* of the non-linked ADs must contain *all* groups from  $T_1$  and  $T_2$ . Every AD in  $\tilde{D}(T_1 T_2)$  is multiplied by all possible ADs formed out of the rest of the groups of the two sets:  $\tilde{S}(\Delta T - T_1)$  corresponds to the ADs made of all groups in the set  $\Delta T - T_1$  (created by removing groups belonging to  $T_1$  from the set  $\Delta T$ ), whereas  $\tilde{S}[T + \Delta T + T_2]$  is obtained by all ADs left after 'removing' the set  $T_2$  from the set  $[T + \Delta T]$ . Equation (28) is schematically illustrated in figure 2.

Dividing each term in equation (28) by  $\tilde{S}$ , we obtain a recurrence relation for the pre-factors sought for:

$$f_{[T]} = \tilde{S}(\Delta T) f_{[T + \Delta T]} + \sum_{T_1 \subset \Delta T} \sum_{T_2 \subset [T + \Delta T]} \tilde{D}(T_1 T_2) \tilde{S}(\Delta T - T_1) f_{[T + \Delta T + T_2]}. \quad (29)$$



**Figure 2.** Schematic diagram illustrating equation (28): all ADs corresponding to the manifold  $[T]$  of electronic groups can be represented as a sum of contributions based on choosing an arbitrary sub-manifold of groups  $\Delta T \subset [T]$ .

It is seen that  $f_{[T]}$  is represented as a linear combination of pre-factors corresponding to *smaller* systems: if  $\aleph_T$  is the number of groups in the manifold  $T$ , then we can write that  $\aleph_{[T]} > \aleph_{[T+\Delta T]} > \aleph_{[T+\Delta T+T_2]}$ . Equation (29) is a generalization of the equations of section 4.1 for the toy model.

Equations like the one written above allow one to obtain the necessary series expansions in the general case. To this end, we attach to every diagram a factor  $\sigma^n$  with the power  $n$  being the order of the AD, i.e. the number of arrows it contains. The expansion we obtain will be with respect to the  $\sigma$  that will be set to unity at the end of the calculation. Note that this method does not take into account an additional factor, which is relevant in the actual calculation, that the contributions of the ADs also depend on the distances between different groups. In the method we propose an expansion with respect to overlap integrals will be obtained.

To illustrate how the method works, we shall obtain the few first terms in the expansion for  $f_{[A]}$ ,  $f_{[A,B]}$  and  $f_{[A,B,C]}$ . Noting that  $\tilde{S}(A) = 1$ , we start, similarly to section 4.1, with  $T = \emptyset$  (empty) and  $\Delta T = A$  in equation (29):

$$1 = f_{[A]} + \sum_{B \in [A]} \tilde{D}(AB) f_{[A,B]} + \sum_{\{B,C\} \in [A]} \tilde{D}(ABC) f_{[A,B,C]} + \sum_{\{B,C,D\} \in [A]} \tilde{D}(ABCD) f_{[A,B,C,D]} + \dots \quad (30)$$

where the curly brackets under the summation signs indicate that we sum over all *sets* of the groups containing two, three, etc, groups in them irrespective of their order in the sets; further,

$$\tilde{D}(AB) = D_2(A, B)\sigma^2 + D_4(A, B)\sigma^4 + \dots \quad (31)$$

$$\tilde{D}(ABC) = D_3(A, B, C)\sigma^3 + D_4(A, B, C)\sigma^4 + D_5(A, B, C)\sigma^5 + \dots \quad (32)$$

contain all ADs composed of groups  $\{A, B\}$  and  $\{A, B, C\}$ , respectively. For convenience, contributions of different orders with respect to  $\sigma$  have been presented separately by the quantities like  $D_n(T)$ . In particular,  $\tilde{D}(AB)$  contains a sum of bubble ADs which only have an even number of arrows:

$$\tilde{D}(AB) = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \\ \text{---} \end{array} + \dots \quad (33)$$

The expansion is finite: it runs until the number of electrons in either of the groups is completely used up. For instance, if a group  $A$  contains only two electrons, there will only be the first

two terms in the expansion. Similarly,  $\tilde{D}(ABC)$  contains a finite sum of all ADs made out of groups  $\{A, B, C\}$ :

$$\tilde{D}(ABC) = \begin{array}{c} \triangle \\ \leftarrow \end{array} + \begin{array}{c} \triangle \\ \leftarrow \end{array} + \begin{array}{c} \triangle \\ \leftarrow \end{array} + \begin{array}{c} \triangle \\ \leftarrow \end{array} + \dots \quad (34)$$

Note that both directions of arrows, where appropriate, are assumed in this expansion. The expansion starts from the AD containing three arrows, the next term contains four arrows, then follows the term with five arrows, etc. For small values of  $n$  there might be only few ADs contained in the given  $D_n(T)$ ; however, the number of the ADs may grow quickly as the order  $n$  becomes larger. The only exception is  $\tilde{D}(AB)$  in which case in any order  $n$  (that is always even) there is exactly one AD in  $D_n(T)$ .

Following the same logic, consider equation (29) for  $T = A$  and  $\Delta T = B$ . This gives

$$f_{[A]} = f_{[A,B]} + \sum_{C \in [A,B]} \tilde{D}(BC) f_{[A,B,C]} + \sum_{\{C,D\} \in [A,B]} \tilde{D}(BCD) f_{[A,B,C,D]} + \dots \quad (35)$$

If  $T = \{A, B\}$  and  $\Delta T = C$ , then we also have

$$f_{[A,B]} = f_{[A,B,C]} + \sum_{D \in [A,B,C]} \tilde{D}(CD) f_{[A,B,C,D]} + \sum_{\{D,E\} \in [A,B,C]} \tilde{D}(CDE) f_{[A,B,C,D,E]} + \dots \quad (36)$$

This process can be continued: at every next step one chooses the set  $T + \Delta T$  of the previous step as a new set  $T$ , and a group from the new set  $[T]$  is chosen as the set  $\Delta T$ .

Expanding all the pre-factors in terms of  $\sigma$  (see equation (25)) and comparing terms with the same powers of  $\sigma$ , we obtain, after setting  $\sigma = 1$ ,

$$\begin{aligned} f_{[A]} = & 1 - \sum_{B \in [A]} D_2(A, B) - \sum_{\{B,C\} \in [A]} D_3(A, B, C) + \sum_{B \in [A]} [D_2(A, B)]^2 \\ & - \sum_{\{B,C,D\} \in [A]} D_4(A, B, C, D) + 2 \sum_{\{B,C\} \in [A]} D_2(A, B) [D_2(A, C) + D_2(B, C)] \\ & - \sum_{B \in [A]} D_4(A, B) - \sum_{\{B,C\} \in [A]} D_4(A, B, C) \\ & + \sum_{\{B,C\} \in [A]} \{D_3(A, B, C) [4D_2(A, B) + D_2(B, C)] - D_5(A, B, C)\} \\ & - \sum_{\{B,C,D,E\} \in [A]} D_5(A, B, C, D, E) \\ & + \sum_{\{B,C,D\} \in [A]} \{6D_3(A, B, C) [D_2(A, D) + D_2(B, D)] \\ & + 3D_3(B, C, D)D_2(A, D) - D_5(A, B, C, D)\} + \dots \end{aligned} \quad (37)$$

The expression for the pre-factor  $f_{[A]}$  was obtained up to the fifth order with respect to overlap and with the terms ordered appropriately. Expansions for  $f_{[A,B]}$  and  $f_{[A,B,C]}$  are obtained up to the fourth order with respect to overlap using the same equations, (30), (35) and (36). Because in the final expression for the RDM-1 the pre-factors are multiplied by the linked ADs (with the open circle) which are also of some order with respect to overlap, third- and second-order expansions are needed for  $f_{[A,B]}$  and  $f_{[A,B,C]}$ , respectively, if the same order expression for the RDM-1 is to be derived. Then, one obtains

$$f_{[A,B]} = 1 - D_2(A, B) - \sum_{C \in [A,B]} [D_2(A, C) + D_2(B, C)] - \sum_{C \in [A,B]} D_3(A, B, C) \\ - \sum_{\{C,D\} \in [A,B]} [D_3(A, C, D) + D_3(B, C, D)] + \dots \quad (38)$$

$$f_{[A,B,C]} = 1 - [D_2(A, B) + D_2(B, C) + D_2(A, C)] \\ - \sum_{D \in [A,B,C]} [D_2(A, D) + D_2(B, D) + D_2(C, D)] + \dots \quad (39)$$

It is seen that in all orders the first-order term vanishes, i.e.  $a_1^{[T]} = 0$ .

Note that the choice of manifolds  $T$  and  $\Delta T$  is somewhat arbitrary. Any choice results in the same expansions. However, the method outlined above is, in our view, the simplest one which leads to a systematic derivation of the expansion coefficients for the pre-factors  $f_{[T]}$  with increasing number of groups in the set  $T$ .

## 5. Application to a quantum cluster embedding problem

### 5.1. Reduced density matrices and energy functional

To illustrate the method proposed above, we first obtain in detail the first three terms of the AD expansion of the RDM-1 and RDM-2. In the former case, we have

$$\rho(x; x') = \sum_A f_{[A]} \begin{array}{c} \text{A} \\ \circ \\ \text{B} \end{array} + \sum_{\{A,B\}} f_{[A,B]} \left[ \begin{array}{c} \text{A} \\ \circ \\ \text{B} \end{array} + \begin{array}{c} \text{A} \\ \circ \\ \text{B} \end{array} + \begin{array}{c} \text{A} \\ \circ \\ \text{B} \end{array} + \begin{array}{c} \text{A} \\ \circ \\ \text{B} \end{array} \right] \\ + \sum_{\{A,B,C\}} f_{[A,B,C]} \left[ \begin{array}{c} \text{A} \\ \circ \\ \text{B} \quad \text{C} \end{array} + \begin{array}{c} \text{A} \\ \circ \\ \text{B} \quad \text{C} \end{array} + \dots \right] + \dots \quad (40)$$

Only three pre-factors are needed; these are: (i)  $f_{[A]}$  (associated with the circle AD); (ii)  $f_{[A,B]}$  (a bubble AD with an open circle); and (iii)  $f_{[A,B,C]}$  (a triangle AD with an open circle). Other pre-factors can be obtained along the same lines. Note that pre-factors do not depend on the particular type (topology  $q$ ; see section 2) of the AD with an open circle; they only depend on the particular electronic groups (the set  $T$ ) involved in the diagram. Due to this, *the same* pre-factors will appear in the AD expansion of the RDM-2 as well. Several first terms of this latter expansion are shown below:

$$\rho(x, y; x', y') = \sum_A f_{[A]} \begin{array}{c} \text{A} \\ \bullet \\ \text{B} \end{array} + \sum_{\{A,B\}} f_{[A,B]} \left[ \begin{array}{c} \text{A} \\ \bullet \\ \text{B} \end{array} + \begin{array}{c} \text{A} \\ \bullet \\ \text{B} \end{array} + \dots \right] \\ + \sum_{\{A,B,C\}} f_{[A,B,C]} \left[ \begin{array}{c} \text{A} \\ \bullet \\ \text{B} \quad \text{C} \end{array} + \begin{array}{c} \text{A} \\ \bullet \\ \text{B} \quad \text{C} \end{array} + \dots \right] + \dots \quad (41)$$

The filled and open black circles designate the variables  $(x, x')$  and  $(y, y')$  of the RDM-2  $\rho(x, y; x', y')$ , respectively [14, 17]. Note that the order (with respect to overlap) of a diagram is exactly equal to the number of arrows on it. The above AD expansions of RDM-1 and RDM-2 allow us to sort out their terms starting with the lowest order with respect to overlap. Thus we can calculate the mean value of a symmetrical operator correct up the desired order of overlap.

The AD expansions for the RDM-1 and RDM-2 given above can be exploited in order to obtain an appropriate expression for the total energy of a many-electron system. The total Hamiltonian contains one- and two-electron parts,  $\hat{h}(1)$  and  $v(1, 2) = |x_1 - x_2|^{-1}$ . In this case it is well known [1] that the total energy can be written via the non-diagonal RDM-1 and a diagonal RDM-2 as follows:  $E = E_1 + E_2$ , where  $E_1 = \int \left[ \hat{h}(1) \rho(1; 1') \right]_{1'=1} d(1)$  and  $E_2 = \frac{1}{2} \int v(1, 2) \rho(1, 2; 1, 2) d(12)$ . Since the final expression is cumbersome, we shall only consider here the energy up to the second order with respect to overlap. Final expressions for the pre-factors given in section 4.2 enable one to write the energy correct up to the fifth order with respect to overlap, if required.

Thus, by truncating the AD expansions of RDM-1 and RDM-2, equations (40) and (41), at the second order with overlap and employing analytical expressions for the diagrams [14], we obtain the one- and two-electron parts of the total energy as follows:

$$E_1 = \sum_A E_{1A} + \sum_{A \neq B} S_{AB} E_{1A} - \sum_{A \neq B} \left[ \int \hat{h}(3) \rho_A(13; 23) \rho_B(2; 1) d(123) + \int \hat{h}(1) \rho_A(1; 2) \rho_B(2; 1) d(12) \right] \quad (42)$$

where  $E_{1A} = \int \left[ \hat{h}(1) \rho_A(1; 1') \right]_{1'=1} d(1)$  and

$$E_2 = \sum_A E_{2A} + \frac{1}{2} \sum_{A \neq B} (J_{AB} - K_{AB}) + \frac{1}{2} \sum_{A \neq B} \left[ S_{AB} (J_{AB} + 2E_{2A}) + \sum_{C(\neq A, B)} (S_{CA} + S_{CB}) J_{AB} \right] - \frac{1}{2} \sum_{A \neq B} \left\{ \int v(3, 4) [\rho_A(13; 23) \rho_B(24; 14) + \rho_A(134; 234) \rho_B(2; 1)] d(1-4) + 2 \int (v(3, 1) + v(3, 2)) \rho_A(13; 23) \rho_B(2; 1) d(123) \right\} - \sum_{A, B, C} \int \rho_A(3; 3) \left[ v(3, 2) \rho_B(1; 2) + \int v(3, 4) \rho_B(14; 24) d(4) \right] \rho_C(2; 1) d(123) \quad (43)$$

where  $E_{2A} = \frac{1}{2} \int v(1, 2) \rho_A(12; 12) d(12)$  is the total intra-electron–electron energy of group  $A$ ,  $S_{AB} = \int \rho_A(2; 1) \rho_B(1; 2) d(12)$  is the overlap between groups  $A$  and  $B$ , while  $J_{AB} = \int v(1, 2) \rho_A(1; 1) \rho_B(2; 2) d(12)$  and  $K_{AB} = \int v(1, 2) \rho_A(1; 2) \rho_B(2; 1) d(12)$  correspond to the Coulomb and exchange interaction between the electrons of the two electron groups.

Note that the one-particle operator here,  $\hat{h}(1)$ , includes the potential from all nuclei (cores) of the whole system, i.e. it also contains a single sum over all groups. We note that a well-behaved expression for the energy is then obtained by separating out these potentials from  $\hat{h}$  operators and then adding the interaction between the nuclei (cores) to the expression given above. This rearrangement is straightforward and, to save space, we do not give the final expression for the energy here. Note also that the first term in equation (42) and the first line in

equation (43) correspond to the strong orthogonality approximation [1, 16]. Therefore, the rest of the terms in the two expressions above result from the overlap effects between the electron groups.

### 5.2. Effective Hamiltonian of an embedded cluster

A promising application of the AD theory is to investigate the electronic structure of extended systems in which a process of interest is well localized (e.g. a point defect on a crystal surface or a reactive site of a biological molecule). Frequently, these types of problems can be solved using a cluster method in which the most important finite fragment of the whole system is treated quantum-mechanically, while the rest of the system (the surrounding environment region) is accounted for on a lower level of theory, the so-called *embedded cluster* method (see [15] and references therein).

As was already mentioned in the introduction, the group function theory is a natural method to derive the embedding equations for the quantum cluster, when the cluster is considered as a single electron group, while the rest of the system (the environment region) is broken down into individual groups in some specific way as well. Previously, this problem has only been solved [3] in the case of the strong orthogonality approximation [1]. The theory developed above can now be used to derive an effective Hamiltonian for the quantum cluster without this artificial restriction, in a general case. As we shall rely on the energy expression obtained in the previous subsection, the derived formulae will be valid up to the second order with respect to overlap between the group functions of the whole system.

For simplicity, we shall assume that the electron GFs in the environment region are ‘frozen’. This restriction can be easily lifted if desired. The reduced density matrices for the embedded cluster are expressed via the cluster wavefunction,  $\psi(x_1, \dots, x_N)$ , as

$$\rho(x_1, \dots, x_n; x'_1, \dots, x'_n) = \frac{N!}{(N-n)!} \int \psi(x_1, \dots, x_n, x_{n+1}, \dots, x_N) \times \psi(x'_1, \dots, x'_n, x_{n+1}, \dots, x_N)^* d(x_{n+1} \cdots x_N) \quad (44)$$

where  $N$  is the total number of electrons in the cluster.

The *optimum* cluster wavefunction,  $\psi$ , requires that the functional  $E[\psi] = E_1[\psi] + E_2[\psi]$  be stationary for the first-order variation of  $\psi$ , subject to the normalization condition  $\langle \psi | \psi \rangle = 1$ . To perform the variational calculation, it is necessary to separate out in the energy expression all terms involving the cluster RDMs of any order, express the latter via the cluster wavefunction according to equation (44) and then evaluate the variational derivative. This procedure results in the following effective Schrödinger equation for the cluster:  $\mathcal{H}^{\text{eff}} |\psi\rangle = \epsilon |\psi\rangle$ , where  $\mathcal{H}^{\text{eff}}$  is the corresponding effective Hamiltonian that takes account of the cluster environment. A rather lengthy calculation gives the following expression for  $\mathcal{H}^{\text{eff}}$ :

$$\mathcal{H}^{\text{eff}} = \mathcal{H} + \mathcal{H}^{\text{ovt}} \quad (45)$$

where

$$\mathcal{H} = \sum_i \left\{ \widehat{h}(i) + \sum_A [\widehat{J}_A(i) - \widehat{K}_A(i)] \right\} + \frac{1}{2} \sum'_{i,j} v(i, j) \quad (46)$$

is the Hamiltonian of the quantum cluster surrounded by an ‘orthogonal’ environment [3] (i.e. within the strong orthogonality approximation) with

$$\widehat{J}_A(i) = \int v(x_i, x) \rho_A(x; x) dx$$

$$\widehat{K}_A(i) = \int dx v(x_i, x) \rho_A(x_i, x) \widehat{P}_{x_i x}$$



being the usual Coulomb and exchange operators associated with group  $A$ , and

$$\mathcal{H}^{\text{ovr}} = \sum_i \widehat{\mathcal{O}}_1(i) + \frac{1}{2} \sum'_{i,j} \widehat{\mathcal{O}}_2(i, j) + \frac{1}{3!} \sum'_{i,j,k} \widehat{\mathcal{O}}_3(i, j, k) \quad (47)$$

a correction due to overlap effects. The latter includes corrections to the one- and two-particle operators,

$$\widehat{\mathcal{O}}_1(i) = \sum_A (\widehat{h}(x_i) + \widehat{J}_A(i)) S_A - \sum_{A \neq B} S_{AB} \widehat{J}_B(i) + \int dx \chi_1(x_i; x) \widehat{P}_{x_i x} \quad (48)$$

$$\widehat{\mathcal{O}}_2(i, j) = v(i, j) \sum_A S_A + \int dx (\chi_2(x_i, x_j; x) \widehat{P}_{x_i x} + (i \leftrightarrow j)) \quad (49)$$

where  $S_A = \int \rho(1; 2) \rho_A(2; 1) d(12)$  is the overlap integral between the cluster and group  $A$ , as well as a three-particle operator:

$$\widehat{\mathcal{O}}_3(i, j, k) = - \sum_A \int dx (v(x_j, x_k) \rho_A(x_i; x) + (i \leftrightarrow k) + (i \leftrightarrow j)) \widehat{P}_{x_i x}. \quad (50)$$

Note that operators  $\widehat{\mathcal{O}}_2(i, j)$  and  $\widehat{\mathcal{O}}_3(i, j, k)$  are symmetrical with respect to a permutation of the electronic coordinates. Here, all summations over  $A, B$  are performed over electronic groups of the environment, i.e. those that surround the cluster.

The operator  $\widehat{P}_{xy}$  replaces the variable  $x$  with  $y$  in whatever function stays on the right of it, i.e.  $\widehat{P}_{xy}\varphi(x) = \varphi(y)$ , that is it performs an exchange function. The corresponding expressions for the kernels  $\chi_1$  and  $\chi_2$  contain summations over the groups in the environment region and are given in the appendix for completeness.

It is seen from equations (45)–(47) that in the strong orthogonality approximation the environment provides an additional (to the isolated cluster Hamiltonian) one-particle operator that contains the Coulomb and exchange interaction between the cluster and every group  $A$  around it; see equation (46). Going beyond this approximation results in an additional nonlocal field, equation (48), modification of the electron–electron interaction within the cluster, equation (49), as well as in the appearance of a fictitious three-electron interaction in the cluster given by equation (50). The described modifications of the cluster Hamiltonian also appear in the strong orthogonality approximation if the environment regions is allowed to polarize [3]. In this case, however, the corresponding corrections are *local* and the cluster resembles a polaron. Although in the present consideration the environment region is frozen, one can see that taking into account overlap between wavefunctions of the quantum cluster and groups of the environment results in similar effects that involve, this time, *nonlocal* operators, i.e. contain *exchange* between the cluster and the environment.

The obtained general properties of the embedded quantum cluster problem should be taken into account for example when constructing model cluster Hamiltonians.

## 6. Conclusions

In this paper, we have developed a general method for calculating the pre-factors in the linked-AD expansion for the mean value of a symmetrical operator. This method is based on the expansion of the pre-factors in a power series with respect to overlap between different groups. The first three pre-factors have been obtained in detail. This progress makes the AD theory applicable to extended systems, and allows us to calculate the mean value of a symmetrical operator correct up to any preferred order with respect to overlap. In particular, an expression for the total energy of a many-electron system consisting of overlapping electron

groups has been obtained in detail that is exact up to the second order with respect to overlap. As a promising application, we have derived the effective Hamiltonian of a quantum cluster surrounded by overlapping electron groups (an embedding problem), that is correct up to the second order of overlap.

It is relevant to note that an expansion of the electron density with respect to overlap in the Hartree–Fock case (with no electron correlation within groups included) is well known [1]. It is obtained (see, e.g. [18]) by representing the overlap matrix  $\mathbf{S}$  as  $\mathbf{S} = \mathbf{1} + \mathbf{\Delta}$  and then expanding  $\mathbf{S}^{-1} = (\mathbf{1} + \mathbf{\Delta})^{-1}$  with respect to the matrix  $\mathbf{\Delta}$ ; the latter contains only overlap between different groups and zeros along the diagonal. The method developed in section 4.2 generalizes this expansion method for the case when group functions are linear combinations of Slater determinants, i.e. when intra-group correlation effects are accounted for in each group. However, it is also known (see, e.g. [18]) that the overlap expansion of the electron density in the Hartree–Fock case *diverges* if the overlap between groups is significant (more explicitly, if there is at least one eigenvalue of  $\mathbf{\Delta}$  which is larger than unity). Therefore, our general method should also have some limitations on its convergence and must be applied with care.

## Appendix

### A.1. Finite ring: an equivalent derivation of the electron density

In the Hartree–Fock theory [1], RDM-1 can be expressed explicitly in terms of orbitals and their overlap matrix,  $\mathbf{S}$ . Since in the ring only a product of two adjacent orbitals is nonzero, the following expression for the electron density (the diagonal elements of the RDM-1) can be obtained:

$$\begin{aligned} \rho(x) &= \sum_{i,j=1}^N \psi_i(x) (\mathbf{S}^{-1})_{ij} \psi_j(x) \\ &= \sum_{i=1}^N [\psi_i(x) (\mathbf{S}^{-1})_{ii} \psi_i(x) + \psi_i(x) (\mathbf{S}^{-1})_{i,i+1} \psi_{i+1}(x) \\ &\quad + \psi_{i+1}(x) (\mathbf{S}^{-1})_{i+1,i} \psi_i(x)]. \end{aligned} \quad (51)$$

Here

$$\mathbf{S} = \begin{bmatrix} 1 & \sigma & & & & & \sigma \\ \sigma & 1 & \sigma & & & & \\ & \ddots & \ddots & \ddots & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & \ddots & \ddots & \ddots & \\ & & & & \sigma & 1 & \sigma \\ \sigma & & & & & \sigma & 1 \end{bmatrix}_{N \times N} \quad (52)$$

is the overlap matrix between the ring orbitals. Note that all the omitted elements in the above expression are zeros. This convention is adopted hereafter. Then, the normalization integral,  $G_N^{\text{Ring}}$ , is simply given by the determinant of the matrix  $\mathbf{S}$ .

Similarly, the normalization integral for the chain is

$$G_N^{\text{Chain}} = \begin{vmatrix} 1 & \sigma & & & & & & & & & \\ \sigma & 1 & \sigma & & & & & & & & \\ & \ddots & \ddots & \ddots & & & & & & & \\ & & \ddots & \ddots & \ddots & & & & & & \\ & & & \ddots & \ddots & \ddots & & & & & \\ & & & & \sigma & 1 & \sigma & & & & \\ & & & & & \sigma & 1 & & & & \\ & & & & & & & \sigma & 1 & & \\ & & & & & & & & & \sigma & 1 \end{vmatrix}_{N \times N}. \quad (53)$$

In order to calculate the RDM-1 (51), one needs the corresponding elements of the inverse of the overlap matrix. Using the explicit structure of the matrix **S** given in equation (52), one obtains

$$(\mathbf{S}^{-1})_{i,i} = \frac{C_{i,i}}{\det \mathbf{S}} = \frac{G_{N-1}^{\text{Chain}}}{G_N^{\text{Ring}}} \quad (54)$$

$$(\mathbf{S}^{-1})_{i,i+1} = (\mathbf{S}^{-1})_{i+1,i} = \frac{C_{i,i+1}}{\det \mathbf{S}} = \frac{-\sigma G_{N-2}^{\text{Chain}} + (-1)^{N+1} \sigma^{N-1}}{G_N^{\text{Ring}}} \quad (55)$$

where  $C_{i,i}$  and  $C_{i,i+1}$  are co-factors of  $S_{i,i}$  and  $S_{i+1,i}$ , respectively. Using equations (54) and (55), we obtain for the electron density (51) an expression identical to equation (14).

Furthermore, owing to the symmetry of the determinants introduced above, it is possible to derive the same recurrence relations as equations (15) and (16). Equation (16) is obtained by opening the determinant of the matrix (52) along its first row (or column), while equation (15) is obtained in the same way from equation (53). The matrix algebra is rather cumbersome and we do not give it here. In contrast, one can appreciate that the algebra of the AD theory as described in section 3 appears to be much simpler.

### A.2. Kernels of the one- and two-particle interactions in the effective Hamiltonian of the quantum cluster

In this appendix we give detailed expressions for the kernels of the one- and two-particle operators (see equations (48) and (49)), of the embedding problem correct to the second order in overlap:

$$\begin{aligned} \chi_1(1; 2) = & - \sum_A \int \widehat{h}(3) \rho_A(13; 23) \, d(3) \\ & + \sum_A \left( E_{QM} + E_A + J_A + \sum_{B(\neq A)} J_{AB} + \widehat{h}(1) - \widehat{h}(2) \right) \rho_A(1; 2) \\ & - \sum_A \int [v(3, 1) + v(3, 2)] \rho_A(13; 23) \, d(3) \\ & - \frac{1}{2} \sum_A \int v(3, 4) \rho_A(134; 234) \, d(34) \\ & - \sum_{A \neq B} \left\{ \int v(3, 4) \rho_A(3; 3) \rho_B(14; 24) \, d(34) \right. \\ & + \int [v(3, 1) + v(3, 2)] \rho_A(3; 3) \rho_B(1; 2) \, d(3) \\ & \left. - \delta_{12} \int \left[ v(2, 5) \rho_A(5; 6) + \int v(2, 4) \rho_A(54; 64) \, d(4) \right] \rho_B(6; 5) \, d(56) \right\} \end{aligned}$$

and

$$\begin{aligned} \chi_2(1, 2; 3) = & - \sum_A \rho_A(1; 3) \widehat{h}(2) - \sum_{A \neq B} \int v(2, 4) \rho_A(4; 4) \rho_B(1; 3) d(4) \\ & - \sum_A \left\{ \int v(2, 4) \rho_A(14; 34) d(4) + [v(2, 1) + v(2, 3)] \rho_A(1; 3) \right\}. \end{aligned}$$

Here  $J_A = \int v(1, 2) \rho(1; 1) \rho_A(2; 2) d(12)$  is the Coulomb interaction between electrons of the cluster and group  $A$ ;  $E_{QM} = E_1^{QM} + E_2^{QM}$  with  $E_1^{QM} = \int [\widehat{h}(1) \rho(1; 1')]_{1'=1} d(1)$  and  $E_2^{QM} = \frac{1}{2} \int v(1, 2) \rho(1, 2; 1, 2) d(12)$  is the energy of the quantum cluster in the Coulomb field of the environment; similarly,  $E_A = E_1^A + E_2^A$  with  $E_1^A = \int [\widehat{h}(1) \rho_A(1; 1')]_{1'=1} d(1)$  and  $E_2^A = \frac{1}{2} \int v(1, 2) \rho_A(1, 2; 1, 2) d(12)$  is the energy of group  $A$ . Note that in both cases these energies do not include the nuclear–nuclear interaction that need to be added and subtracted to make the expression within the brackets in the second term of  $\chi_1(1; 2)$  to be well defined.

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