RUSSELL–SAUNDERS STATES ARISING FROM CONFIGURATIONS OF EQUIVALENT ELECTRONS

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A short method is given for the classification of the atomic Russell–Saunders coupling terms arising from an \((l)^N\) configuration consisting of \(n\) equivalent electrons. The method uses Young diagrams.

1. INTRODUCTION

The classification of the \(L–S\) coupling states of an atom or ion having more than two electrons outside a closed shell, is a cumbersome task if one uses the procedure of Slater \([1]\). An alternative and shorter route is presented which arrives at the same results.

In order to clarify the method a brief outline is presented to illustrate the connection between the irreducible representations of the general linear group \(GL(n)\) and the symmetric group \(S_n\). Let \(V\) be an \(n\)-dimensional linear space and \(V \otimes_k\) its \(k\)-fold (contravariant) tensorial product. As is well known \([2,3]\), we can characterize the irreducible \(GL(n)\)-subspaces of \(V \otimes_k\) with the aid of Young diagrams. This is so because all the partners in an irreducible representation of \(GL(n)\) can be generated by the action of a Young projector (ref. \([2]\), p. 102) on the basis of \(V \otimes_k\). Let the Young projector \(Y(\lambda)\) be constructed from the \(p\)th standard tableau \(\delta(\lambda)\) with shape \(\lambda\). Let \(Y(\lambda)\) operate on the tensor \(F_{\mu_1 \mu_2 \ldots \mu_k} \in V \otimes_k\), \(1 \leq \mu_j \leq n, 1 \leq j \leq k\). We can represent \(Y(\lambda) = \delta(\lambda)\) graphically by the Young tableau that is obtained by replacing the digit \(j\) by the index \(i_j\) in \(\delta(\lambda)\). By substituting in \(\delta(\lambda)\) all the possible index sets \(\{i_j | 1 \leq j \leq k, 1 \leq i_j \leq n\}\) we generate a basis set for an irreducible \(GL(n)\)-subspace.

Of course, not all the \((n^k)\) tensors yield linearly independent basis vectors; only those basis vectors are linearly independent in which the graphical representations satisfy the following two conditions:

1-1 Going from left to right in a row the indices may not increase;
1-2 Going down a column the indices must decrease.

The irreducible \(GL(n)\)-spaces generated in this way are irreducible under the subgroups \(U(n)\) and \(SU(n)\) of \(GL(n)\) as well. An immediate consequence of these rules for eigenfunctions of the total spin angular momentum \(S^2\) is that these functions can only be represented by Young diagrams of at most two rows. As is easy to prove, the Young diagram \([\frac{1}{2}(k+s), \frac{1}{2}(k-s)]\) corresponds to a \((s+1)\)-dimensional representation of \(SU(2)\).

2. \(L–S\) COUPLING CASE

Let us consider an atom with the electron configuration \((l)^K\). According to the Russell–Saunders rules we form from a product of \(k\) one-electron spin functions an eigenfunction \(X(1, \ldots, k)\) of \(S^2\) with eigenvalue \(\frac{1}{2}(s+1)\). This function can be represented by a Young tableau with pattern \([\frac{1}{2}(k+s), \frac{1}{2}(k-s)]\). Next we form a spatial product \(\psi(1, \ldots, k)\) of \(k\) orbitals with eigenvalue \(l(l-1)\) of \(L^2\), i.e., we construct an element of the \(k\)-fold tensorial product of the \((2l+1)\)-dimensional carrier space of the Irreducible representation \(D^l\) of the full rotation group \(O(3)\). If one now anti-symmetrizes the function \(\psi(1, \ldots, k) \otimes X(1, \ldots, k)\) according to the Pauli principle, one finds \([4]\) that the only non-vanishing components of \(\psi\) are those tensors that can be represented by Young tableaux with the shape \([\frac{1}{2}(l-k-s)^2, \frac{1}{2}(l-s)]\). Thus, the Pauli principle together with the fact that the atomic wavefunction ought to be an eigenfunction of \(S^2\) causes the spatial part of the wavefunction

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to belong to specific irreducible representation spaces of SU(2I + 1). As pointed out in the introduction, it is very easy to write down the spatial wavefunctions that satisfy this symmetry restriction. However, since the hamilton operator contains spatial electron-electron interaction terms, the total k-electron wavefunction ought to transform according to irreducible representations of the group O(3) ⊂ SU(2I + 1). That means that we have to decompose the irreducible SU(2I + 1)-subspaces with respect to O(3). It is possible, using a formula derived by Gosinski and Öhrn [5], to find out which irreducible O(3)-subspaces are contained in an irreducible SU(2I + 1)-space.

Their formula is however difficult to apply, because a knowledge of the characters of all the involved representations is required. A faster way is the following: write down the possible basis vectors of the irreducible SU(2I + 1) space that corresponds to a spin multiplicity s + 1. That is, construct all the possible tensors in the Young tableau representation using the shape \[2^{(k-s)}\] taking into account the rules 1-1 and 1-2. Tabulate these tensors according to the quantum number \(M_L\) of the z-component of the angular momentum. From this table it is immediately clear which representations are contained in the SU(2I + 1)-subspace.

In order to make the argument concrete the triplet functions of a (d)\(^4\) configuration are derived. The orbital part should transform according to the Young tableau \([2, 1^2]\), so we get Table 1. We see that a (d)\(^4\) configuration gives rise to the following triplets:

\[3_P, \ 3_P, \ 3_D, \ 3_F, \ 3_F, \ 3_G, \ 3_H.\]

One can check the total multiplicity \(f\) of the orbital state by modifying Robinson's formula (ref. [6], eq. 3.282) to give

\[
f = \frac{(s + 1)}{\frac{1}{2}(k + s)} + 1 \left(\frac{2I + 1}{\frac{1}{2}(k + s)}\right) \left(\frac{2I + 2}{\frac{1}{2}(k - s)}\right).
\]

In this example: \(s = 2, \ k = 4, \ I = 2\), hence \(f = (3.4)\frac{5}{1} = 45\). This agrees with the sum of the multiplicities of \(L\)-states:

\[
f = 2 \times 3 + 5 + 2 \times 7 + 9 + 11 = 45.
\]

**REFERENCES**

CLASSIFICATION OF INTERACTION OPERATORS
WITH RESPECT TO MANY-PARTICLE PERMUTATION SYMMETRY

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Two procedures are developed for the classification of interaction operators with respect to the permutation symmetry of a many (N) particle system, which is a necessary first step for deriving selection rules for matrix elements of spin dependent operators over many-particle wavefunctions. The first method, based on character relations in the symmetric group SN, is applied to one- and two-particle operators. The second, using Young diagrams is easily applied to the general case of n-particle interaction operators.

1. Introduction

Recently, Mushor [1] has derived selection rules for matrix elements of spin-dependent operators over many-electron wavefunctions, only using the property that such operators should be symmetric under permutations of the electrons, whereas the wavefunctions must be antisymmetric. The formalism works for symmetric wavefunctions as well and, therefore, can be applied to all systems containing N identical particles. It is based on the decomposition of the configuration space and the spin space separately into sub-spaces which span the irreducible representations of the symmetric group SN. A symmetric/antisymmetric wavefunction can be written as a sum of space functions which transform according to the irreducible representations of SN, each term multiplied by a spin function which is a basis vector of the same/the associate representation [2, 3]. If the wavefunction is an eigenfunction of the total spin operator S2 it corresponds to one specific irreducible representation. An analogous expansion can be made for the symmetric space--spin operators. After this decomposition of the wavefunctions and the operator, matrix elements can be calculated by integrating over space and spin coordinates separately and applying the Wigner-Eckart theorem for the permutation group. The reduced matrix elements describe the dynamics of the problem; the 3-j symbols contain all information regarding the symmetry. Matrix elements are zero, by vanishing of all 3-j symbols, if the threefold (inner) product of the irreducible representations spanned by the components of the bra-vector, the operator and the ket-vector does not include the symmetric representation. Since the operator only contains some specific irreducible representations of SN, this results in certain spin selection rules between the bra-vector and the ket-vector [1].

Methods for calculating non-vanishing 3-j symbols of the permutation group are given by Gallup [4], Sullivan [5], Cooper and Mushor [6]. In order to apply this procedure for the simplification of matrix elements explicitly one must find out which irreducible representations of SN are carried by the separate space and spin operators that constitute the N-particle interaction operator.

(i) One-particle operators

\[ \{ f(i) \mid i = 1, \ldots, N \} \]

are containted in the general interaction operator

\[ O_1 = \sum_{i=1}^{N} a(r_i) b(a_i) \]

which describes, e.g., spin orbit coupling or the Fermi hyperfine interaction.
(ii) Two-particle operators

\[ \{ f(i,j) | i = 1, ..., N; j = 1, ..., i - 1 \} \]

occur in interactions of the type

\[ O_2 = \sum_{i=1}^{N} \sum_{j=1}^{i-1} g(r_i, r_j) h(a_i, a_j). \]

They can be symmetric, \( f(i,j) = f(j,i) \), such as electron-electron, spin-spin coupling, or antisymmetric, \( f(i,j) = -f(j,i) \), in case of vector forces [7]. Non-symmetric two-particle operators, appearing in the spin-other-orbit coupling [8], can be written as sums of a symmetric and an antisymmetric part. An important class of two-particle spin operators is given by various effective hamiltonians, symmetric if they are of the Heisenberg type [9], antisymmetric in some more extended models [10].

(iii) Many-particle operators

\[ \{ f(i,j,k,...) | N \geq i > j > k > ... \geq 1 \} \]

involving interactions between more than two particles simultaneously, are not found in any “physical” hamiltonian. Still they do arise in effective interaction operators [11, 12].

In this letter we first use the character relations in order to prove the decomposition of the spaces spanned by the one-particle and two-particle operators, given by Musher [1] and Gallup [4]. We then treat the general case of \( n \)-particle operators in the \( N \)-particle Hilbert space.

2. One- and two-particle operators

(a) The one-particle operators:

\[ \{ f(i) | i = 1, ..., N \} \]  

(1)

carry an \( N \)-dimensional (reducible) representation \( \Gamma_1 \) of the symmetric group \( S_N \), which should be decomposed as a direct sum of irreducible representations. The character of this “permutation representation” \( \Gamma_1 \) for a certain class of \( S_N \) is derived by acting with a permutation from this class on the basis of 1-particle operators. The character equals the number of basis vectors mapped on itself. The class structure of \( S_N \) is completely determined by the cycle structure of the permutations, so that we can denote an arbitrary class of permutations consisting of \( k \) 1-cycles, \( l \) 2-cycles, \( m \) 3-cycles, etc. as:

\[ (k, l, m, ...) = (1^k, 2^l, 3^m, ...) \]

(2)

with

\[ k + 2l + 3m + ... = N. \]

If an operator from this class acts on the basis (1) all 2-cycles and larger cycles interchange operators. Each 1-cycle leaves one operator invariant. So the character of this permutation representation is:

\[ \chi_{\{\}}^{[N]} = k. \]

(3)

This character must be written as a sum of irreducible characters of \( S_N \), which can be derived by an algorithm described in Hamermesh [13]. Using the partition notation for the irreducible representations of \( S_N \) one finds that

\[ \chi_{\{\}}^{[N]} = 1. \]

(4)

\[ \chi^{[1,1]}_{\{\}} = k - 1. \]

(5)

so that the unique decomposition of the representation \( \Gamma_1 \) is given by:

\[ \Gamma_1 = [N] \oplus [N - 1, 1]. \]

(6)

(b) The two-particle operators:

\[ \{ f(i,j) | i = 1, ..., N; j = 1, ..., i - 1 \} \]  

(7)

span a \( \frac{1}{2} N(N - 1) \) dimensional representation. Let us again act with a permutation operator of the arbitrary class \( (1^k, 2^l, 3^m, ...) \) on all \( f(i,j) \). The \( k \) 1-element partitions leave a certain \( f(i,j) \) invariant if they include both \( i \) and \( j \). A sequence of \( k \) numbers contains \( \frac{1}{2} k(k - 1) \) different pairs \( (i,j) \) with \( i > j \), so that the 1-element partitions in the permutation operator leave \( \frac{1}{2} k(k - 1) \) operators \( f(i,j) \) unaltered. Besides, if we assume that the operators \( f(i,j) \) are all symmetric or all antisymmetric under the transposition \( (ij) \), an \( f(i,j) \) is left invariant or turned into \( -f(i,j) \), respectively, by this transposition. Therefore, every 2-cycle in the permutation operator maps one \( f(i,j) \) on itself in the symmetric case or on its negative for antisymmetric operators. Since all larger cycles necessarily interchange the \( f(i,j) \), the characters of the representations spanned by the symmetric and antisymmetric 2-particle operators are, respectively:

\[ \chi_{\{\}}^{[1,1]} = \frac{1}{2} k(k - 1) + l. \]

(8)
\[ \chi_{k,l,m, \ldots}^{\text{anti}} = \frac{1}{2}k(k-1) - l. \]  

Inspecting the irreducible characters of \( S_N \) given by Hamermesh [13]:

\[ \chi_{N-2,2} = \frac{1}{2}(k-1)(k-2) + l - 1, \]

\[ \chi_{N-2,1^2} = \frac{1}{2}(k-1)(k-2) - l, \]

we find that:

\[ \Gamma_2^\text{sym} = [N] \oplus [N-1,1] \oplus [N-2,2], \]

\[ \Gamma_2^\text{anti} = [N-1,1] \oplus [N-2,1^2]. \]

Although possible in principle, the treatment of three- or more-particle operators in a similar manner would become very laborious. For this reason we shall consider the general case of \( n \)-particle operators by an alternative technique, which basically is derived from character relations as well [14].

3. General theory

The general problem is to find, which representations are carried by the set of all \( n \)-particle operators in \( N \)-particle space (\( 1 \leq n \leq N \)). Without loss of generality the \( n \)-particle operators are assumed to be symmetry adapted with respect to the permutation group \( S_n \); they are irreducible tensor operators which transform according to the representation \( [\lambda] \) of \( S_n \) (i.e., the symmetric or the antisymmetric one in case of 2-particle operators). If this would not be the case for any practical set of operators we could always expand them as linear combinations of such symmetry adapted operators. We denote these operators by:

\[ \{ f_k^{[\lambda]}(I_n) \}_{k=1, \ldots, f_\lambda}, \]

where \( I_n \) stands for a set of \( n \) different particle coordinates (taken from the total set \( I_N \) of \( N \) particle coordinates) and \( f_\lambda \) is the dimension of the irreducible representation \( [\lambda] \). Special cases of this formula are given by the expressions (1) and (7). We factorize the \( N \)-particle Hilbert space as a twofold tensorial product, one factor being the space of functions on \( I_n \), the other one the space of functions on the set of coordinates which do not occur in \( I_n \). This difference set is denoted by \( I_N \setminus I_n \). This factorization of the \( N \)-particle Hilbert space corresponds to an equivalent factorizing of the operators on this space. So we write the operators \( f_k^{[\lambda]}(I_n) \) in \( N \)-particle space as:

\[ f_k^{[\lambda]}(I_n) \otimes 1(I_N \setminus I_n), \]

where \( 1(I_N \setminus I_n) \) stands for the identity operator in the space of the particles in the difference set \( I_N \setminus I_n \).

Consider a particular one of these operators, for instance:

\[ f_k^{[\lambda]}(1, \ldots, n) \otimes 1(n+1, \ldots, N). \]

It is apparent that \( 1(n+1, \ldots, N) \) transforms according to the symmetric representation of \( S_{N-n} \), corresponding to the partition \( [N-n] \). Since \( f_k^{[\lambda]} \) transforms according to the representation \( [\lambda] \) of \( S_n \), the operator given by (16) must carry the (irreducible) representation \( [\lambda] \otimes [N-n] \) of the productgroup \( S_n \times S_{N-n} \), which is a subgroup of \( S_N \). The total set of \( n \)-particle operators in \( N \)-particle space can be generated from this particular operator (16) by the coset generators of \( S_n \times S_{N-n} \) in \( S_N \). The representation spanned by these operators is thus obtained by inducing the representation \( [\lambda] \otimes [N-n] \) to the permutation group \( S_N \). It is symbolically denoted by \( [\lambda] \otimes [N-n] \uparrow S_N \).

The rules for decomposing such representations which have been given by Littlewood [14], are as follows: After writing the Young diagram for the irreducible representation \( [\lambda] \), one adds the boxes of the (single row) diagram \( [N-n] \) one by one to the boundary of \( [\lambda] \) so that:

(i) the augmented diagram remains a proper Young diagram,

(ii) not more than one box is added to each column of \( [\lambda] \).

For example, let us treat the two-electron operators again (\( n = 2 \)). If they are symmetric, \( [\lambda] = [2] \) and the decomposition reads:

\[ \Gamma_2^\text{sym} = [2] \otimes [N-2] \otimes [N] \oplus [N-1,1] \oplus [N-2,2]. \]

For antisymmetric operators with \( [\lambda] = [1^2] \), we find:

\[ \Gamma_2^\text{anti} = [1^2] \otimes [N-2] \otimes [N-1,1] \oplus [N-2,1^2]. \]
4. Conclusion

We have derived two methods for decomposing the representation spanned by the \( n \)-particle operators in \( N \)-particle Hilbert space into irreducible representations of \( S_N \). The second method using Young diagrams is much easier to handle than the first one, based on character relations. Since this decomposition can be applied to both the space and spin operators separately, general spin-dependent operators can be decomposed and their matrix elements simplified by the techniques described in the introduction.

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Transformation Properties of Antisymmetric Spin Eigenfunctions under Linear Mixing of the Orbitals

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After recalling the duality between the general linear group $GL(m)$, represented by its $N$-fold inner product, and the permutation group $S_N$, we have given a survey of its quantum chemical consequences. It causes the one-to-one correspondence between the total spin quantum number and the permutation symmetry of $N$-electron spin functions, and, via the Pauli principle which imposes permutation symmetry on the spatial part also, it leads to specific properties of antisymmetric spin eigenfunctions under orbital transformations. Such functions can be classified according to the irreducible representations of $GL(m)$. For special orbital transformations, often occurring in quantum chemistry, which mix only orbitals in different subsets among each other, we have derived how the transformation of the $N$-electron wavefunctions simplifies, by a reduction of the representations of $GL(m)$. The theory is illustrated by an example and some applications are discussed.

I. INTRODUCTION

The last years have shown among theoretical chemists a renewed interest in the applications of the permutation group to many-body problems. Kotani et al.\textsuperscript{1} and Johnston\textsuperscript{2} revived the early work of Hund, London, Heitler, Wigner, and, especially, Weyl.\textsuperscript{3} The theory was worked out further by Matsen and co-workers\textsuperscript{4} in a series on “spin-free quantum chemistry”. It was applied to variational calculations by Goddard,\textsuperscript{5} Harris,\textsuperscript{6} and Morrison and Gallup,\textsuperscript{7} whereas van der Avoird,\textsuperscript{8} Amos and Mushere\textsuperscript{9} and Klein\textsuperscript{10} continued the work of Eisen-schitz and London\textsuperscript{11} on permutation symmetry adapted perturbation theory.

One aspect of the theory is missing in this recent work: The duality between the representations of the permutation group $S_N$ on the one hand and the general linear group in $m$ dimensions $GL(m)$ on the other. These groups are related via their representations carried by $N$th rank tensor space. Still, this relationship is of paramount importance. In the first place it forms the basis of the connection between the spin quantum number and permutation symmetry: $N$-electron eigenfunctions of $S^2$, which carry irreducible representations of $GL(2)$ and its subgroup $SU(2)$, must span certain irreducible representations of the permutation group $S_N$. Secondly, the Pauli principle, requiring the antisymmetry of the total many-electron wavefunction, imposes the permutation symmetry on the spatial part as well. Using the duality between $S_N$ and $GL(m)$ again, it follows that the spatial function must have specific behavior under orbital transformations, which can be studied by considering the group $GL(m)$.

The global representation theory of $GL(m)$ on which this paper is based, originates from Schur and has been outlined in great detail by Weyl,\textsuperscript{3} who was the first to recognize its quantum mechanical importance. The books by Boerner\textsuperscript{12} and Murnaghan\textsuperscript{13} give a good survey of the mathematical background.

In many practical cases one is not interested in general orbital transformations, but, given a partitioning of the orbitals in different subsets, in those transformations which mix only orbitals belonging to the same subset. Examples are given by:

- the hybridization of orbitals on the separate atoms in a molecular Valence Bond calculation,
- orthogonalization of orbitals in different sets by intraset transformations (According to the pairing theorem such transformations can orthogonalize an orbital in a definite set to all orbitals except one in another set.),
- mixing schemes in pair-correlated DODS methods, such as AMO\textsuperscript{14} or extended VB,\textsuperscript{15}
- Roothaan’s procedure\textsuperscript{16} of simplifying the open-shell Hartree–Fock problem by transformation of the closed and open shell orbitals separately.

In this paper we have derived which antisymmetrized eigenfunctions of $S^2$ are mixed under such “partitioned” orbital transformations and indicated a way to calculate the mixing coefficients. The theory is outlined for a system consisting of two parts, but, by induction, is easily extensible to many subsystems. It could be considered as a supplement to Matsen and Klein’s “aggregate theory,”\textsuperscript{17} regarding the transformation properties of aggregate states. Before we proceed to our results we shall give a brief survey of the general formalism which is extensively, but rather untrasparently, described by Weyl.\textsuperscript{3}

II. REVIEW OF THE DUALITY BETWEEN $S_N$ AND $GL(m)$

For the construction of the wavefunction, let us begin with an $m$-dimensional orbital set spanning a linear
space \( V_m^* \),
\[
V_m^* = \{ \phi_i(r) \mid i = 1, \ldots, m \}. \tag{1}
\]
The general linear group \( GL(m) \) consists of all non-singular linear mappings (orbital transformations) \( \gamma \),
\[
\gamma : V_m^* \rightarrow V_m^*. \tag{2}
\]
Formation of all \( N \)-electron product functions amounts to constructing a tensorial product space spanned by \( N \)th rank (purely contravariant) tensors,
\[
V_m^* \otimes N^* = \{ \Phi_{i_1, i_2, \ldots, i_N} \mid i_1, i_2, \ldots, i_N = 1, \ldots, m \}, \tag{3}
\]
where
\[
\Phi_{i_1, i_2, \ldots, i_N} = \phi_{i_1}(r_1) \otimes \phi_{i_2}(r_2) \otimes \cdots \otimes \phi_{i_N}(r_N).
\]
Similarly, the \( N \)-electron spin space \( V_s^* \otimes N^* \) is an \( N \)-fold tensorial product of 2-dimensional one-electron spin spaces \( V_s^* \).

The linear space \( V_m^* \otimes N^* \) is stable under both the permutation group \( S_N \) and the \( N \)-fold inner product group \( [GL(m)]^N \). The latter consists of the tensor products of mappings \( [\gamma]^N \),
\[
[\gamma]^N : V_m^* \otimes N^* \rightarrow V_m^* \otimes N^*, \tag{4}
\]
which are defined by
\[
[\gamma]^N \Phi_{i_1, i_2, \ldots, i_N} = \gamma \phi_{i_1}(r_1) \otimes \gamma \phi_{i_2}(r_2) \otimes \cdots \otimes \gamma \phi_{i_N}(r_N), \tag{5}
\]
that is, by a simultaneous transformation of all orbitals in \( \Phi_{i_1, i_2, \ldots, i_N} \) under \( \gamma \). If \( D(\gamma) \) is the matrix of \( \gamma \), then \( [D(\gamma)]^N \), the \( N \)th power Kronecker product of \( D(\gamma) \), is the matrix of \( [\gamma]^N \). The group consisting of these Kronecker product matrices is a faithful representation of \( GL(m) \) (and of the isomorphic group \( [GL(m)]^N \)) carried by \( N \)th rank tensor space. This tensor space can be decomposed with respect to the permutation group \( S_N \) using the matrix group elements or Wigner operators (which generate minimal ideals of the group algebra of \( S_N \)):
\[
W_{ij}^{[N]} = (f_{ij}/N!) \sum_{P \in S_N} D_{ij}^{[N]}(P^{-1}) P. \tag{6}
\]
Here \( D_{ij}^{[N]} \) is a matrix element of the \( f_{ij} \) dimensional irreducible matrix representation \( [\lambda] \) of \( S_N \) (which can be denoted by a partition of \( N \)). Because the elements of \( S_N \) commute with all the elements of the group \( [GL(m)]^N \), it follows that a complete reduction of \( V_m^* \otimes N^* \) is \( S_N \) along the following complete reduction under \( [GL(m)]^N \) and, consequently, under \( GL(m) \):
\[
V_m^* \otimes N^* = \sum_{\text{partitions of } N} \oplus R^{(\lambda)} \tag{7}
\]
with
\[
R^{(\lambda)} = \sum_{i=1}^{n(\lambda)} \bigoplus R^{(\lambda)}_i = \sum_{j=1}^{f_{ij}} \bigoplus R^{(\lambda)}_j.
\]
\( R^{(\lambda)} \) spans the \( f_{ij} \) dimensional representation \( [\lambda] \) of \( S_N \) which occurs \( n(\lambda) \) times in \( V_m^* \otimes N^* \), whereas \( R^{(\lambda)} \) spans the \( n(\lambda) \) dimensional representation \( \lambda \) of \( GL(m) \) occurring \( f_{ij} \) times. Here Robinson's notation is used. Both dimensions, \( f_{ij} \) and \( n(\lambda) \), are easily calculated by means of the hook graphs and \( m \) graphs, respectively. Schematically this decomposition \( (7) \) is shown in Fig. 1.

Henceforth we assume that the different spaces \( R^{(\lambda)}, i = 1, \ldots, n(\lambda) \), which span the irreducible representations \( [\lambda] \) of \( S_N \), carry identical matrix representations. Weyl's proof shows that, in this case, the spaces \( R^{(\lambda)}, i = 1, \ldots, f_{ij} \), carry identical matrix representations \( D^{(\lambda)} \) of \( GL(m) \), so that we obtain the following decomposition of \( [D(\gamma)]^N \):
\[
[D(\gamma)]^N = \sum_{\text{partitions of } N} \oplus f_{ij} D^{(\lambda)}(\gamma). \tag{8}
\]
Since the elements of \( D^{(\lambda)}(\gamma) \) are integral functions (\( \lambda \)th order homogeneous polynomials) of the elements of \( D(\gamma) \), these irreducible representations of \( GL(m) \) are called integral. The reason that this one-to-one correspondence between the irreducible representations of \( S_N \) and \( GL(m) \) has important consequences in the quantum mechanics of \( N \)-electron systems is explained in the next two sections.

III. SPIN QUANTUM NUMBER AND PERMUTATION SYMMETRY

The \( \xi \)-component of the spin operator, \( S_\xi \), for one electron is related to the unitary mappings in two-dimensional spin space \( V_s^* \) by
\[
U_\xi(\phi) = \exp(i\phi S_\xi), \tag{9}
\]
where $U(\phi)$ can be thought to represent a rotation around the $\xi$ axis over angle $\phi$. These "rotations" form the group $SU(2)$ of all two-dimensional unitary transformations with unit determinant. In case of $N$ electrons the same formula (9) holds for the tensor product operators $[U(\phi)]^N$, constituting the group $[SU(2)]^N$ of mappings in $V^* \otimes N$.

Using Formula (9) it is easily proved that the group $[SU(2)]^N$ commutes with the total spin operator $S^z$ and, invoking Schur's lemma, that $N$-electron spin functions which are basis vectors for the irreducible representations of $[SU(2)]^N$, and of $SU(2)$, are eigenfunctions of $S^z$. The duality between the representations of $[U(2)]^N$ and $N$ and the property that irreducible representations of $U(2)$ stay irreducible under the subduction $U(2) \downarrow SU(2)$, then leads to the one-to-one correspondence between the irreducible representations of $S_N$ and the total spin quantum number.

Eigenfunctions of $S^z$ are basis vectors for the irreducible representations of $S_N$, corresponding to partitions of $N$, graphically represented by Young diagrams. The dimensionality 2 of the space spanned by these functions of $S_N$ for $N=1$, $2$, and the index $j=1$, $\cdots$, $f_{N+\delta,N-N-\delta}$.

**IV. TRANSFORMATION PROPERTIES OF THE SPATIAL WAVEFUNCTIONS**

If one neglects spin-dynamics, then $S$ and $M_z$ are good quantum numbers and the spin part of the $N$-electron wavefunction must be an eigenfunction of $S^z$. In order to construct the spatial wavefunction one must first select an appropriate configuration $|\Phi_{N,w}|$, where $N$ corresponds to the set of specific orbital indices $N_i = \{i_1, i_2, \cdots, i_N\}$. The total $N$-electron wavefunction, which must be antisymmetrized according to the Pauli principle, can then be written as

$$\Psi_{N,w,S,M_z} = \sum_{i_1} |[N/2+S,N/2-S], M_z, i_1 \rangle \otimes W_{N,w}^{[N/2+S,N/2-S]} |\Phi_{N,w} \rangle.$$  

In this expression $[2^{N/2-S}, 12^S]$ is the associate (two-column) representation of $[\sqrt{N}/2+S, \sqrt{N}/2-S]$. The index $k$ of the Wigner operator has to be chosen such that the resulting tensor is not equal to zero. In general, several choices of $k$, resulting in tensors with different parentage, are possible.

Summarizing, it follows that spin symmetry together with the Pauli principle imposes definite permutation symmetry on the spatial part of the wavefunction. The latter symmetry in turn, because of the duality between $S_N$ and $GL(m)$, causes a reduction of $V^* \otimes N$ under $GL(m)$.

When neglecting spin terms in the Hamiltonian, a general Hamiltonian matrix element takes the form

$$\langle \psi_{I,w',S',M',I'} | H | \psi_{I,w,S,M,I} \rangle = \delta_{S' \otimes M', M, I} \beta \delta_{I', I} + \gamma \delta_{I' \otimes M', M, I} + \delta_{I' \otimes M', M, I} \Phi_{I,w},$$

where $[\lambda]$ stands for $[2^{N/2-S}, 12^S]$.

For arriving at this result we used the property that the Wigner operators commute with $H$ and the relation

$$W_{N,w}^{[N/2+S,N/2-S]} = \delta_{[N/2+S,N/2-S]} \Phi_{N,w}.$$  

Formulas (12) and (13) show in the first place that the carrier spaces $R_j(N)$, $j=1, \cdots, f_{N,w}$, of $GL(m)$ are non-interacting for different ($\lambda$) and different $j$. Secondly, instead of writing the matrix elements over antisymmetric space–spin functions $|\psi\rangle$, one can also write matrix elements over the space functions $W_{N,w}^{[N/2+S,N/2-S]} |\Phi_{N,w} \rangle$ only. The reason is that the matrix elements over such space functions are independent of $j$, and identical (except for multiplication by a constant) to the matrix elements over the space–spin functions. Concluding, we can take just one of the carrier spaces $R_j(N)$ of $GL(m)$ in order to construct all matrix elements in the secular problem. Neglecting spin dynamics, we may replace the Pauli principle and the spin symmetry by the single postulate: A physically allowable $N$-electron spatial wavefunction must be expanded in partner basis elements of an integral representation of $GL(m)$, characterized by a Young diagram with an at most two columns.

Although this postulate is equivalent to Matsen’s, which concerns the permutation group $S_N$, the formulation in terms of $GL(m)$ emphasizes directly the spatial transformation properties of the wavefunction. This postulate has one drawback: We change the degeneracy of the system from $2S+1$ to $f_{N,w}^{[N/2+S,N/2-S]}$, where the latter degeneracy cannot be resolved by any physical means whatever (Ref. 3, p. 321).

Let us illustrate the quantum chemical application of this theory by an example. The $O_2$ molecule counts 10 atomic orbitals in the $K$ and $L$ shells that can be considered in a valence bond calculation, or the same number of molecular orbitals if we start with an MO treatment on that basis. Suppose we wish to construct an antisymmetric wavefunction for the triplet ground...
state of $O_2$ containing 16 electrons. This triplet function must be a basis element of the representation $(2^2, 1^2)$ of $GL(10)$. A simplification is obtained by noting that this representation has the same dimension as the representation $(2^2, 1^2)$ of $SU(10)$, which is equivalent to the "hole" representation $(2, 1^2)$ of $SU(10)$.

This hole representation is defined such that its Young diagram added to the original diagram as in Fig. 2 yields the Young diagram for $m$ doubly occupied orbitals.

The dimension $n_{(\bar{S}, \bar{L})}$, which equals the number of triplet configurations that can be constructed from the given orbital basis, is easily calculated by Robinson's formula

$$n_{(\bar{S}, \bar{L})} = \frac{G_{(\bar{S}, \bar{L})}(m)}{H_{(\bar{S}, \bar{L})}},$$

where $G_{(\bar{S}, \bar{L})}(m)$ is the product of numbers in the $m$ graph and $H_{(\bar{S}, \bar{L})}$ is the product of hook lengths. The dimension is 990.

This means that an orbital transformation of the original 10 orbital basis set, for instance a Löwdin orthogonalization of the VB orbitals or a DODS mixing of the MO's, would mix 990 triplet states of $O_2$. If the applied orbital transformation $D(\gamma)$ is predetermined, as for the Löwdin orthogonalization, the weights of all mixed configurations are fixed: they are the matrix elements of $D(\gamma)$

$$D(\gamma)_{(nN-m^2)},$$

In the case of the DODS procedure, the matrix elements of $D(\gamma)$ are used as variation parameters. The theory of this section then tells immediately that the DODS approach is equivalent to a full configuration interaction with somewhat restricted CI coefficients that are homogeneous polynomials of the DODS parameters.

V. PARTITIONED ORBITAL TRANSFORMATIONS

So far we have outlined the basic theory derived by Schur and Weyl. From this theory follows the manner in which an antisymmetric spin eigenfunction behaves under arbitrary orbital transformations. In many practical cases, however (examples are given in the introduction), one can divide the orbitals in different subsets and restrict the transformations between orbitals of the same subset. In these cases the matrix $D(\gamma)$ has a blocked form. We have derived explicitly how the transformation of the many-electron wave-

Fig. 2. Young diagram for the triplet $(S = 1)$ state of $O_2$; number of electrons $N = 16$, number of orbitals $m = 10$.

function simplifies under such orbital transformations. The result is described in this section for a two-subset partitioning of the orbital set, but, by induction, can be easily extended to the general case.

A division of the orbital set into two subsets is equivalent to the following decomposition of the orbital space:

$$V_m = V_{m_1} \oplus V_{m_2}.$$  

We consider orbital transformations of the form

$$\gamma = \gamma_1 \oplus \gamma_2,$$  

where $\gamma_1$ is the restriction of $\gamma$ to $V_{m_1}$ and $\gamma_2$ to $V_{m_2}$. The mappings $\gamma$ of this form constitute a group which we denote by $GL(m_1 + m_2)$. Since $m_1 + m_2 = m$, this group is clearly a subgroup of $GL(m)$. Thinking in terms of matrices instead of linear mappings, $GL(m_1 + m_2)$ can be defined as the group of matrices with the blocked structure

$$D(\gamma) = D(\gamma_1) \oplus D(\gamma_2),$$  

where $D(\gamma_1)$ is a $m_1 \times m_1$ matrix and $D(\gamma_2)$ a $m_2 \times m_2$ matrix.

The problem we have to solve is to find the behavior of the irreducible representations $\lambda$ of $GL(m)$ under the subduction $GL(m) \downarrow GL(m_1 + m_2)$. First we decompose the $N$th rank tensor space $V_m \otimes^N$ by a generalization of Newton's binomial theorem for noncommuting factors:

$$V_m \otimes^N = (V_{m_1} \otimes V_{m_2}) \otimes^N = \sum_{n=0}^{N} \sum_{i=1}^{\binom{N}{i}} \oplus C_i(V_{m_1} \otimes) \otimes (V_{m_2} \otimes)^{N-i}.  \quad (18)$$

The elements $C_i \in S_N$ which take care of the proper ordering of the factors in the tensorial products are the coset generators of the subgroup $S_n \otimes S_{N-n}$ in $S_N$. Note
that this decomposition of $V_n \otimes N$ is joined by a reduction of $[\gamma]^N \in [GL(m_1 + m_2)]^{\otimes N}$, namely,

$$[\gamma]^N V_n \otimes N = ([\gamma_1 V_{m_1} \otimes \gamma_2 V_{m_2}] \otimes N$$

$$= \sum_{n=0}^{N^n} \sum_{k=1}^{N^{N-n}} \theta C_k \left( [\gamma_1 V_{m_1}] \otimes N \right) \otimes \left( [\gamma_2 V_{m_2}] \otimes N^{N-n} \right)$$

$$= \sum_{n=0}^{N^n} \sum_{k=1}^{N^{N-n}} \theta C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} (V_{m_1} \otimes N)$$

$$\otimes (V_{m_2} \otimes N^{N-n})$$

$$= \sum_{n=0}^{N^n} \sum_{k=1}^{N^{N-n}} \theta C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} C_{k-1}^{-1}$$

$$\times C_k (V_{m_1} \otimes N) \otimes (V_{m_2} \otimes N^{N-n}).$$

Hence,

$$[\gamma_1 : \otimes N^n] = \sum_{n=0}^{N^n} \sum_{k=1}^{N^{N-n}} \theta C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} C_{k-1}^{-1}$$

where the summand is the restriction of $[\gamma_1 : \otimes N^n]$ to $C_k (V_{m_1} \otimes N) \otimes (V_{m_2} \otimes N^{N-n}).$

If we choose the basis elements in each of the spaces $C_k (V_{m_1} \otimes N) \otimes (V_{m_2} \otimes N^{N-n})$ such that they are obtained from an original basis in $\left( V_{m_1} \otimes N \right) \otimes (V_{m_2} \otimes N^{N-n})$ by the permutations $C_k$, it follows that all elements $C_k [\gamma_1]^n \otimes [\gamma_2]^{N-n} C_{k-1}$ for

$$k = 1, \ldots, \binom{N}{n}$$

have the same matrix,

$$[D(\gamma_1)]^N \otimes [D(\gamma_2)]^{N-n}. \tag{21}$$

This is easily proved since $C_k$ is a linear operator which does not act on the transformation coefficients of $[D(\gamma_1)]^N \otimes [D(\gamma_2)]^{N-n}$. We thus arrive at a reduction of the matrix representation of $GL(m)$ carried by the complete tensor space $V_n \otimes N$ under $GL(m_1 + m_2)$.

We must now look for the reduction of the irreducible representations $(\lambda)$ of $GL(m)$ under $GL(m_1 + m_2)$. To this end we reduce the spaces $V_{m_1} \otimes N$ and $V_{m_2} \otimes N^{N-n}$ according to Formula (7):

$$V_{m_1} \otimes N = \sum_{(\mu) \in \text{partitions of } N} \sum_{i=1}^{f_{(\mu)}} \otimes R^{(i)}_{\mu},$$

$$V_{m_2} \otimes N^{N-n} = \sum_{(\nu) \in \text{partitions of } N-n} \sum_{j=1}^{f_{(\nu)}} \otimes R^{(j)}_{\nu}, \tag{22}$$

where $R^{(i)}_{\mu}$ is irreducible under $[GL(m_1)]^{\otimes N}$ and $R^{(j)}_{\nu}$ is irreducible under $[GL(m_2)]^{\otimes N-n}$. Therefore the tensor product space $R^{(i)}_{\mu} \otimes R^{(j)}_{\nu}$ is irreducible under $[GL(m_1)]^{\otimes N} \otimes [GL(m_2)]^{\otimes N-n}$ and, consequently, under $GL(m_1 + m_2)$. Since we just derived [see Expression (21)] that all spaces $C_k (V_{m_1} \otimes N) \otimes (V_{m_2} \otimes N^{N-n})$ span the same matrix representation of $GL(m_1 + m_2)$, it follows that all spaces $C_k (R^{(i)}_{\mu} \otimes R^{(j)}_{\nu})$ for

$$k = 1, \ldots, \binom{N}{n}, \quad i = 1, \ldots, f_{(\mu)}, \quad j = 1, \ldots, f_{(\nu)}$$

are irreducible under $GL(m_1 + m_2)$ and span the same matrix representation $D^{(i)}_{\mu} \otimes D^{(j)}_{\nu}$.

Let us imagine that we place the $n(\mu) \times n(\nu)$ basis vectors of $R^{(i)}_{\mu} \otimes R^{(j)}_{\nu}$ in rows. Taking these rows for $i = 1, \ldots, f_{(\mu)}$, $j = 1, \ldots, f_{(\nu)}$, we obtain a scheme comparable to Fig. 1. We construct identical schemes for the spaces $C_k (R^{(i)}_{\mu} \otimes R^{(j)}_{\nu})$ and place these directly under the first scheme, getting

$$\binom{N}{n}$$

blocks with each $f_{(\mu)} \times f_{(\nu)}$ rows. As shown above, each row carries the same irreducible matrix representation $D^{(i)}_{\mu} \otimes D^{(j)}_{\nu}$ of $GL(m_1 + m_2)$. Using Weyl's result [Eq. (7)] again, we find that each column in the first block spans the irreducible representation $[\mu] \otimes [\nu]$ of $S_N \otimes S_{N-n}$. The columns of the next blocks are generated from the first block by the coset generators $C_k$ of $S_N \otimes S_{N-n}$ in $S_N$. We can prove that a full column spans the induced representation of $S_N$ denoted by $[\mu] \otimes [\nu] \uparrow S_N$. Every one of the $n(\mu) \times n(\nu)$ different columns spans an identical induced representation, thus assuring that all these induced representations can be reduced by the same basis transformation. But, if we perform the same basis transformation on all columns, we do not disturb the matrix representation of $GL(m_1 + m_2)$ afforded by the rows.

Let the reduction of every column be written as follows:

$$[\mu] \otimes [\nu] \uparrow S_N = \sum_{(\lambda) \text{ partitions of } N} m_{\mu \nu \lambda} [\lambda], \tag{23}$$

and let us perform on the columns the basis transformation corresponding to this reduction. In our scheme we then have blocks in which the columns span the irreducible representations $[\lambda]$ of $S_N$, the same block appearing $m_{\mu \nu \lambda}$ times. The rows still span the representation $D^{(i)}_{\mu} \otimes D^{(j)}_{\nu}$ of $GL(m_1 + m_2)$. This result is
expressed mathematically as

\[
\sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(R_{\mu}\otimes R_{\nu}) = \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(R_{\mu}\otimes R_{\nu}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}) = \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(R_{\mu}\otimes R_{\nu}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}).
\]

Note that the space \(R_{\mu}\otimes R_{\nu}\) cannot be written as a tensor product, although it spans the representation \(D^{(\lambda)} \otimes D^{(\sigma)}\).

We now consider the complete reduction of the full space \(V_m \otimes N\) under \(GL(m_1 + m_2)\):

\[
V_m \otimes N = \sum_{n=0}^{N} \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes (V_{\nu}\otimes^{N-n}) \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\sigma(R_{\mu}\otimes R_{\nu}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}).
\]

Substituting Formula (24) yields

\[
V_m \otimes N = \sum_{n=0}^{N} \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes (V_{\nu}\otimes^{N-n}) \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\sigma(R_{\mu}\otimes R_{\nu}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}).
\]

Comparing this to the original reduction of \(V_m \otimes N\) under \(GL(m)\),

\[
V_m \otimes N = \sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}),
\]

we find

\[
R_{\mu}(\lambda) = \sum_{n=0}^{N} \sum_{\lambda} \sum_{\mu} \sum_{\nu} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}).
\]

This reduction is accompanied by a decomposition of the matrix representation:

\[
D^{(\lambda)}(\gamma_1 \otimes \gamma_2) = \sum_{n=0}^{N} \sum_{\lambda} \sum_{\mu} \sum_{\nu} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}) \otimes D^{(\lambda)}(\gamma_1) \otimes D^{(\lambda)}(\gamma_2).
\]

With this result we have fulfilled our aim: the decomposition of the irreducible representations \(\langle \lambda \rangle\) of \(GL(m)\) with respect to \(GL(m_1 + m_2)\). They are expressed in tensor products of irreducible representations \(\langle \mu \rangle\) and \(\langle \nu \rangle\) of \(GL(m_1)\) and \(GL(m_2)\), respectively, with multiplicity coefficients that are derived from an induction problem in \(S_N\). According to Frobenius' reciprocity theorem we can also obtain the coefficients from the subduction

\[
\sum_{\lambda} \sum_{\mu} \sum_{\nu} \sum_{\sigma} \Theta C_\lambda(V_{\mu}\otimes^{n}) \otimes \Theta C_\sigma(R_{\mu}\otimes R_{\nu}).
\]

where \(m_{\mu\lambda}\) is the multiplicity.

Generally, this induction/subduction problem is not multiplicity free, i.e., \(m_{\mu\lambda}\) can be larger than 1. If we restrict the problem to many-electron systems, however, only representations are allowed with Young diagrams of two columns at most, and \(m_{\mu\lambda}\) can just become 0 or 1. A constructive method of calculating these multiplicity factors has been given by Littlewood and by Robinson. Extensive tables can be found in Appendix B of Ref. 25.

For demonstrating the application of our result (29) we again turn to the example of the \(O_2\) molecule. Suppose that we first wish to separate the core orbitals and then to perform an orbital transformation (e.g., hybridization or orthogonalization) which mixes only the valence orbitals of each atom among each other. For the separation of the two core orbitals we consider the reduction of the triplet representation \(\langle 2', 1^\prime \rangle\) of \(GL(10)\) under \(GL(2+8)\):

\[
\langle 2', 1^\prime \rangle = \langle 1 \rangle \otimes \langle 2', 1 \rangle
\]

triplet \(O_2\) doublet core doublet valence
(16 electrons) (15 el.) (15 el.)
dimension 990 = 2 \times 8

\[
\oplus \langle 2 \rangle \oplus \langle 2', 1^\prime \rangle \oplus \langle 1^\prime \rangle \oplus \langle 2' \rangle
\]

singlet c. triplet v. triplet c. singlet v.
(2) (14) (2) (14)
+ 3 \times 28 + 1 \times 36

\[
\oplus \langle 1^\prime \rangle \oplus \langle 2', 1^\prime \rangle \oplus \langle 2', 1 \rangle \oplus \langle 2' \rangle
\]

triplet c. triplet v. doublet c. doublet v.
(2) (14) (3) (13)
+ 1 \times 28 + 2 \times 168

\[
\oplus < 2, 1 > \oplus \langle 2, 1^\prime \rangle \oplus \langle 2' \rangle \oplus \langle 2', 1^\prime \rangle
\]

doublet c. quartet v. singlet c. triplet v.
(3) (13) (4) (12)
+ 2 \times 56 + 1 \times 378

We are only interested in those states with 4 electrons in the core forming a singlet, so that we are left with 12
electrons in the 8 valence orbitals carrying the triplet representation \( (2^e, 1^t) \) of \( GL(8) \). Formula (14) shows that we find 378 such states. The second step of our procedure amounts to the reduction of the latter representation under \( GL(4+4) \), which reads (indicating the atoms by A and B):

\[
\begin{align*}
(2^e, 1^t) &= (2, 1^t) \otimes (2^e) \\
\text{valence triplet} & \quad \text{triplet} \quad \text{singlet} \quad \text{B}^\pm \\
\text{(12 electrons)} & \quad \text{(4 el.)} \quad \text{(8 el.)} \\
\text{dimension 378} & \quad 15 \times 1 \\
\otimes & \quad (2, 1^t) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \\
\text{quartet} & \quad \text{doublet} \quad \text{doublet} \quad \text{doublet} \quad \text{doublet} \\
(5) & \quad (7) \quad (5) \quad (7) \\
+ & \quad 4 \times 4 + 20 \times 4 \\
\otimes & \quad (2^e) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \\
\text{singlet} & \quad \text{triplet} \quad \text{triplet} \quad \text{triplet} \quad \text{triplet} \\
(6) & \quad (6) \quad (6) \quad (6) \\
+ & \quad 10 \times 6 + 6 \times 6 \\
\otimes & \quad (2^e, 1^t) \otimes (2^e) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \\
\text{triplet} & \quad \text{singlet} \quad \text{doublet} \quad \text{doublet} \quad \text{B}^\pm \\
(6) & \quad (5) \quad (7) \quad (5) \\
+ & \quad 6 \times 10 + 4 \times 20 \\
\otimes & \quad (2^e, 1^t) \otimes (2^e, 1^t) \otimes (2^e) \otimes (2^e, 1^t) \\
\text{doublet} & \quad \text{quartet} \quad \text{singlet} \quad \text{triplet} \quad \text{triplet} \quad \text{B}^\pm \\
(7) & \quad (5) \quad (8) \quad (4) \\
+ & \quad 4 \times 4 + 1 \times 15
\end{align*}
\]

One could imagine that the secular problem including all configurations mixed by \( GL(8) \) is too large. In this case, we can, for instance, consider only the triplet ground state which is formed by covalent interaction between the atomic ground state triplets. We then find 36 states which transform as

\[
\begin{align*}
(2^e) \otimes (2^e, 1^t) \otimes (2^e, 1^t) \\
\text{core atom A} \quad \text{atom B} \quad \text{singlet} \quad \text{triplet} \quad \text{triplet} .
\end{align*}
\]

It is important to note, as we remarked before, that the product notation for the representations does not imply that the wavefunctions are simple tensorial products; they should have the proper symmetry also with respect to permutations exchanging electrons between subsystems. Still, they are basis elements of tensorial product representations. We have developed a method\(^{[6]}\) to construct such wavefunctions by means of reduced Wigner operators, which is closely related to the aggregate theory of Matsen and Klein.\(^{[4]}\)

**VI. DISCUSSION**

Starting from Weyl's theory which describes the behavior of antisymmetric spin eigenfunctions under general orbital transformations, we have derived how this behavior simplifies for partitioned orbital mixings. This simplification can be considerable, as in the example of the preceding section, where a full valence bond calculation is restricted to include only covalent states. Both the general result and its specification for partitioned transformations have numerous applications in quantum-mechanical methods applied to atoms and molecules.

An example for the use of the general result is given by a complete orthogonalization of a linearly independent basis set. This orthogonalization of the orbital set can significantly change the interaction energy between atoms or molecules calculated with a limited number of atomic or molecular orbital configurations. In practice, this effect was noticed by Magnasco and Musso\(^{[5]}\) in their computation of the interaction between two \( H_2 \) molecules and by Vonsovsky and Karpenko\(^{[18]}\) in discussing superexchange by Anderson's model. The results of both studies depend sensitively on whether the atomic orbitals are orthogonalized or not. Weyl's theory tells in this case which configurations should be included in order to obtain a result which is independent of orbital mixing and, in case one takes fewer configurations, which new ones are introduced and how the weights are changed by a given orbital transformation.

Our special result for partitioned orbital transformations has been used in two different subjects so far:

(1) In connection with Roothaan's open-shell Hartree-Fock method\(^{[14]}\) we have proved, very compactly, that

an antisymmetric spin eigenfunction is invariant under mixing of the closed-shell orbitals,

an antisymmetric spin eigenfunction transforms under mixing of the open-shell orbitals as if the closed shells were not present.

Using the latter theorem one shows very easily that by mixing of the open shells also non-degenerate states (with the same spin multiplicity but different spatial symmetry) can be mixed.

(2) We have derived the explicit relation between a pair-correlated DODS method and the CI approach. Particularly, the effect that various matrix elements in the DODS secular equations do not depend on some mixing parameters could be explained.
These results will be elaborated in a forthcoming publication.28

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17. This is a group theoretical generalization of the theorem that two commuting operators have a set of common eigenfunctions. In his proof of this relation (7), Weyl used the property that the enveloping algebra of $[GL(m)]^W$ is the commuting algebra of the group algebra of $S_N$. Since the enveloping algebra of $[U(m)]^W$ is also the enveloping algebra of $[U(m)]^W$, one finds that the (integral) representations (Λ) of the general linear group $GL(m)$ stay irreducible under the restriction of $GL(m)$ to $U(m)$, the group of unitary transformations (see Refs. 12 and 13).
22. The first part of this assertion is a consequence of the theorem that the tensor products of the irreducible representations of two different groups form the irreducible representations of their outer product group. This theorem was proved by Weyl (Ref. 3, p. 104) for the compact group $U(m)$, but it is also valid for integral representations of $GL(m)$ which stay irreducible under $U(m)$ (see Ref. 17). The second statement holds because $[GL(m_1)]^W \otimes [GL(m_2)]^W$ is isomorphic to $GL(m_1) \otimes GL(m_2)$, which in its turn is isomorphic to $GL(m_1+m_2)$.
23. This result is a generalization of Weyl's branching theorem (Ref. 3, p. 391).
Transformation Properties of Many-Electron Wave Functions with Special Attention to the Relation Between Pair-Correlated DODS and Configuration Interaction

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Abstracts

A method is presented that leads to a simple derivation of the explicit relation between pair-correlated DODS schemes (e.g., the alternant molecular orbital method and the extended valence bond method) and configuration interaction.

This result is based on a reduction formula for the representations of the general linear group, $GL(m)$, carried by the $N$-electron function space. Generally, this paper deals with the effect of "partitioned" orbital transformations on states with "local" permutation symmetry.

On présente une méthode qui fournit une dérivation simple de la relation explicite entre les procédés de type DODS-paires corrélées (par ex. la méthode des orbitales moléculaires alternantes et la méthode de la mésomérie généralisée) et l'interaction des configurations.

Ce résultat est basé sur une formule de réduction pour les représentations du groupe linéaire général, $GL(m)$, portées par l'espace des fonctions de $N$ électrons. En général l'article traite l'effet des transformations d'orbitales "partitionnées" sur les états avec une symétrie de permutation "locale".

Eine Methode wird vorgelegt, die zu einer einfachen Herleitung der expliziten Beziehung zwischen paar-korrellierten DODS-Verfahren (z.B. der Methode mit alternierenden Molekülorbitalen und der verallgemeinerten Valenzbindungsmethode) und Konfigurationswechselwirkung führt.

Das Ergebnis gründet sich auf eine Reduktionsformel für die Darstellungen der allgemeinen linearen Gruppe, $GL(m)$, die von dem Raum der $N$-Elektronenfunktionen getragen werden. Im allgemeinen behandelt der Artikel die Wirkung von "partinionierten" Orbitaltransformationen auf Zustände mit "lokaler" Permutationssymmetrie.

1. Introduction

Starting from a molecular calculation by the Hartree–Fock self-consistent field procedure, various methods exist for the computation of the remaining correlation energy. One of the traditional methods is the configuration interaction technique, which permits the Hartree–Fock single configuration wave
function (which is an antisymmetrized $N$-electron eigenfunction of the total spin operator $S^2$ in restricted Hartree–Fock) to be mixed with excited configuration wave functions (of the same spin multiplicity). Excited configurations are constructed from the original configuration by promoting electrons from occupied to virtual Hartree–Fock orbitals. By Hartree–Fock orbitals we do not necessarily understand the canonical Hartree–Fock orbitals; they may localized, for instance, and are even not required to be orthogonal.

Other methods for calculating correlation energy follow the different orbitals for different spins (doDs) scheme described by Löwdin [1]. $N$ different orbitals are obtained, for instance, by linear mixing between occupied and virtual Hartree–Fock orbitals. The correct $N$-electron wave function is formed from a product of such orbitals and a spin function product by antisymmetrization and spin projection. The mixing coefficients of the orbitals are considered as variation parameters which must be energy-optimized. Special forms of this doDs method mix each occupied Hartree–Fock orbital with just one virtual orbital, which should already account for a substantial part of the pair-correlation energy between the electrons in the doubly occupied Hartree–Fock orbital. Examples of such methods, which we shall call pair-correlated doDs, are given by the alternant molecular orbital method [2] and by the extended valence bond method [3, 4].

Although it can be readily recognized that the mixing between virtual and occupied orbitals introduces excited configurations into the Hartree–Fock wave function, so that doDs methods are in principle equivalent to configuration interaction with somewhat restricted interaction coefficients, it is not so easy to derive these coefficients explicitly. In a recent paper [5] we have reviewed the group-theoretical treatment of general orbital transformations as given by Weyl [6], and we have presented a new result which permits us to simplify the relation with CI considerably for pair-correlated doDs-methods. This is worked out in the present paper.

Our result is not restricted to the special orbital transformations occurring in pair-correlated doDs, and we have also indicated the specific transformation properties of some currently used $N$-electron wave functions.

2. Transformation Properties of $N$-Electron Wave Functions

We discuss $N$-electron wave functions that are composed of spatial orbitals and spin functions. They are considered to satisfy the Pauli principle, and to be eigenfunctions of the total spin operator $S^2$ with multiplicity $2S + 1$. Given a certain basis set of $m$ orbitals we can construct $n_{\langle i \rangle}$ linearly independent $N$-electron wave functions for a given $S$ and $S_z$ where $n_{\langle i \rangle}$ is determined by $m$, $N$ and $S$ as described in ref. [5]. A linear transformation of the orbitals (e.g., a doDs mixing) will mix these $N$-electron wave functions among each other.

The formal theory for general orbital transformations was treated by Weyl [6] using the duality between the group $GL(m)$ of all linear (nonsingular) orbital
transformations and the permutation group $S_N$. This duality rests on the commutability of simultaneous orbital transformations for all $N$-electrons and the electron permutations. It implies that $N$-electron basis functions for a certain irreducible representation $[\lambda]$ of $S_N$ are also basis functions for an irreducible representation of $GL(m)$, denoted by $\langle \lambda \rangle$. Now, we know that spatial wave functions which span a certain irreducible representation $[\lambda]$ of $S_N$, must combine with spin functions spanning the associate representation $[\tilde{\lambda}]$ (because of the antisymmetry of the total wave function) and, moreover, that this is uniquely connected to the spin functions being eigenfunctions of $S^z$ with definite $S$.

Combining these results, we find that the antisymmetric eigenfunctions of $S^z$ with fixed $S$ form a basis for an irreducible representation $\langle \lambda \rangle$ of $GL(m)$. The irreducibility of $\langle \lambda \rangle$ implies that a general orbital transformation $D(\gamma)$ (a nonsingular $m \times m$ matrix) will mix all $n_{\langle \lambda \rangle}$ $N$-electron antisymmetric wave functions belonging to the same $S$ and $S^-$. The mixing coefficients are the matrix elements of $D(\gamma)^{\{\lambda\}}$, the irreducible matrix representation $\langle \lambda \rangle$ of $GL(m)$ (dimension $n_{\langle \lambda \rangle}$). They are $N$th order homogeneous polynomials in the matrix elements of $D(\gamma)$, which can be derived after the actual construction of the $N$-electron basis functions of $\langle \lambda \rangle$.

Because orbital transformations do not affect the spin part of the wave functions, the theory is most easily formulated in a spinfree manner. The irreducible representations $[\lambda]$ of $S_N$, and also $\langle \lambda \rangle$ of $GL(m)$, are denoted by partitions of $N$ or Young diagrams. The two-valuedness of the electron spin permits only two-row diagrams $[\frac{1}{2}N + S, \frac{1}{2}N - S]$ for the electron spin functions, so that the spatial wave functions must be basis elements of a two-column representation $[\lambda] = [2^{1/2N-S}, 1^{2S}]$ of $S_N$ [7]. Such wave functions can be constructed by acting with the Wigner operators:

\begin{equation}
W_{jk}^{[\lambda]} = \frac{f^{[\lambda]}}{N!} \sum_{P \in S_N} D(P^{-1})_{k,j} P
\end{equation}

on an $N$-fold orbital product which corresponds to the desired electron-configuration $f^{[\lambda]}$ is the dimension of the irreducible representation $[\lambda]$ of $S_N$). By the theory of ref. [5] it is easily proved that the $N$-electron eigenfunctions of $S^z$ with given $S$, taken as a basis for the irreducible representations $\langle \lambda \rangle = \langle 2^{1/2N-S}, 1^{2S} \rangle$ of $GL(m)$, generate a matrix representation $D(\gamma)^{\langle \lambda \rangle}$ that is exactly identical to the one which is generated by the spinfree basis projected by $W_{jk}^{[\lambda]}$ for arbitrary, but fixed $j$. We denote the latter basis for the representation $\langle \lambda \rangle$ of $GL(m)$ by:

\begin{equation}
\psi_i^{\langle \lambda \rangle}(1, \cdots, N) = W_{jk}^{[\lambda]} \Phi_i(1, \cdots, N); \quad i = 1, \cdots, n_{\langle \lambda \rangle}
\end{equation}

with

\begin{equation}
\Phi_i(1, \cdots, N) = \varphi_{i_1}(1) \varphi_{i_2}(2) \cdots \varphi_{i_N}(N)
\end{equation}

The index $I$ in principle runs over all orbital occupations $(i_1 = 1, \cdots, m; i_2 = 1, \cdots, m; \cdots; i_N = 1, \cdots, m)$. Different choices of index $k$ with fixed $I$ project wave
functions which are either linearly independent or identical (except for a scalar factor which might be zero). The number of linearly independent wave functions that can be projected equals \( n_{\lambda} \).

Once we have constructed the spinfree basis functions of \( \langle \lambda \rangle \) we can proceed with the explicit derivation of the elements of the matrix \( D(\gamma)^{\langle \lambda \rangle} \) by inspecting the result of an arbitrary orbital transformation \( D(\gamma) \) on these basis functions. If we realize that each orbital product in principle transforms into \( m^N \) products we can understand that this derivation is certainly not trivial. The complexity of the problem rapidly increases with \( N \) and \( m \). For instance, a transformation of four orbitals in a four electron system mixes twenty singlet configurations with coefficients that are fourth order polynomials; for the singlet states of eight electrons in eight orbitals we need already a 1764 dimensional transformation matrix of eighth order polynomials. If we wish to find the explicit relation between a DODS treatment and a \( \alpha \) approach the expressions for the elements of these transformation matrices must be derived. Therefore it is very useful that we can simplify the transformation properties considerably if we restrict ourselves, for instance, to pair-correlated DODS.

3. Partitioned Orbital Transformations

The orbital transformations occurring in pair-correlated DODS are given by a direct sum of \( 2 \times 2 \) matrices which mix every occupied Hartree–Fock orbital with one virtual orbital. They form a special case of “partitioned” orbital transformations, for which we have derived a simplified transformation formula for the \( N \)-electron wave functions. Partitioned orbital transformations are defined as follows:

\[
D(\gamma) = D(\gamma_1) \oplus D(\gamma_2)
\]

where \( D(\gamma_1) \) mixes only \( m_1 \) orbitals and \( D(\gamma_2) \) mixes only \( m_2 \) orbitals among each other \((m_1 + m_2 = m)\).

Transformations of this type form a group \( GL(m_1 + m_2) \) which is a subgroup of \( GL(m) \). We derived in ref. [5] that the restriction to this subgroup reduces the irreducible representation \( \langle \lambda \rangle \) of \( GL(m) \) in the following way:

\[
D(\gamma)^{\langle \lambda \rangle} \downarrow GL(m_1 + m_2) = \sum_{n=0}^{N} \left( \sum_{(\mu)} \left( \sum_{(\nu)} \oplus m_{\mu\nu}\lambda D(\gamma_1)^{\langle \mu \rangle} \otimes D(\gamma_2)^{\langle \nu \rangle} \right) \right)
\]

where \( \langle \mu \rangle \) are those irreducible representations of \( GL(m_1) \), the group of transformations \( D(\gamma_1) \), labelled by partitions of \( n \) and \( \langle \nu \rangle \) those irreducible representations of \( GL(m_2) \) labelled by partitions of \( (N - n) \). The outer direct products \( \langle \mu \rangle \otimes \langle \nu \rangle \) are irreducible representations of the outer product group \( GL(m_1) \otimes GL(m_2) \), which is isomorphic to \( GL(m_1 + m_2) \). The multiplicity coefficients
\( m_{\nu \lambda} \) are obtained from an induction problem in the permutation group, namely the induction of the representations of the product group \( S_n \otimes S_{N-n} \) to the full permutation group \( S_N \):

\[
[\mu] \otimes [\nu] \uparrow S_N = \sum_{\text{partitions } \lambda} \oplus m_{\mu \nu \lambda}[\lambda]
\]

This reduction of the irreducible representations \( \langle \lambda \rangle \) of \( GL(m) \) for partitioned orbital transformations implies that no longer all \( n_{\langle \lambda \rangle} \) basis functions of \( D(\gamma^{(\lambda)}) \) are mixed among each other, but only the \( n_{\langle \mu \rangle} \times n_{\langle \nu \rangle} \) basis functions of the product representations \( D(\gamma_1^{(\mu)}) \otimes D(\gamma_2^{(\nu)}) \). The last number usually is considerably smaller and, moreover, the form of the mixing coefficients for \( N \)-electron wave functions will be much simpler.

In order to obtain these mixing coefficients explicitly we have to construct the \( N \)-electron basis functions of \( D(\gamma_1^{(\mu)}) \otimes D(\gamma_2^{(\nu)}) \). These functions must simultaneously be basis elements of a two-column representation \( [\lambda] \) of \( S_N \). Wave functions which satisfy the latter condition (which is the spinfree equivalent of the total wave function satisfying the Pauli principle and being an eigenfunction of \( S^2 \)), we shall call Pauli kets. The duality between \( GL(m) \) and \( S_N \) implies that Pauli kets must also be basis elements of a two-column representation \( D(\gamma^{(\lambda)}) \) of \( GL(m) \) (see ref. [5]). Our special Pauli kets must therefore simultaneously be basis elements for \( \langle \lambda \rangle \) of \( GL(m) \) and for \( \langle \mu \rangle \otimes \langle \nu \rangle \) of \( GL(m_1 + m_2) \). We say that they are "sequence-adapted" to the two-membered sequence \( GL(m) \to GL(m_1 + m_2) \).

Let us start the construction of these Pauli kets by taking the basis functions for the irreducible representations \( D(\gamma_1^{(\mu)}) \) and \( D(\gamma_2^{(\nu)}) \), which are also basis functions of the representations \( [\mu] \) of \( S_n \) and \( [\nu] \) of \( S_{N-n} \), respectively. (Again, because of the duality between the general linear group and the permutation group). Such basis functions can be obtained by projection with the Wigner operators of \( S_n \) and \( S_{N-n} \) (compare formula (2)):

\[
\Psi_p^{\langle \mu \rangle}(1, \cdots, n) = W_{qr}^{[\mu]} \Phi_p(1, \cdots, n); \quad p = 1, \cdots, n_{\langle \mu \rangle}
\]

\[
\Psi_s^{\langle \nu \rangle}(n+1, \cdots, N) = W_{tu}^{[\nu]} \Phi_s(n+1, \cdots, N); \quad s = 1, \cdots, n_{\langle \nu \rangle}
\]

The (tensorial) products of these basis functions

\[
\{\Psi_p^{\langle \mu \rangle} \otimes \Psi_s^{\langle \nu \rangle}; \ p = 1, \cdots, n_{\langle \mu \rangle}, \ s = 1, \cdots, n_{\langle \nu \rangle}\}
\]

form a basis for the representations \( D(\gamma_1^{(\mu)}) \otimes D(\gamma_2^{(\nu)}) \) of \( GL(m_1 + m_2) \). They are not Pauli kets, however, although they are adapted to the permutation symmetry of the group \( S_n \otimes S_{N-n} \), because they do not span an irreducible representation of the full permutation group \( S_N \). Pauli kets can be generated by acting with the left coset generators \( \{C_i; \ i = 1, \cdots, (n)\} \) of the subgroup \( S_n \otimes S_{N-n} \) in \( S_N \) on the product functions, which yields a basis for the induced representation.
\([\mu] \otimes [\nu] \uparrow S_N\), and a subsequent basis transformation which corresponds to the reduction (5). This induction-reduction process with respect to \(S_N\) does not influence the transformation properties of the wave functions, so that they still form a basis for \(D(\gamma_1)^{[\mu]} \otimes D(\gamma_2)^{[\nu]}\). In fact, this construction forms an essential part of the derivation of formula (4), as described in ref. [5].

One way to obtain the proper Pauli kets is by direct action with the Wigner operators \(W^{[\lambda]}_{Jk}\) of the full permutation group \(S_N\) on the product functions \(\Psi_p^{[\mu]} \otimes \Psi_s^{[\nu]}\). Thus, we can be sure of the correct permutation symmetry. It is better, however, to take advantage of the permutation symmetry which is already present in the product functions by using the "reduced Wigner operators":

\[
\tilde{W}^{[\lambda]}_{JK} = \frac{f_{[\lambda]}}{f_{[\mu]} f_{[\nu]}} \left( \frac{N}{n} \right)^{-1} \sum_{i=1}^{N} D(C_i^{-1})_{[\lambda]}^{[\mu]} C_i
\]

with \(J = (\mu', \nu', v, w)\) and \(K = (\mu, \nu, v, q, t)\)

In this formula \(D^{[\lambda]}\) must be an irreducible matrix representation of \(S_N\) which is "sequence adapted" to the subgroup \(S_{n} \otimes S_{N-n}\). A method for deriving such representations is described by Matsen and Klein (ref. [8], Appendix 3). Acting with the reduced operators, which only contain the coset generators \(C_i\) of \(S_{n} \otimes S_{N-n}\) in \(S_N\), on a function which is already symmetry adapted to \(S_{n} \otimes S_{N-n}\) we can obtain the same result as by acting with the full Wigner operator. This is expressed by the following relation:

\[
W^{[\lambda]}_{(\mu', v', v, w)(\mu, v, q, t)} = \sum_{q=1}^{N} \sum_{l=1}^{N} \tilde{W}^{[\lambda]}_{(\mu', v', v, w)(\mu, v, q, l)} \tilde{W}^{[\mu]}_{q \upsilon} \tilde{W}^{[\nu]}_{1 \upsilon}
\]

The form of a sequence-adapted representation, the derivation of expression (8) and the meaning of all indices is shown in the Appendix.

Using this property of the reduced Wigner operators, we can write the resulting Pauli kets as follows:

\[
\Psi^{[\mu] \otimes [\nu]}_{p, s}(1, \cdots, N)
\]

\[
= \sum_{q=1}^{N} \sum_{l=1}^{N} \tilde{W}^{[\lambda]}_{(\mu', v', v, w), (\mu, v, q, l)} \Psi^{[\mu]}_{p}(1, \cdots, n) \otimes \Psi^{[\nu]}_{s}(n + 1, \cdots, N)
\]

where \(p = 1, \cdots, n_{(\mu)}\), \(s = 1, \cdots, n_{(\nu)}\) and the functions on the right-hand side are given by (6). The reduced Wigner operator being a linear combination of left coset generators, Equation (9) is the algebraic analogue of the induction-reduction process described before.

* This problem of obtaining the correct overall permutation symmetry for wave functions which are already permutation symmetry adapted to certain subsystems forms the basis of what is called by Matsen and Klein "the aggregate theory" [8, 9].
It is easily proved [5], by using the commutation of the matrices representing \(GL(m_1 + m_2)\) and the coset generators \(C_i\), that expression (9) indeed produces basis elements for the irreducible representation \(\langle \mu \rangle \otimes \langle \nu \rangle\) of \(GL(m_1 + m_2)\). Moreover, it produces proper Pauli kets with the representation \([\lambda]\) of \(S_N\) and \(\langle \lambda \rangle\) of \(GL(m)\), so that we now have obtained basis vectors which are adapted to the sequence \(GL(m) \supset GL(m_1 + m_2)\). Equation (4) then shows the way to obtain a full basis of \(GL(m)\).

The irreducibility of the representations \(\langle \mu \rangle \otimes \langle \nu \rangle\) with respect to the group of partitioned orbital transformations \(GL(m_1 + m_2)\) implies that the basis functions which we have now constructed give maximum simplification of the transformation matrix for the \(N\)-electron wave functions. Moreover, their expression by means of the reduced Wigner operators appears to be particularly convenient for deriving the remaining matrix elements explicitly. This we will demonstrate by an example in the next section.

We conclude this section by summarizing the above considerations in a corollary, while at the same time extending the theory to an arbitrary number of subsystems. Assume that the spatial wave function \(\Phi^{(1)}(1, \cdots, n_1)\) is an orbital product, or a linear combination of orbital products, constructed from the first \(m_1\) orbitals of the \(m\)-dimensional orbital basis. (It forms an element of the \(n_1\)-fold tensor product space \(V_{m_1} \otimes \cdots \otimes V_{m_1}\)). Analogously, \(\Phi^{(2)}(n_1 + 1, \cdots, n_1 + n_2)\) is constructed from the second set of \(m_2\) orbitals. We continue until \(\Phi^{(k)}(N - n_k + 1, \cdots, N)\), which is built from the last set of \(m_k\) orbitals.

\[
(m_1 + m_2 + \cdots + m_k = m; \ n_1 + n_2 + \cdots + n_k = N)
\]

Let the Wigner operator \(W^{[1]}_{JK}\) be constructed on the basis of an irreducible representation \([\lambda]\) of \(S_N\) that is sequence adapted to

\[
S_N \supset S_{n_1} \otimes S_{n_2} \otimes \cdots \otimes S_{n_k}
\]

The column index \(K\) of the Wigner operator corresponds with the irreducible representation \([\mu_1] \otimes [\mu_2] \otimes \cdots \otimes [\mu_k]\) of the subgroup (see Appendix). By an easy generalization of the contents of this section one can show that the Pauli ket

\[
\Psi = W^{[1]}_{JK} \Phi^{(1)}(1, \cdots, n_1) \otimes \Phi^{(2)}(n_1 + 1, \cdots, n_1 + n_2)
\]

\[
\cdots \otimes \Phi^{(k)}(N - n_k + 1, \cdots, N)
\]

is an element in the basis of the irreducible representation \(\langle \mu_1 \rangle \otimes \langle \mu_2 \rangle \otimes \cdots \otimes \langle \mu_k \rangle\) of the group \(GL(m_1 + m_2 + \cdots + m_k)\). If the functions \(\Phi^{(i)}\) are already symmetry adapted to the permutation group \(S_{n_i}(i = 1, \cdots, k)\), we can use the reduced Wigner operators in order to replace (10) by an expression which is the generalization of (9) to an arbitrary number of subsystems.
By constructing basis functions that are sequence adapted to the permutation group sequence \( S_n \supset S_{n_1} \otimes \cdots \otimes S_{n_k} \)—Matsen and Klein [8] call such functions “aggregate states”—we have obtained a basis that is also sequence adapted to the orbital transformation groups \( GL(m) \supset GL(m_1 + m_2 + \cdots + m_k) \). In other words, by fixing the parentage of the Pauli kets with respect to the permutation groups \( S_{n_1} , S_{n_2} , \cdots , S_{n_k} \), we have completely determined their transformation behaviour under partitioned orbital transformations belonging to the group \( GL(m_1 + m_2 + \cdots + m_k) \).

4. Relation between Pair-Correlated DODS and CI

The matrix of a pair-correlated DODS transformation is a direct sum of \( 2 \times 2 \) matrices (not necessarily orthogonal), which mix pairs of orbitals that for physical reasons are chosen to be coupled. Matrix elements are the mixing coefficients which serve, according to the DODS formalism on a finite basis, as variation parameters. Mathematically, this pair-correlated DODS matrix is an element of a matrix group isomorphic to \( GL(2 + 2 + \cdots + 2) \). In order to project Pauli kets transforming to irreducible representations of this group, one needs, according to the above prescription, representations \([\lambda]\) of \( S_N \) adapted to \( S_2 \otimes S_2 \otimes \cdots \otimes S_2 \). This type of representation is known as Serber representation [10]. The corollary of the previous section states that the DODS wave function projected by a Wigner operator on basis of a Serber representation transforms according to an irreducible representation of \( GL(2 + 2 + \cdots + 2) \). Knowing this, we can readily derive the explicit expansion of the DODS wave function in terms of configurations, without necessity to write out the projection of any wave function involved in the expansion.

Let us illustrate the characteristic features of the theory by a rather simple example: the DODS treatment of a four electron system. Due to the simplifications which the theory permits for pair-correlated DODS, this treatment can easily be extended to larger systems.

We start with a basis set of four orbitals \( \{ \varphi_1, \varphi_3, \varphi_2, \varphi_4 \} \), e.g., two occupied and two virtual molecular orbitals from a SCF-LCAO calculation. (In the AMO method these MO's are the canonical ones, in extended valence bond they are localized.) The DODS scheme allows these four orbitals to be mixed in order to form four different orbitals \( \{ \psi_1, \psi_3, \psi_2, \psi_4 \} \), in each of which one electron is placed. This can be achieved by a \( 4 \times 4 \) orbital transformation matrix \( D(\gamma) \). The theory for general orbital transformations then tells us that we mix twenty singlet configurations: the SCF ground state with two doubly occupied MO's: \( \varphi_1^2 \varphi_2^2 \) and all excited singlet configurations which can be constructed within the given basis. The mixing coefficients of the four-electron configurations, which form a \( 20 \times 20 \) matrix, are fourth order homogeneous polynomials of the elements of \( D(\gamma) \).

If we restrict ourselves to pair-correlated DODS the matrix \( D(\gamma) \) has the following
typical form:

\[
D(\gamma) = \begin{pmatrix}
d_{11} & d_{13} & 0 & 0 \\
d_{31} & d_{33} & 0 & 0 \\
0 & 0 & d_{22} & d_{24} \\
0 & 0 & d_{42} & d_{44}
\end{pmatrix} = D(\gamma_1) \oplus D(\gamma_2)
\]

In this example the occupied orbitals \(\varphi_1\) and \(\varphi_2\) are mixed with the virtual orbitals \(\varphi_3\) and \(\varphi_4\), respectively. Partitioned orbital transformations of this type cause the following reduction of the twenty-dimensional singlet representation of \(GL(4)\) into outer direct products of representations of \(GL(2)\):

\[
\langle 2^2, 0^2 \rangle = \langle 2^2 \rangle \otimes \langle 0^2 \rangle \oplus \langle 2, 1 \rangle \otimes \langle 1, 0 \rangle \oplus
\]

\[
(12) \quad \oplus \langle 2, 0 \rangle \otimes \langle 2, 0 \rangle \oplus \langle 1^2 \rangle \otimes \langle 1^2 \rangle \oplus
\]

\[
\oplus \langle 1, 0 \rangle \otimes \langle 2, 1 \rangle \oplus \langle 0^2 \rangle \otimes \langle 2^2 \rangle
\]

with dimensionality \(20 = 1 \times 1 + 2 \times 2 + 3 \times 3 + 1 \times 1 + 2 \times 2 + 1 \times 1\). In order to indicate clearly to which group the representations belong we have placed zeros for the nonoccurring rows in the Young diagrams. Note that the representation \(D(\gamma)^{0^2}\) is the identity representation of \(GL(2)\) and that the representation \(D(\gamma)^{1,0}\) is identical to \(D(\gamma)\) itself.

Because in the \(\text{dOoD}\) scheme we assign four different orbitals to the four electrons, thus placing two electrons in each orbital pair, the \(\text{dOoD}\) four-electron singlets can only span the representations \(\langle 2, 0 \rangle \otimes \langle 2, 0 \rangle\) or \(\langle 1^2 \rangle \otimes \langle 1^2 \rangle\). (The other representations occurring in (12) correspond physically with one or two orbitals being doubly occupied.) In fact, from the configuration \(\varphi_1\varphi_3\varphi_2\varphi_4\) we can construct two linearly independent singlet wave functions, one of which spans the representation \(\langle 1^2 \rangle \otimes \langle 1^2 \rangle\), whereas the other one is a basis element of \(\langle 2, 0 \rangle \otimes \langle 2, 0 \rangle\). In order to derive the explicit relation between the \(\text{dOoD}\) wave functions and a \(\text{CI}\) basis we construct these wave functions and show their transformation behaviour.

In the first step we use the Wigner operators of the group \(S_2\) :

\[
W^{[2,0]} \varphi_1 \varphi_3 = \frac{1}{2} (\varphi_1 \varphi_3 + \varphi_3 \varphi_1) = d_{11}d_{13} W^{[2,0]} \varphi_1 \varphi_1 +
\]

\[
(13) \quad + d_{31}d_{33} W^{[2,0]} \varphi_3 \varphi_3 + (d_{11}d_{33} + d_{13}d_{31}) W^{[2,0]} \varphi_1 \varphi_3
\]

\[
W^{[1^2]} \varphi_1 \varphi_3 = \frac{1}{2} (\varphi_1 \varphi_3 - \varphi_3 \varphi_1) = (d_{11}d_{33} - d_{13}d_{31}) W^{[1^2]} \varphi_1 \varphi_3
\]

We note that for the triplet state several terms cancel. One proceeds analogously for the other electron pair.

The next step is to find an irreducible matrix representation \([2^2, 0^2]\) of \(S_4\).
which is sequence adapted to $S_2 \otimes S_2$. Accidentally, in this case the Serber representation is identical with the Young–Yamanouchi representation [11, 12]. We do not need this Serber representation explicitly, we only need to know the parentage of its different columns. The operator $W_{11}^{[2,0]^0}$ has the parentage $[2,0] \otimes [2,0]$, whereas $W_{12}^{[2,0]^0}$ corresponds with $[1^2] \otimes [1^2]$. Therefore, we can write the DQDS wave functions as follows:

\begin{align*}
\Psi^{(2,0)\otimes(2,0)} &= W_{11}^{[2,0]^0} \psi_1 \psi_3 \psi_2 \psi_4 \\
&= \tilde{W}_{11}^{[2,0]^1} (W^{[2,0]} \psi_1 \psi_3) \otimes (W^{[2,0]} \psi_2 \psi_4) \\
(14) \Psi^{(1^2)\otimes(1^2)} &= W_{12}^{[2,0]^0} \psi_1 \psi_3 \psi_2 \psi_4 \\
&= \tilde{W}_{12}^{[2,0]^1} (W^{[1^2]} \psi_1 \psi_3) \otimes (W^{[1^2]} \psi_2 \psi_4)
\end{align*}

Substituting the formula (13) and using relation (8) again, we can easily express the DQDS wave functions in terms of the MO configurations that form the basis of a CI treatment (they should be Pauli kets also):

\begin{align*}
\Psi^{(2,0)\otimes(2,0)} &= d_{11} d_{13} d_{22} d_{24} W_{11}^{[2,0]^0} \varphi_1 \varphi_1 \varphi_2 \varphi_2 \\
&+ d_{11} d_{13} d_{42} d_{44} W_{11}^{[2,0]^0} \varphi_1 \varphi_1 \varphi_4 \varphi_4 \\
&+ d_{31} d_{32} d_{22} d_{24} W_{11}^{[2,0]^0} \varphi_3 \varphi_3 \varphi_2 \varphi_2 \\
&+ d_{31} d_{32} d_{42} d_{44} W_{11}^{[2,0]^0} \varphi_3 \varphi_3 \varphi_4 \varphi_4 \\
&+ d_{11} d_{13} (d_{22} d_{44} + d_{24} d_{42}) W_{11}^{[2,0]^0} \varphi_1 \varphi_1 \varphi_2 \varphi_4 \\
&+ (d_{11} d_{33} + d_{13} d_{31}) d_{22} d_{24} W_{11}^{[2,0]^0} \varphi_1 \varphi_3 \varphi_2 \varphi_2 \\
&+ d_{31} d_{33} (d_{22} d_{44} + d_{24} d_{42}) W_{11}^{[2,0]^0} \varphi_3 \varphi_3 \varphi_2 \varphi_4 \\
&+ (d_{11} d_{33} + d_{13} d_{31}) d_{22} d_{44} W_{11}^{[2,0]^0} \varphi_1 \varphi_3 \varphi_4 \varphi_4 \\
&+ (d_{11} d_{33} + d_{13} d_{31}) (d_{22} d_{44} + d_{24} d_{42}) W_{11}^{[2,0]^0} \varphi_1 \varphi_3 \varphi_2 \varphi_4 \\
(15) \Psi^{(1^2)\otimes(1^2)} &= (d_{11} d_{33} - d_{13} d_{31}) (d_{22} d_{44} - d_{24} d_{42}) W_{11}^{[2,0]^0} \varphi_1 \varphi_3 \varphi_2 \varphi_4
\end{align*}

This result tells us explicitly which configurations are mixed in a pair-correlated DQDS wave function and how the mixing coefficients vary as a function of the orbital mixing coefficients.

In the special case of the AMO method, where the orbital transformation matrices have the form:

\begin{align*}
D(\gamma_1) &= \begin{pmatrix} \cos \vartheta_1 & \cos \vartheta_1 \\ \sin \vartheta_1 & -\sin \vartheta_1 \end{pmatrix}, & D(\gamma_2) &= \begin{pmatrix} \cos \vartheta_2 & \cos \vartheta_2 \\ \sin \vartheta_2 & -\sin \vartheta_2 \end{pmatrix}
\end{align*}

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various terms cancel and we find the following simple relation:

\[
\Psi^{(2,0) \otimes (2,0)} = \cos^2 \vartheta_1 \cos^2 \vartheta_2 W_{11}^{[2,0; 0]} \varphi_1 \varphi_2 \varphi_3 \varphi_4 \\
- \cos^2 \vartheta_1 \sin^2 \vartheta_2 W_{11}^{[2,0; 0]} \varphi_1 \varphi_2 \varphi_3 \varphi_4 \\
- \sin^2 \vartheta_1 \cos^2 \vartheta_2 W_{11}^{[2,0; 0]} \varphi_3 \varphi_2 \varphi_1 \varphi_4 \\
+ \sin^2 \vartheta_1 \sin^2 \vartheta_2 W_{11}^{[2,0; 0]} \varphi_3 \varphi_2 \varphi_1 \varphi_4 \\
\Psi^{(1^2) \otimes (1^2)} = 4 \cos \vartheta_1 \sin \vartheta_1 \cos \vartheta_2 \sin \vartheta_2 W_{12}^{[2,0; 0]} \varphi_1 \varphi_2 \varphi_3 \varphi_4
\]

No singly or triply excited states occur in the singlet AMO wave functions.

This example can be easily extended to systems with more than four electrons by using the results of the previous section, formula (10) in particular. The complete pair-correlated AMO wave functions can be built up from the singlets and triplets of formula (13) by using the reduced Wigner operators based on the Serber representations of \( S_N \). If one wants to derive which configurations occur in a certain AMO wave function and to calculate the configuration interaction coefficients as functions of the orbital mixing coefficients, it is not necessary to construct these complete wave functions, however. Only knowing their parentage with respect to \( S_2 \otimes S_2 \otimes \cdots \otimes S_2 \), i.e., the singlet and triplet states from which they are built, is sufficient.

5. Transformation of Some Common Antisymmetric Spin Eigenfunctions

We have seen in the previous section that the transformation properties of antisymmetric spin eigenfunctions under pair-correlated AMO mixing become particularly simple if we project such wave functions by means of Wigner operators based on the Serber representations of \( S_N \). Although Serber functions have found recent interest in quantum chemistry [13], many other projectors have been used in the literature to construct antisymmetric eigenfunctions of \( S^2 \). We shall briefly discuss the transformation properties of some of these other Pauli kets also.

The general section about partitioned orbital transformations tells us that the transformation behaviour of Pauli kets can be largely simplified if one knows the permutational genealogy of their projectors.

Let us first look at some Wigner operators based on the orthogonal Young–Yamanouchi representations [12], called orthogonal units by Rutherford [11]. We shall label the basis functions for a given irreducible representation \( [\lambda] = [2^{1/2N-S}, 1^S] \) of \( S_N \) according to decreasing Yamanouchi symbols, using Hamermesh’s [14] definition of these symbols. It follows immediately from the construction rules for the Young–Yamanouchi representations (ref. [14], Section 7-7) and from the form of the first standard Young tableau that the Wigner operator \( W_{11}^{[2]} \) is invariant under all transpositions \( (12), (34), \cdots, (N-2S-1, N-2S) \)
and spans an antisymmetric representation of all permutations among the last 2S electrons. Thus, the Wigner operator $W^{[1]}_{2,1}$ generates spatial functions that carry the representation

$$\left[2\right] \otimes \left[2\right] \otimes \cdots \otimes \left[2\right] \otimes \left[1^{2S}\right]$$

of the group $S_2 \otimes S_2 \otimes \cdots \otimes S_2 \otimes S_{2S}$. Such functions are also sequence adapted to

$$GL(m) \supset GL(m_1 + m_2 + \cdots + m_{1/2N-S} + m_{1/2N-S+1})$$

and transform according to the representation:

$$\langle 2 \rangle \otimes \langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^{2S} \rangle$$

of the latter group.

In order to get nontrivial results the partitioning of the orbital basis $(m = m_1 + m_2 + \cdots + m_{1/2N-S+1})$ must satisfy the relations

$$m_1, m_2, \ldots, m_{1/2N-S} \geq 1; \quad m_{1/2N-S+1} \geq 2S$$

This projector is used by Goddard in his GL-method [15].

Basis functions projected by this operator transform identically to one of the Serber basis functions under $GL(m_1 + m_2 + \cdots + m_{1/2N})$, namely according to

$$\langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^{2} \rangle \otimes \cdots \otimes \langle 1^{2} \rangle$$

$$\frac{1}{2}N - S \text{ factors} \quad S \text{ factors}$$

Consequently, this projector connects pair-correlated doubs and ci in the manner described in the previous section.

Another Wigner operator with a physically interesting parentage is $W^{[1]}_{f_{[\lambda]} f_{[\lambda]}}$ where $f_{[\lambda]}$ is the dimension of the irreducible representation $[\lambda] = \left[2^{1/2N-S}, 1^{2S}\right]$. It is sequence-adapted to $S_N \supset S_{1/2N+S} \otimes S_{1/2N-S}$ and corresponds to the representation $\left[1^{1/2N+S}\right] \otimes [1^{1/2N-S}]$. Pauli kets which are projected by this operator transform according to $\langle 1^{1/2N+S} \rangle \otimes \langle 1^{1/2N-S} \rangle$ of $GL(m_1 + m_2)$. The partitioning of the orbital basis must satisfy $m_1 \geq \frac{1}{2}N + S$, $m_2 \geq \frac{1}{2}N - S$. If the equal signs hold, the irreducible representation $\langle 1^{1/2N+S} \rangle \otimes \langle 1^{1/2N-S} \rangle$ is one-dimensional, and the functions carrying $\langle 1^{1/2N+S} \rangle$ and $\langle 1^{1/2N-S} \rangle$ are simply Slater determinants composed of $\frac{1}{2}N + S$ and $\frac{1}{2}N - S$ spatial orbitals, respectively. In general, this projector corresponds to a physical system with antiferromagnetic coupling between two subsystems with $\frac{1}{2}N + S$ and $\frac{1}{2}N - S$ parallel spins. This projector is also of importance if one fills up degenerate doubs orbitals according to Hund’s rules [16].
Also a common way of constructing antisymmetric eigenfunctions of $S^2$ is by acting with the Young operators \([17]\), $P_i N_i$ or $N_i P_i$, either on the spin part or on the spatial part of a wave function.

Each Young operator corresponds with a standard Young tableau ($i = 1, \cdots, f_{[\lambda]}$); the operator $N_i$ is a product of antisymmetrizers over the electron indices occurring in the columns of tableau $i$, $P_i$ symmetrizes over indices occurring in rows. These Young operators, which project nonorthogonal bases, can be related to the spinfree Wigner operators. In case they project spin functions, the first step involves transferring the permutational symmetry from spin to spatial coordinates by using one of the relations:

\[
A(I \otimes P_i N_i^{[\lambda]}) = A(P_i N_i^{[\lambda]} \otimes I)
\]
\[
A(I \otimes N_i P_i^{[\lambda]}) = A(N_i P_i^{[\lambda]} \otimes I)
\]

(18)

where the first factor acts on the spatial coordinates and the second on the spin coordinates, $I$ is the identity operator and $A$ is the antisymmetrizer over spatial and spin coordinates. The representation $[\lambda]$ is associate to $[\lambda]$ and $i = f_{[\lambda]} + 1 - i$ counts according to increasing Yamanouchi symbols. These two relations are easily proved following the arguments of Heldmann \([18]\). Furthermore, one can show, using elements of Goddard’s proof \([19]\), that the following expansions must hold:

\[
N_i P_i^{[\lambda]} = \sum_{i=1}^{f_{[\lambda]}} c_i W_{i,i}^{[\lambda]}
\]

(19)

\[
P_{f_{[\lambda]}} N_{f_{[\lambda]}}^{[\lambda]} = \sum_{i=1}^{f_{[\lambda]}} c_i' W_{i,f_{[\lambda]}}^{[\lambda]}
\]

Because the second index of the Wigner operators determines their permutational genealogy, and therewith the transformation properties of projected wave functions, and we have already discussed the Wigner operators $W_{11}^{[\lambda]}$ and $W_{f_{[\lambda]}, f_{[\lambda]}}, \ f_{[\lambda]}$, relations (18) and (19) are sufficient to uncover these properties for the given Young operators.

The projector $N_{f_{[\lambda]}} P_{f_{[\lambda]}}^{[\lambda]}$ acting on a spin function $\alpha \beta \alpha \beta \cdots \alpha \beta \alpha \alpha \cdots \alpha$ generates the Boys–Reeves "spin-bonded" functions \([20]\). Using (18) and (19) we conclude that such functions transform according to $\langle 2 \rangle \otimes \langle 2 \rangle \otimes \cdots \otimes \langle 2 \rangle \otimes \langle 1^{2S} \rangle$ under $GL(m_1 + m_2 + \cdots + m_{1/2N-S} + m_{1/2N-S+1})$. The projector $P_1 N_1^{[\lambda]}$ acting on:

\[
\frac{\alpha \alpha \cdots \alpha \beta \beta \cdots \beta}{\frac{1}{2}N + S} \quad \frac{\alpha \alpha \cdots \alpha \beta \beta \cdots \beta}{\frac{1}{2}N - S}
\]

yields the same result as the Löwdin operator \([21]\) acting on this function \([22]\). The Pauli kets corresponding to this choice transform as $\langle 1^{1/2N+S} \rangle \otimes \langle 1^{1/2N-S} \rangle$
under $GL(m_1 + m_2)$. If we have just $N$ orbitals, these Pauli kets are invariant (except for a scalar factor) under mixing the spin-up and the spin-down orbitals among themselves. This result lies at the basis of the pairing theorem [23, 24].

6. Conclusion

In this paper we have treated the effect of orbital transformations on some commonly used many-electron wave functions, that are antisymmetric eigenfunctions of $S^2$. Especially, orbital mixings occurring in pair-correlated dops-schemes were considered in more detail, in order to find the explicit relation between such schemes and the configuration interaction method. Orbital transformations were regarded as elements of the general linear group, $GL(m)$, and their effects were studied group theoretically. Although some of the transformation properties that we have discussed in this paper have already been derived for special cases [2, 25], the group theoretical approach places these results in a general and more formal framework. It gives much deeper insight as it clearly shows the relation between the permutational characteristics of wave functions and their transformation behaviour. Moreover, by using a group-theoretical formula that we have derived for the subduction of the representations of $GL(m)$, we can very often simplify complicated transformation matrices to a large extent and, thus, save much labour.

Appendix

We have shown in this paper that the transformation properties of $N$-electron wave functions under partitioned orbital transformations can actually be simplified if we construct basis functions of the type (9) by means of the "reduced" Wigner operators which satisfy relation (8). We will now show the derivation of this relation (8) and explain the meaning of all occurring indices. (A similar result has been derived by Klein et al. [9], using the theory of semi-simple algebras, and by Jahn [26] and Gerrat [16], who both restrict their attention to one- and two-column representations only).

Start with an irreducible representation $\left[\lambda\right]$ of $S_N$ which is "sequence adapted" to the subgroup $S_n \otimes S_{N-n}$.

By definition such a representation $\left[\lambda\right]$ is completely decomposed if it is restricted to the subgroup $S_n \otimes S_{N-n}$. Therefore we can write for an arbitrary element $PQ$ of this subgroup ($P \in S_n$, $Q \in S_{N-n}$):

\begin{equation}
D(PQ)_{[\lambda]} = \sum_{(\mu) \text{part.}} \sum_{(v) \text{part.}} \oplus m_{\lambda \mu \nu} D(P)_{[\mu]} \otimes D(Q)_{[v]}
\end{equation}

(A1)

(According to Frobenius' theorem the multiplicity coefficients in this subduction
problem are equal to those occurring in the induction (5): 

\[ m_{\lambda \mu \nu} = m_{\mu \nu \lambda} \]

The matrix \( D(PQ)^{[\lambda]} \) has a diagonal blocked form with the Kronecker products \( D(P)^{[\mu]} \otimes D(Q)^{[\nu]} \) occurring \( m_{\lambda \mu \nu} \) times on the diagonal (see Figure 1). If we want to write out relation (A1) in terms of matrix elements we necessarily have to introduce a large number of indices. The rows of the matrix \( D(PQ)^{[\lambda]} \) are numbered by:

- \( \mu \) (running over partitions of \( n \))
- \( \nu \) (running over partitions of \( N - n \)),
- \( \alpha = 1, \cdots, m_{\lambda \mu \nu} \) (numbering multiple occurrences of \( [\mu] \otimes [\nu] \)),
- \( r = 1, \cdots, f_{[\mu]} \) (running over the rows of \( D(P)^{[\mu]} \)),
- \( u = 1, \cdots, f_{[\nu]} \) (running over the rows of \( D(Q)^{[\nu]} \)).

All these indices can be collected in one index \( K \), numbering the rows of \( D(PQ)^{[\lambda]} \), such that there is a unique relation \( K = (\mu, \nu, \alpha, r, u) \). In the same manner we label the columns by \( L = (\mu', \nu', \alpha', q, t) \). Then, the following relation is obtained:

\[ (A2) \quad D(PQ)^{[\lambda]}_{KL} = \delta_{\mu \mu'} \delta_{\nu \nu'} \delta_{\alpha \alpha'} D(P)^{[\mu]}_{r q} D(Q)^{[\nu]}_{u t} \]

with \( K = (\mu, \nu, \alpha, r, u) \) and

\[ L = (\mu', \nu', \alpha', q, t) \]

Although this factorization is only valid for the matrices \( D(PQ)^{[\lambda]} \) representing the subgroup \( S_n \otimes S_{N-n} \), we must realize that the sequence-adapted representation \( D(R)^{[\lambda]} \) is defined for all \( R \in S_N \). So, the labelling \( K = (\mu, \nu, \alpha, r, u), L = (\mu', \nu', \alpha', q, t) \) can be carried through for all \( R \in S_N \).
We now write a Wigner operator for the (sequence-adapted) representation $[\lambda]$ of $S_N$:

\[(A3)\]

\[W^{[\lambda]}_{JK} = \frac{f_{[\lambda]}}{N!} \sum_{P \in S_N} D(R^{-1})^{[\lambda]}_{KJ} P R \]

Every permutation $R \in S_N$ can be written as $R = C_l P Q$, where $P \in S_n$, $Q \in S_{N-n}$ and \(\{C_l ; l = 1, \cdots, \binom{N}{n}\}\) are the (left) coset generators of $S_n \otimes S_{N-n}$ in $S_N$. Replacing the summation over all $R \in S_N$ by a threefold sum over $P \in S_n$, $Q \in S_{N-n}$ and $l = 1, \cdots, \binom{N}{n}$ we obtain

\[(A4)\]

\[W^{[\lambda]}_{JK} = \frac{f_{[\lambda]}}{N!} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} \sum_{l=1}^{\binom{N}{n}} D(Q^{-1} P^{-1})^{[\lambda]}_{KJ} C_l P Q \]

\[= \frac{f_{[\lambda]}}{N!} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} \sum_{l=1}^{\binom{N}{n}} f^{[\lambda]}_{l} \sum_{L=1}^{\binom{N}{n}} D(Q^{-1} P^{-1})^{[\lambda]}_{KL} D(C_l^{-1})^{[\lambda]}_{LJ} C_l P Q \]

Substitution of expression (7) for the reduced Wigner operator yields

\[(A5)\]

\[W^{[\lambda]}_{JK} = \frac{f_{[\mu]} f_{[\nu]}}{n! (N-n)!} \sum_{L=1}^{\binom{N}{n}} \tilde{W}^{[\lambda]}_{JL} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} D(Q^{-1} P^{-1})^{[\lambda]}_{KL} P Q \]

Since the permutation $Q^{-1}P^{-1}$ is an element of the group $S_n \otimes S_{N-n}$ we can use the decomposition formula (A2):

\[(A6)\]

\[W^{[\lambda]}_{JK} = \frac{f_{[\mu]} f_{[\nu]}}{n! (N-n)!} \sum_{L=1}^{\binom{N}{n}} \tilde{W}^{[\lambda]}_{JL} \sum_{P \in S_n} \sum_{Q \in S_{N-n}} \delta_{\mu\mu'} \delta_{\nu\nu'} \delta_{\alpha\alpha'} D(P^{-1})^{[\mu]}_{rq} D(Q^{-1})^{[\nu]}_{ut} P Q \]

Remember that $K = (\mu, \nu, \alpha, r, u)$ and $L = (\mu', \nu', \alpha', q, t)$. Because of the Kronecker delta's the summation over $L = (\mu', \nu', \alpha', q, t)$, which is in fact a fivefold summation, can be reduced to a twofold sum. Moreover, we can substitute formula (1) for the Wigner operators of $S_n$ and $S_{N-n}$ to obtain the final result:

\[(A7)\]

\[W^{[\lambda]}_{JK} = \sum_{q=1}^{f_{[\lambda]}} \sum_{t=1}^{f_{[\nu]}} W^{[\lambda]}_{JL} W^{[\mu]}_{qr} W^{[\nu]}_{tu} \]

where $K = (\mu, \nu, \alpha, r, u)$, $L = (\mu, \nu, \alpha, q, t)$ and $J = 1, \cdots, f_{[\lambda]}$ is some arbitrary index, which could also be written as a contraction of the same type: $J = (\mu', \nu', \alpha', v, w)$.

If we restrict ourselves to two-column representations of the permutation group, the induction-subduction problem (Equations (5) and (A1)) is multiplicity-free: $m_{\lambda\mu\nu}$ must be 0 or 1. In that case we can drop the indices $\alpha$ and $\alpha'$ to obtain Equation (8).
Formula (A7) can be easily generalized to an arbitrary number of subsystems. Suppose that we have \( n_1 \) electrons occupying the first \( m_1 \) orbitals, \( n_2 \) electrons in the second set of \( m_2 \) orbitals, etc., and \( n_k \) electrons in the last \( m_k \) orbitals, as in Equation (10). Irreducible representations of \( S_{n_1}, S_{n_2}, \ldots, S_{n_k} \) are denoted by \([\mu_1], [\mu_2], \ldots, [\mu_k]\) and their rows and columns are numbered by \( r_i = 1, \ldots, f[\mu_i] \) and \( q_i = 1, \ldots, f[\nu_i] \), respectively, for \( i = 1, \ldots, k \). The reduced Wigner operator \( \tilde{W}_{\ell K}^{[\lambda]} \), which contains the left coset generators of the subgroup \( S_{n_1} \otimes S_{n_2} \otimes \cdots \otimes S_{n_k} \) in \( S_N \), is constructed on a representation \([\lambda]\) that is sequence-adapted to this subgroup. The rows and columns of \([\lambda]\) are numbered by \( K = (\mu_1, \mu_2, \ldots, \mu_k, \alpha, r_1, r_2, \ldots, r_k) \) and \( L = (\mu'_1, \mu'_2, \ldots, \mu'_k, \alpha', q_1, q_2, \ldots, q_k) \). The rows of \([\lambda]\) are numbered by \( (\mu_1, \ldots, \mu_k, \alpha, r_1, \ldots, r_k) \) and \( L = (\mu_1, \ldots, \mu_k, \alpha, q_1, \ldots, q_k) \). This equation can be substituted into expression (10) in order to obtain a generalization of (9) for an arbitrary number of sub-systems.

\[
W^{[\lambda]}_{JK} = \sum_{q_1=1}^{f[\nu_1]} \sum_{q_2=1}^{f[\nu_2]} \cdots \sum_{q_k=1}^{f[\nu_k]} \tilde{W}^{[\lambda]}_{JL} \tilde{W}^{[\mu_1]}_{q_1r_1} \tilde{W}^{[\mu_2]}_{q_2r_2} \cdots \tilde{W}^{[\mu_k]}_{q_kr_k}
\]

where \( K = (\mu_1, \ldots, \mu_k, \alpha, r_1, \ldots, r_k) \), \( L = (\mu_1, \ldots, \mu_k, \alpha, q_1, \ldots, q_k) \) and \( J = (\mu'_1, \ldots, \mu'_k, \alpha', q_1, \ldots, q_k) \). This equation can be substituted into expression (10) in order to obtain a generalization of (9) for an arbitrary number of sub-systems.

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The referee has drawn our attention to a recent paper [27] which is concerned with the transformation properties of \( N \)-electron wave functions under general orbital transformations (with rectangular matrices). Moreover, he mentioned that the equivalence between Young operators (\( PN \) or \( NP \)) and Löwdin projected determinants [19, 22] was also pointed out by Gallup [28].

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PART II:

INTERMOLECULAR FORCES
CHAPTER II.1. INTRODUCTION

The study of intermolecular forces impinges on many of the natural sciences. For example, intermolecular forces determine the thermodynamical properties of gases and liquids, they establish to a large extent the conformation and dynamical behaviour of the polymers, including the biopolymers, they control the structure of molecular crystals and biomembranes, etc. In all these examples one is mostly interested in the behaviour of the system at temperatures not much higher than room temperature, and consequently in the region of the intermolecular potential surface that reaches up to a few thousand calories per mole.

Calculations on such weak interactions are difficult mainly because of the following two reasons:

- The interactions are very small compared to the total energy of the system (the ratio is in the order of 1 to $10^6$). One must realize in this respect that many quantum chemical methods compute interaction energies by subtracting energies that include the contributions of all the electrons in the system, including the inner shell electrons.

- The interaction itself is a delicate balance between a relatively strong repulsive and an equally strong attractive force.

The repulsive force has an exponential behaviour with an onset at a relatively short intermolecular distance $R$, therefore it is typically a short range force. The attractive force has a much longer range; accordingly the term long range force is frequently used as a synonym for intermolecular attraction. The physical origin of these forces has been explained qualitatively a long time ago, but it is only recently that quantitative calculations have come within reach.

The repulsive part of the potential, proposed by Van der Waals to account for the properties of imperfect gases, has been discussed by Eisenschitz and London [1]. They showed that the short range repulsion has the same quantum mechanical origin as chemical bonding, viz. the exchange phenomenon. The one-structure valence bond treatment of the hydrogen molecule is well-suited to illustrate this, because $H_2$ is a chemically bonded system in its singlet ground state, whereas the triplet state exhibits a repulsion which is characteristic for the complexes studied in this thesis. The $H_2$ singlet energy, then, is given by the formula [2]:

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\[ E_S(R) = \frac{C(R) + A(R)}{1 + S(R)} \]

and the triplet energy by:

\[ E_T(R) = \frac{C(R) - A(R)}{1 - S(R)}. \]

The presence of the Coulomb term \( C(R) \) in these formulas can be rationalized quantum mechanically as well as classically. The exchange term \( A(R) \) (and also the overlap term \( S(R) \)) originates from the fact that electrons are indistinguishable, which means that the molecular wave function must be antisymmetric under permutation of all electrons. This typically quantum mechanical observation has been discussed in a more formal setting in sec. I.6.2 of this dissertation. Now, explicit calculation of \( A(R) \) and \( C(R) \) shows that \( A(R) \) is negative and much larger than \( C(R) \), at least for distances down to the equilibrium distance. Further \( S(R) \ll 1 \). So, \( A(R) \) gives rise to a strong (chemical) bonding in the singlet state, whereas the very same term causes a strong repulsion in the triplet state.

In principle it is feasible to exhibit the origin of the exchange repulsion also for larger systems than \( \text{H}_2 \), but because of the multitude of integrals arising in such an exhibition this would be very tedious and not very illuminating. However, all calculations performed to date bear out that the valence bond method (and also the Hartree-Fock method for that matter) always predicts exchange repulsion between systems without unsaturated valencies.

As a possible explanation for the long range intermolecular attraction several possibilities had already been proposed before the advent of quantum mechanics. Keesom [3] had attempted an explanation in terms of electrostatic interactions between permanent moments on the interacting systems. Debije [4] had suggested that induction might be an important factor. In 1930 London [5] came with a quantum mechanical treatment which unified into one single consistent theory the Keesom and Debije forces together with a force unknown until that time. London called this new force "dispersion force", because of the noticeable resemblance of his theory with the Kramers-Heisenberg dispersion theory. (It is interesting that a simple semi-classical version of London's theory [6], which considers an interacting dimer as two coupled harmonically oscillating dipoles, has also a strong likeness with the classical Drude-Lorentz theory of dispersion. Hence the name of the newly discovered force may be explained by the quantum mechanical as well as the classical analogy).
London's theory rests on two fundamental ideas: a Rayleigh-Schrödinger perturbation expansion of the interaction energy and a multipole expansion of the interaction operator. We will consider these points in somewhat more detail in the following chapters. This will be done because the calculations performed in the course of this work have been guided by London's theory, which therefore has considerable impact on this work. Furthermore, London's theory in its elegant irreducible tensor formulation, does not belong to the standard equipment of the average quantum chemist. Irreducible tensors allow, as we will see, the presentation of all the formulas in closed form.

The discussion of the long range intermolecular forces is followed by a few reprinted papers, the oldest of which presents computations on a charge transfer complex. Here the complete neglect of differential overlap (CNDO) method, a semi-empirical Hartree-Fock LCAO-MO method, has been employed. Although it is generally felt that the H-F model does not yield dispersion energy, it is accepted that the model is capable of giving electrostatic, induction and charge transfer interactions. So, reasonable answers may be obtained from H-F calculations on complexes in which charge transfer forces are thought to be the main bonding factor.

As for an approximation which neglects the differential overlap occurring in the integrals, it must be noted that in such a method the Coulomb integrals arising in the H-F equations do not vanish and so the CNDO method might in principle be able to give a reasonable account of the electrostatic forces. Moreover at the time the calculations were undertaken (autumn 1969) it was already known that CNDO usually gives fair results for hydrogen bonded complexes.

However, the paper shows rather unexpectedly that the transfer of charge from the donor to the acceptor is highly exaggerated, giving rise to unphysical interactions. Via a Mulliken population analysis the origin of these interactions could be traced back to the effect of charge transfer; at the same time this population analysis established also that no sort of intermolecular chemical bond was formed.

The other three articles reprinted below are chiefly based on the multi-structure valence bond method, although also CNDO and ab initio SCF calculations are reported for the ethylene dimer. The VB calculations were performed by computer programs especially developed for this purpose. (As a matter of fact the writing and debugging of these programs was the most time consuming part of the work performed for this dissertation). See
ref. 7 (reprinted in this thesis) for a short description of the programs. The basis in the VB calculations consists of canonical valence bond structures, defined in sec. I.5.4, and there called standard Weyl-Rumer tensors.

The unperturbed monomer states entering the VB calculations were all obtained from H-F calculations on the free monomers. To that end a standard SCF program (IBMOL-V) was employed. This program fulfilled all our needs, including the calculation of excited states. Because SCF-LCAO-MO calculations on open- and closed-shell systems have become a routine matter in most laboratories, and because the corresponding theory can be found in any textbook on quantum chemistry, it is unnecessary to go into details about this part of the work. The same holds for the integration of atomic orbitals. See for instance ref. 8 for a discussion of these topics.

All the VB calculations have been performed within an orthogonalized basis of monomer orbitals. For He-He and the ethylene dimer we have investigated whether the intermolecular orthogonalization formed not too drastic an approximation. This was done by transforming the VB structures back to the original basis of non-orthogonal monomer orbitals. We used to that end matrices in irreps of GL(n). The explicit construction of such matrices has been described in sec. I.5.7 of this thesis.
CHAPTER II.2. THE MULTIPole EXPANSION OF 1/r_{12}

In order to introduce the physical problem that forms the topic of this chapter, we consider a system of two point charges \( q_1 \) and \( q_2 \). We further take two coordinate systems: one with an origin at A and another one obtained by translation of the system at A along a vector \( \hat{\mathbf{R}} \). The second system has an origin at B. So, the vector \( \hat{\mathbf{R}} \) points from the origin of system A to the origin of system B. The coordinate vector of \( q_1 \) with respect to the system of axes at A is denoted by \( \hat{\mathbf{r}}_{1a} \); \( \hat{\mathbf{r}}_{1b} \) is the coordinate vector of \( q_1 \) with respect to the system of axes at B. So we have \( \hat{\mathbf{r}}_{1a} = \hat{\mathbf{r}}_{1b} + \hat{\mathbf{R}} \). The coordinate vectors of \( q_2 \) are analogously denoted by \( \hat{\mathbf{r}}_{2a} \) and \( \hat{\mathbf{r}}_{2b} \). Now, Coulomb's law states that the electrostatic interaction between \( q_1 \) and \( q_2 \) is proportional to:

\[
\frac{1}{r_{12}} \equiv 1/|\hat{\mathbf{r}}_{1a} - \hat{\mathbf{r}}_{2a}| = 1/|\hat{\mathbf{r}}_{1a} - (\hat{\mathbf{r}}_{2b} + \hat{\mathbf{R}})|.
\]

If the length \( \mathbf{R} \) of \( \hat{\mathbf{R}} \) is larger than \( r_{1a} + r_{2b} \) the electrostatic interaction can be expanded into a series in \( 1/R \). Each term in this series represents an interaction between a multipole centered on A and one centered on B; therefore this series is called the multipole expansion of the interaction.

In this chapter this multipole expansion will be derived.

Obviously, the multipole expansion is an unnecessarily complicated way of expressing the interaction between two point charges. However, if we have a continuous charge distribution \( \rho_a \) around A and another continuous charge distribution \( \rho_b \) around B, then the multipole expansion furnishes a convenient means of computing the interaction between \( \rho_a \) and \( \rho_b \). For in that case we let \( q_1 \) stand for \( \rho_a (\hat{\mathbf{r}}_{1a}) d\mathbf{x} d\mathbf{y} d\mathbf{z} \) and \( q_2 \) for \( \rho_b (\hat{\mathbf{r}}_{2b}) d\mathbf{x} d\mathbf{y} d\mathbf{z} \), expand the interaction and integrate term-wise over both the charge distributions. Provided \( \mathbf{R} \) is always larger than \( r_{1a} + r_{2b} \), that is, provided \( \rho_a \) and \( \rho_b \) do not overlap, we have found a converging and physically appealing manner of expanding the interaction between \( \rho_a \) and \( \rho_b \).

Quantum mechanically the multipole expansion of \( 1/r_{12} \) enables the expansion of the interaction part of a Hamiltonian describing a system of two non-penetrating atoms or molecules.

There are two essentially different ways of writing the multipole series. The first employs Cartesian coordinate systems at the origins A and B and expresses the interaction completely in terms of Cartesian tensors. The "geometrical" variables do not appear in closed form but in
operator expressions of the type [9]:

\[ T_{\alpha\beta...\gamma} \equiv \nabla_\alpha \nabla_\beta \cdots \nabla_\gamma \left( \frac{1}{r} \right). \]

The operators \( \nabla_\alpha, \nabla_\beta, \ldots, \nabla_\gamma \) standing for the Cartesian components of the nabla operator, \( T_{\alpha\beta...\gamma} \) is a Cartesian tensor. The Cartesian approach has the disadvantage that the final formula is highly redundant. This follows from the fact that the components of Cartesian tensors span reps and not irreps of the full rotation group \( \text{SO}(3) \), and accordingly the problem has not been disentangled to its limit. (The group \( \text{SO}(3) \) arises in this connection as the invariance group of \( 1/r^2 \)). Rotational invariance is of course preserved upon expansion, and so the terms in the multipole expansion are all invariant under rotation. Reduction of the tensor components under \( \text{SO}(3) \) will indeed bring a considerable simplification, because out of the \( \frac{1}{2}(n + 1)(n + 2) \) different components of a Cartesian multipole moment tensor of rank \( n \) only \( 2n + 1 \) contribute to the interaction.

The second manner of writing the multipole expansion makes use of irreducible tensors, thus assuring a maximal disentanglement of the problem. An additional advantage of this approach is that the expansion is not only in closed form, but also solely in terms of spherical harmonics and Clebsch-Gordan coefficients, which can both be found in many tables. Furthermore we can often profit by the fact that the Wigner-Eckart theorem can be applied directly in ensuing calculations.

A disadvantage of the irreducible tensor notation is that the derivation of the multipole expansion, as for instance given by Rose [10], is rather involved, whereas the Cartesian derivation can be followed by everybody who knows how to differentiate a function of \( x, y \) and \( z \). However, a considerably shorter derivation will be presented subsequently, which, as far as I am aware, has not been given before. The final result is presented in the form of a theorem (the second theorem of this chapter).

Firstly, we establish some notation and some necessary definitions. In the following we will adhere to Edmonds [11] with regard to all conventions, including for instance the phases of Clebsch-Gordan coefficients and of spherical harmonics, the definition of standard bases for irreps of \( \text{SO}(3) \), etc.
Definitions.
1. The function $Y_{\ell,m}(\hat{r})$ is a spherical harmonic of the order $\ell$. See for an explicit definition ref. 11, formula 2.5.5. The vector $\hat{r}$ is a unit vector with the polar coordinates $\theta$ and $\phi$.
2. The function:
   \[ S_{\ell,m}(\hat{r}) \equiv r^\ell Y_{\ell,m}(\hat{r}) \]
   is a regular solid harmonic.
   The same function considered as a multiplicative operator is a multipole operator.
3. The function:
   \[ Z_{\ell,m}(\hat{r}) = r^{-\ell-1} Y_{\ell,m}(\hat{r}) \]
   is an irregular solid harmonic.
4. Let the set
   \[ \mathbf{T}_{\ell}(\hat{r}) \equiv \{ T_{\ell,m}(\hat{r}) | m = -\ell, \ldots, +\ell \} \]
   consist of $2\ell + 1$ quantities defined with respect to a set of coordinates in $\mathbb{R}^3$. Describe a rotation of $\mathbb{R}^3$ by:
   \[ \mathbf{r}' = R \mathbf{r} \]
   and let $D^{(\ell)}(R)$ be the matrix representing $R$ in the $(2\ell+1)$-dimensional irrep of $SO(3)$. If the set $\mathbf{T}_{\ell}$ satisfies the transformation equations:
   \[ T_{\ell,m}(\mathbf{r}') = \sum_{m' = -\ell}^{+\ell} T_{\ell,m'}(\mathbf{r}) D^{(\ell)}(R^{-1})_{m'm}, \quad m = -\ell, \ldots, +\ell \]
   then $\mathbf{T}_{\ell}(\hat{r})$ is an irreducible tensorial set of the order $\ell$. Examples of irreducible tensorial sets are spherical harmonics, angular momentum operators, multipole operators, etc.
5. Let $\mathbf{U}_{\ell_1}$ and $\mathbf{V}_{\ell_2}$ be irreducible tensorial sets. The irreducible product of these sets is defined by
   \[ \left[ \mathbf{U}_{\ell_1} \times \mathbf{V}_{\ell_2} \right]^{(\ell)}_{m} \equiv \sum_{m_1,m_2} U_{\ell_1,m_1} V_{\ell_2,m_2} (\ell_1,m_1;\ell_2,m_2 | \ell,m), \quad m = -\ell, \ldots, +\ell \]
   where $(\ell_1,m_1;\ell_2,m_2 | \ell,m)$ is a Clebsch-Gordan coefficient. Clearly an irreducible product is an irreducible tensorial set.
6. Inserting the value of $(\ell,m;\ell,-m|0,0)$ one gets:
   \[ \left[ \mathbf{U}_{\ell} \times \mathbf{V}_{\ell} \right]^{(0)}_{0} = (-1)^\ell (2\ell + 1)^\ell \sum_{m} (-1)^m U_{\ell,-m} V_{\ell,m}. \]
7. Let $\hat{r} = (x,y,z)$ be a vector in $\mathbb{R}^3$. Its spherical coordinates are defined by:
   \[ r_+ = -1/\sqrt{2} (x + iy), \quad r_0 = z, \quad r_- = 1/\sqrt{2} (x - iy) \]
In the sequel spherical coordinates of vectors will be labelled by \( m \) or \( \mu \).

8. The inner product of two vectors \( \mathbf{r} \) and \( \mathbf{r}' \) can be written thus:

\[
\mathbf{r} \cdot \mathbf{r}' = \sum_{m} (-1)^m r_m r'_m = -\sqrt{3} \left[ \mathbf{r} \times \mathbf{r}' \right]_0 ^{(0)}
\]

The following lemma will be needed in the proof of the translation formula for irregular solid harmonics.

**Lemma.**

\[
[\ldots[\mathbf{r} \times \mathbf{r}]^{(2)} \times \mathbf{r}]^{(3)} \times \mathbf{r}]^{(4)} \ldots \times \mathbf{r}]_m^{(k)} = \sqrt{4\pi} \left[ \frac{2^k}{(2k + 1)!} \right]^{\frac{1}{2}} k! S_{k,m}(\mathbf{r}).
\]

**Proof.** First note that \( r_m = \sqrt{4\pi/3} S_{1,m}(\mathbf{r}) \), \( m = -1, 0, +1 \), and therefore:

\[
[\ldots[\mathbf{r} \times \mathbf{r}]^{(2)} \times \mathbf{r}]^{(3)} \ldots \times \mathbf{r}]_m^{(k)} = (\sqrt{4\pi/3})^k \left[ \ldots[\mathbf{s}_1 \times \mathbf{s}_1]^{(2)} \times \mathbf{s}_1]^{(3)} \ldots \mathbf{s}_1 \right]_m^{(k)}.
\]

The right hand side can be easily evaluated by recursion from the relation:

\[
[\mathbf{s}_j \times \mathbf{s}_1]_m^{(j+1)} = \sqrt{3/4\pi} \left[ \frac{j + 1}{2j + 3} \right]^{\frac{1}{2}} S_{j+1,m}
\]

which we now derive:

\[
[\mathbf{s}_j \times \mathbf{s}_1]_m^{(j+1)} = \sum_{m_1,m_2} \left( j,m_1;1,m_2 \mid j+1,m \right) S_{j,m_1} S_{1,m_2}.
\]

Insert into the right hand side the Gaunt series (ref. 11, formula 5.1.6):

\[
[\mathbf{s}_j \times \mathbf{s}_1]_m^{(j+1)} = \sum_{m_1,m_2} \left( j,m_1;1,m_2 \mid j+1,m \right) \sum_{\ell,m'} \left( j,m_1;1,m_2 \mid \ell,m' \right) \times
\]

\[
\times (j,0;1,0 \mid \ell,0) \times \left[ \frac{3(2j + 1)}{4\pi(2j + 3)} \right]^{\frac{1}{2}} S_{\ell,m'}.
\]

Using the fact that the C-G coefficients constitute a real orthogonal matrix and inserting

\[
(j,0;1,0 \mid j+1,0) = \left[ \frac{j + 1}{2j + 1} \right]^{\frac{1}{2}}
\]

we arrive at:

\[
[\mathbf{s}_j \times \mathbf{s}_1]_m^{(j+1)} = \sqrt{3/4\pi} \left[ \frac{j + 1}{2j + 3} \right]^{\frac{1}{2}} S_{j+1,m}.
\]

If we apply this relation repeatedly, for \( j = 1, \ldots, k - 1 \), we get:

\[
[\ldots[\mathbf{s}_1 \times \mathbf{s}_1]^{(2)} \times \mathbf{s}_1]^{(3)} \ldots \times \mathbf{s}_1}_m^{(k)} = (\sqrt{3/4\pi})^{k-1} \left[ \frac{3 \cdot k! \cdot k! \cdot 2^k}{(2k + 1)!} \right]^{\frac{1}{2}} S_{k,m}.
\]
Using \( S_{1,m} = \sqrt{3/4\pi} r_m \) we obtain immediately the relation to be proved.

The now following theorem gives a translation formula for irregular solid harmonics.

**Theorem.**

\[
Z_{\ell,m}^\pm (r_1, r_2) = \sqrt{4\pi} \sum_{k=0}^{\infty} \frac{(2\ell + 2k)^{1/2}}{(2k)^{1/2}} (2k + 1)^{-3/2} \left( Z_{\ell+k}^\pm (r_2) \times S_k^\pm (r_1) \right)_m. 
\]

**Proof.** Expand according to Taylor:

\[
Z_{\ell,m}^\pm (r_1, r_2) = \sum_{k=0}^{\infty} \frac{1}{k!} (r_1 \cdot \hat{r}_2)^k Z_{\ell,m}^\pm (r_2).
\]

To evaluate the terms in the expansion we use the gradient formula (ref. 12, p. 150):

\[
\sum_{\mu} (-1)^\mu \frac{\partial}{\partial \mu} Z_{\ell,m}^\pm (r_2) = \frac{1}{2(\ell + 1)(\ell + 1)} \sum_{\mu} (\ell + 1, \mu + 1, \mu - 1 | \ell, m) \times Z_{\ell+1,m}^\pm (r_2) \frac{\partial}{\partial \mu} r_2,
\]

which written more compactly reads:

\[
(r_1 \cdot \hat{r}_2)^k Z_{\ell,m}^\pm (r_2) = \frac{1}{2(\ell + 1)(\ell + 1)} \left( \left[ \left( Z_{\ell+1}^\pm (r_2) \times \frac{\partial}{\partial \mu} r_2 \right)_m \right] \right)^{(\ell)}. 
\]

Repeated application of \( r_1 \cdot \hat{r}_2 \) gives:

\[
(r_1 \cdot \hat{r}_2)^k Z_{\ell,m}^\pm (r_2) = c_{k\ell m} \left[ \left[ \left[ Z_{\ell+k}^\pm (r_2) \times \frac{\partial}{\partial \mu} r_2 \right] \times \frac{\partial}{\partial \mu} r_1 \right] \times \frac{\partial}{\partial \mu} r_1 \right] \times \ldots \times \frac{\partial}{\partial \mu} r_1 \right]^{(\ell)}_m 
\]

and one easily derives for the constant \( c_{k\ell m} \):

\[
c_{k\ell m} = \left( \frac{(2\ell + 2k)!}{(2\ell)! 2^k} \right)^{1/2}.
\]

The coupling scheme originating from the application of \( (r_1 \cdot \hat{r}_2)^k \) is equivalent to the quantum mechanical coupling case of adding \( k \) particles, all with quantum number \( j = 1 \), to a state with \( j = \ell + k \) in such a manner that a state with \( j = \ell \) results. This same state can also be obtained by first coupling the \( k \) particles to a state of maximal multiplicity, i.e. with \( j = k \), and then coupling this state with \( j = \ell + k \) to give \( j = \ell \).

This is so because there is only one state with quantum numbers \( j = \ell \) and \( j_z = m \) and genealogy \( (\ell + k, 1, 1, \ldots, 1 | \ell) \). So:

\[
\left[ \left[ \left[ Z_{\ell+k}^\pm (r_2) \times \frac{\partial}{\partial \mu} r_2 \right] \times \frac{\partial}{\partial \mu} r_1 \right] \times \frac{\partial}{\partial \mu} r_1 \right] \times \ldots \times \frac{\partial}{\partial \mu} r_1 \right]^{(\ell)}_m =
\]

\[
= \left[ Z_{\ell+k}^\pm (r_2) \times \left[ \left[ \left[ r_1 \times \frac{\partial}{\partial \mu} r_1 \right] \times \frac{\partial}{\partial \mu} r_1 \right] \times \ldots \times \frac{\partial}{\partial \mu} r_1 \right]^{(k)}_m \right]^{(\ell)}.
\]
From the lemma just proved:
\[
\left[ \ldots \left( \mathbf{r}_1 \times \mathbf{r}_1 \right)^{(2)} \mathbf{r}_1 \right]_{(3)} \ldots \mathbf{r}_1_{(m)}^{(k)} = \sqrt{4\pi} \left[ \frac{2^k}{(2k + 1)!} \right]^{\frac{1}{2}} k! S_{k,m}(r_1) \]

and so:
\[
\left( \mathbf{r}_1 \cdot \mathbf{v}_2 \right)^k Z_{l,m}(\mathbf{r}_2) = \sqrt{4\pi} k! \left( \frac{2L + 2k}{2k} \right)^{\frac{L}{2}} (2k + 1)^{-\frac{L}{2}} \left[ Z_{l+k,l}(\mathbf{r}_2) \mathbf{S}_k(\mathbf{r}_1) \right]_{(l)} \]

Substitution of this expression into the Taylor expansion gives the desired result.

We have now at our disposal the necessary machinery to state and prove the essential result of this chapter.

**Theorem (The multipole expansion of 1/|r_1|).**

\[
\frac{1}{r_{12}} = (4\pi)^{3/2} \sum_{l_a=0}^{\infty} \sum_{l_b=0}^{\infty} (-1)^{l_a} \left( \frac{2L}{2l_a} \right)^{L} \left[ (2l_a + 1)(2l_b + 1)(2L + 1) \right]^{-\frac{L}{2}} \times \]
\[
\times \sum_{M=-L}^{+L} (-1)^M Z_{L-M}(\mathbf{R}) \left[ \mathbf{S}_{l_a}(\mathbf{r}_2) \times \mathbf{S}_{l_b}(\mathbf{r}_1) \right]_{(l)} \]

Here: \( L = l_a + l_b \); \( \mathbf{r}_1a, \mathbf{r}_2b \) and \( \mathbf{R} \) are the vectors introduced in the beginning of this chapter, and the lengths of the vectors satisfy:
\( R > r_{1a} + r_{2b} \).

**Proof.** Apply the Laplace expansion of 1/|r_1| [13, p. 79]:

\[
\frac{1}{r_{12}} = \sum_{l_a=0}^{\infty} 4\pi(2l_a + 1)^{-\frac{L}{2}} (-1)^{l_a} \left[ \mathbf{Z}_{l_a}(\mathbf{r}_2a) \times \mathbf{S}_{l_a}(\mathbf{r}_1a) \right]_{(0)} \]

Because, as discussed in the beginning of this chapter, \( R > r_{1a} + r_{2b} \) it follows that always \( r_{2a} > r_{1a} \). This has been used in the Laplace expansion just given. Substituting \( \mathbf{r}_2a = \mathbf{r}_2b + \mathbf{R} \), and applying the foregoing theorem we find:

\[
\frac{1}{r_{12}} = (4\pi)^{3/2} \sum_{l_a=0}^{\infty} \sum_{l_b=0}^{\infty} (-1)^{l_a} \left[ (2l_a + 1)(2l_b + 1) \right]^{-\frac{L}{2}} \left( \frac{2l_a + 2l_b}{2l_a} \right)^{L} \times \]
\[
\times \left[ \mathbf{Z}_{l_a+l_b}(\mathbf{R}) \times \mathbf{S}_{l_b}(\mathbf{r}_2b) \right]_{(l)} \left[ \mathbf{S}_{l_a}(\mathbf{r}_1a) \right]_{(0)} \]

There is only one state with \( j = 0, j_z = m \) and genealogy \( (l_a, l_b, l_a, l_b) \) and so we can write, substituting \( L = l_a + l_b \):

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\[
\left[ \hat{S}^\ell_L (\hat{R}) \times \hat{S}^\ell_{1a} (\hat{R}_{2b}) \right]^{(L)} \times \hat{S}^\ell_{2b} (\hat{R}_{1a}) \right]^{(0)} = \left[ \hat{S}^\ell_L (\hat{R}) \times \hat{S}^\ell_{1b} (\hat{R}_{2b}) \times \hat{S}^\ell_{2a} (\hat{R}_{1a}) \right]^{(L)} \right]^{(0)} =
\]
\[
= (-1)^{L(2L + 1) + 1} \sum_{M} (-1)^{M} Z_{L,-M} (\hat{R}) \left[ \hat{S}^\ell_{b} (\hat{R}_{2b}) \times \hat{S}^\ell_{a} (\hat{R}_{1a}) \right]^{(L)} .
\]

(Of course one can prove the validity of this recoupling more explicitly by evaluation of the associated 6j-symbol).

Substituting this result in the expansion of 1/\(r_{12}\) we have proved the theorem.

Notes.

1. The expression \( [\hat{S}^\ell_{b} (\hat{R}_{2b}) \times \hat{S}^\ell_{a} (\hat{R}_{1a})]^{(L)} \) represents physically the coupling of a multipole moment of order \( \ell_{b} \) on B with a multipole moment of order \( \ell_{a} \) on A to a total moment of maximal order L.

2. The terms in the expansion are invariant under SO(3) as it, of course, must be.

3. The multipole expansion in this form clearly separates the "geometrical" variables \( \hat{R} \) from the "structure" variables contained in the irreducible product of moments.

4. To exhibit more clearly the 1/\(R\)-dependence of the terms, we use the fact that the range \( 0 < \ell_{a} < \infty, 0 < \ell_{b} < \infty \) is also covered by \( 0 \leq L < \infty, 0 \leq \ell_{b} \leq L \). Eliminating \( \ell_{a} \) we get:

\[
1/r_{12} = (4\pi)^{3/2} \sum_{L=0}^{\infty} \sum_{L,-M} (-1)^{L} Y_{L,-M} (\hat{R}) \times \sum_{\ell_{b}=0}^{L} \sum_{M=-L}^{+L} c_{L,\ell_{b}} \left[ \hat{S}^\ell_{b} (\hat{R}_{2b}) \times \hat{S}^\ell_{L,-\ell_{b}} (\hat{R}_{1a}) \right]^{(L)}
\]

where:

\[
c_{L,\ell_{b}} = (-1)^{L} \left( \frac{2L}{2\ell_{b}} \right)^{L} \left[ (2L - 2\ell_{b} + 1)(2\ell_{b} + 1)(2L + 1) \right]^{L/2}.
\]

For instance the physical interactions: hexadecupole-monopole coupling \((\ell_{a} = 4, \ell_{b} = 0)\), octupole-dipole coupling \((\ell_{a} = 3, \ell_{b} = 1)\), and quadrupole-quadrupole coupling \((\ell_{a} = 2, \ell_{b} = 2)\) all have an \(R^{-5}\) dependence.
CHAPTER II.3. LONG RANGE FORCES

In this chapter general formulas for the long range interaction between two systems (atoms or molecules) will be derived. As has been shown in ref. 7, these formulas form an asymptotic expansion (for large $R$) of the VB interaction energy. From the outset we make the assumption that the monomer wave functions do not overlap. This has two immediate consequences:

- All intermolecular exchange integrals vanish, and so we are relieved of the difficult task of intermolecular antisymmetrization.
- The multipole expansion derived in the preceding chapter is applicable.

Let us choose two parallel space fixed coordinate systems $A$ and $B$ located at the centers of mass of the subsystems $A$ and $B$, respectively. The vector $\mathbf{r}$ connects the origins. The particles (nuclei and electrons) of $A$ are labelled by $\alpha$. Their charge is denoted by $q_\alpha$ and their position vector with respect to the coordinate system at $A$ by $\mathbf{r}_\alpha$. Similarly $\mathbf{r}_\beta$ gives the position with respect to the system at $B$ of particle $\beta$, belonging to monomer $B$ and having charge $q_\beta$. Monomer $A$ may be rotated over a set of Euler angles $\omega_A = (\alpha_A, \beta_A, \gamma_A)$ and monomer $B$ over $\omega_B = (\alpha_B, \beta_B, \gamma_B)$. Subsequently expressions will be derived for the first and second order interaction energy as a function of $\mathbf{R}$, $\omega_A$ and $\omega_B$. It is apparent that these coordinates are redundant in a description of the complete interaction potential surface. For example just $\mathbf{R}$ and $\omega_B$ are sufficient.

Write the Hamiltonian of the system as:

$$H = H^A + H^B + V^{AB}$$

(1)

where:

$$V^{AB} = \sum_{\alpha, \beta} \sum_{\ell_A = 0}^{+\lambda} \sum_{\ell_B = 0}^{+\lambda} c_{\ell_A \ell_B} A_B (\ell) \mu Z_{\lambda, -\mu} (\mathbf{R}) \times$$

$$\times \left[ \frac{q_\alpha q_\beta}{\mathbf{r}_{\alpha}} \mathbf{r}_{\beta} \right] \mu \sum_{\ell}^{(r)} \mu \right) (\lambda)$$

(3)

where:

$$\lambda = \ell_A + \ell_B$$

(4)
\[ c_{A}^{\ell} \cdot c_{B}^{\ell} = (-1)^{\ell} \frac{(4\pi)^{3/2}}{2\ell + 1} \left( \frac{(2\ell_A + 1)(2\ell_B + 1)(2\ell_A + 2\ell_B + 1)}{2\ell_A} \right)^{1/2} \left( \frac{2\ell_A + 2\ell_B}{2\ell_A} \right)^{1/2}. \] (5)

Let \( \{|a\rangle \} \) be a complete and discrete set of eigenstates of \( H^A \):

\[ H^A |a\rangle = E_a |a\rangle, \quad a = 0, 1, 2, \ldots, \infty \] (6)

and similarly on B:

\[ H^B |b\rangle = E_b |b\rangle, \quad b = 0, 1, 2, \ldots, \infty. \] (7)

Define a multipole (transition) moment on A:

\[ \langle a | \vec{\ell}_A | a' \rangle \equiv \{ |a \rangle, m_A \langle a' \rangle ; m_A = -\ell_A, \ldots, +\ell_A \} \] (8)

where:

\[ \langle a | \ell_A, m_A \langle a' \rangle \equiv \langle a | \sum_{\alpha} q^\alpha_{\ell_A, m_A} \left( r^\alpha_{\ell_A, m_A} \right) |a' \rangle. \] (9)

In exactly the same way the multipole transition moment \( \langle b | \vec{\ell}_B | b' \rangle \) is defined.

The transition moments are irreducible tensorial sets. Rotation of molecule A over \( \omega_A \) gives the following mapping:

\[ \langle a | \vec{\ell}_A | a' \rangle \rightarrow \langle a | \vec{\ell}_A \cdot \omega^{-1}_A (\omega^{-1}_A) |a' \rangle \] (10)

where:

\[ \langle a | \vec{\ell}_A \cdot \omega^{-1}_A (\omega^{-1}_A) |a' \rangle \equiv \sum_{m_A} \langle \ell_A \rangle_{m_A} (\omega^{-1}_A)_{m_A m_A} \langle a | \ell_A, m_A \langle a' \rangle. \] (11)

Here \( D_{\ell_A} \) is the \((2\ell_A + 1)\)-dimensional irrep of \( SO(3) \). In an analogous manner one proceeds for the transition moments on B.

Up to second order perturbation the interaction energy \( \Delta E^{AB} \) becomes:

\[ \Delta E^{AB} = \Delta E^{(1)} + \Delta E^{(2)} \] (12)

\[ \Delta E^{(1)} = \langle 00 | V^{AB} | 00 \rangle \] (13)

\[ \Delta E^{(2)} = \sum_{a,b=0} \langle \ell_A \rangle^{-1} \langle 00 | V^{AB} | ab \rangle \langle ab | V^{AB} | 00 \rangle \] (14)

\[ \Delta E_{ab} \equiv \langle E_{a=0} - E_{a'} \rangle + \langle E_{b=0} - E_{b} \rangle. \] (15)

In eq. (13) and (14) a product ket \( |a\rangle \otimes |b\rangle \) is written as \( |ab\rangle \), with the first quantum number labelling a ket on A and the second a ket on B. The same holds for the bra.
The first order interaction energy can be written as an explicit function of \( \vec{r}, \omega_A \) and \( \omega_B \), when we insert the multipole expansion (3) into (13) and use the rotation property (10):

\[
\Delta E^{(1)} (\omega_A, \omega_B, \vec{r}) = \sum_{\ell_A=0}^{\infty} \sum_{\ell_B=0}^{\infty} c_{\ell_A \ell_B}^{\ell_0 \ell_0} (-1)^{\mu} Z_{\lambda, \mu}^{\ell_0 \ell_0} (\vec{r}) \times \\
\times \left[ \langle 0 | \hat{D}_A^{\ell_A} (\omega_A^{-1}) | 0 \rangle \alpha \langle 0 | \hat{D}_B^{\ell_B} (\omega_B^{-1}) | 0 \rangle \beta \right]^{(\lambda)}
\]

where \( \lambda \equiv \ell_A + \ell_B \) and \( c_{\ell_A \ell_B}^{\ell_0 \ell_0} \) is the coefficient defined in eq. (5). The expression between square brackets stands for the coupling of a \( 2\ell_A \)-pole on A with a \( 2\ell_B \)-pole on B to a resulting tensor of maximal degree \( \lambda \equiv \ell_A + \ell_B \). The resulting tensor is coupled with an irregular harmonic to form an SO(3) scalar.

So, the terms with fixed \( \ell_A \) and \( \ell_B \) in this expansion of the first order energy represent a tensor interaction [14] between a (rotated) permanent moment on A and a (rotated) permanent moment on B. The total interaction is zero if one of the monomers has no permanent multipole moment, that is, if one of the subsystems is a neutral atom in an S-state. Interpreting the wave function squared as a classical charge distribution, eq. (16) can also be looked upon as the multipole expansion of the classical electrostatic interaction energy. So, in fact we have found a general expression for the tensor force which was considered by Keesom [3] up to quadrupole-quadrupole interaction (\( \ell_A = \ell_B = 2 \)).

Because of the orthogonality relation in the full rotation group:

\[
\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} D^{(0)}(\alpha \beta \gamma)^* \delta^{(2)}(\alpha \beta \gamma)_{mn} \, d\alpha \sin \beta \, d\beta \, d\gamma = \delta_{\alpha 0} \delta_{\beta 0} \delta_{\gamma 0}
\]

(see ref. 11, eq. 4.6.1) and because \( D^{(0)}(\alpha \beta \gamma)_{00}^* = 1 \), it follows that the first order energy, averaged over all orientations of one of the subsystems, is zero. This is not to imply that powers of the first order interaction also vanish upon orientational averaging. The electrostatic energy does give a contribution to the second virial coefficient of an imperfect gas, but only in second and higher order of \( (1/kT) \).
The second order energy becomes after insertion of the multipole expansion (3) into eq. (14):

\[ \Delta E^{(2)}(\mathbf{R}) = \sum \sum c_{\lambda, \lambda'} c_{\lambda, \lambda'}^{*} (\Delta c_{ab})^{-1} Q^{(\ell, \ell'; \lambda, \lambda'; a, b = 0, A, B A, B a, b = 0, A, B A, B)} \]

\[ Q^{(\ell, \ell'; \lambda, \lambda'; a, b = 0, A, B A, B)} = \sum_{\mu=-\lambda}^{\lambda} \sum_{\mu'=-\lambda}^{\lambda} (-1)^{\mu+\mu'} Z_{\lambda, -\mu}(\mathbf{R}) Z_{\lambda', -\mu'}(\mathbf{R}) T_{\lambda, \mu} T_{\lambda', \mu'}^{*} \]

where:

\[ T_{\lambda, \mu} = \langle 0| \mathbf{r}_{A}^{\lambda} | a \rangle \times \langle 0| \mathbf{r}_{B}^{\lambda} | b \rangle \] \]

\[ T_{\lambda', \mu'}^{*} = \langle a| \mathbf{r}_{A}^{\lambda'}| 0 \rangle \times \langle b| \mathbf{r}_{B}^{\lambda'}| 0 \rangle \].

This expression for the second order energy has two disadvantages: the \( \mathbf{R} \)-dependence is given as a product of two irregular solid harmonics, which is inconvenient; furthermore this expression becomes a rather complicated function of \( \omega_{A} \) and \( \omega_{B} \) after substitution of rotation matrices in the manner of the first order energy (16). Therefore we will rewrite this expression, so that all interactions are given in terms of irreducible tensorial products.

Consider the quantity \( Q^{(\ell, \ell'; \lambda, \lambda'; a, b = 0, A, B A, B)} \) defined in equation (19). Write:

\[ Z_{\lambda, -\mu} Z_{\lambda', -\mu'} = \sum_{L, M} (L, M| \lambda, -\mu; \lambda', -\mu') \left[ \mathbf{r}_{L}^{\lambda} \times \mathbf{r}_{\lambda'}^{\lambda'} \right]_{M}^{(L)} \]

\[ T_{\lambda, \mu} T_{\lambda', \mu'}^{*} = \sum_{L', M'} (L', M'| \lambda, \mu; \lambda', \mu') \left[ \mathbf{r}_{L}^{\lambda} \times \mathbf{r}_{\lambda'}^{\lambda'} \right]_{M'}^{(L')} \].

Use:

\[ (L, M| \lambda, -\mu; \lambda', -\mu') = (-1)^{\lambda+\lambda'+L} (L, -M| \lambda, \mu; \lambda', \mu') \],

apply the orthogonality of C-G coefficients and we get:

\[ Q^{(\ell, \ell'; \lambda, \lambda'; a, b = 0, A, B A, B)} = (-1)^{\lambda+\lambda'} \sum_{L} (-1)^{L} \sum_{M} \left[ \mathbf{r}_{L}^{\lambda} \times \mathbf{r}_{\lambda'}^{\lambda'} \right]_{M}^{(L)} \left[ \mathbf{r}_{L}^{\lambda} \times \mathbf{r}_{\lambda'}^{\lambda'} \right]_{M}^{(L')} \].

From the Gaunt series (ref. 11, eq. 5.1.6) one derives easily:

\[ \left[ \mathbf{r}_{L}^{\lambda} \times \mathbf{r}_{\lambda'}^{\lambda'} \right]_{M}^{(L)} = \frac{(2\lambda+1)(2\lambda'+1)}{4\pi(2L+1)} \left( \begin{array}{c} L \lambda \lambda' \mu \end{array} \right)_{-M}^{L} \left( \begin{array}{c} L \lambda \lambda' \mu \end{array} \right)_{M}^{L+2} \mathbf{Y}_{L, -M}(\mathbf{R}). \]
The product \([\tilde{T}_A^\lambda \times \tilde{T}_{A'}^\lambda']_M^{(L)}\) is in fact a fourfold irreducible product (see (20) and (21)). We can recouple this product:

\[
[[\langle 0 | \tilde{T}_A^\lambda | a \rangle \times \langle 0 | \tilde{T}_B^\lambda | b \rangle]^{(\lambda)} \times [\langle a | \tilde{T}_A^\lambda | 0 \rangle \times \langle b | \tilde{T}_B^\lambda | 0 \rangle]^{(\lambda')} \]_M^{(L)} = \\
= \sum \sum (l_A^\lambda, l_B^\lambda) L, (l_A^\lambda', l_B^\lambda') L, (l_A^\lambda, l_B^\lambda') \lambda, (l_A^\lambda', l_B^\lambda') \lambda, \lambda, L \times \\
\times \left[ \tilde{M}_{(l_A^\lambda, l_A^\lambda')} L_A \times \tilde{M}_{(l_B^\lambda, l_B^\lambda')} L_B \right]^{(L)}_M.
\]

Here:

\[
L_A = |l_A - l_A'|, \ldots, l_A + l_A' \\
L_B = |l_B - l_B'|, \ldots, l_B + l_B'
\]

\[
\tilde{M}_{(l_A^\lambda, l_A^\lambda')} \equiv [[\langle 0 | \tilde{T}_A^\lambda | a \rangle \times \langle a | \tilde{T}_A^\lambda | 0 \rangle]^{(L_A)} \\
\tilde{M}_{(l_B^\lambda, l_B^\lambda')} \equiv [[\langle 0 | \tilde{T}_B^\lambda | b \rangle \times \langle b | \tilde{T}_B^\lambda | 0 \rangle]^{(L_B)}.
\]

The recoupling coefficient is (ref. 11, eq. 6.4.2):

\[
(l_A^\lambda, l_B^\lambda') L, (l_A^\lambda', l_B^\lambda') L, (l_A^\lambda, l_B^\lambda') \lambda, (l_A^\lambda', l_B^\lambda') \lambda, \lambda, L = \\
= \left[ (2L_A + 1)(2L_B + 1)(2\lambda + 1)(2\lambda' + 1) \right]^{\frac{1}{2}} \begin{pmatrix} l_A & l_A' & L_A \\ l_B & l_B' & L_B \\ \lambda & \lambda' & L \end{pmatrix}
\]

(29)

The expression between curly brackets is the Wigner 9j-symbol. Substitution of (25), (26) and (29) into (24) yields:

\[
Q(l_A^\lambda, l_B^\lambda'; l_A^\lambda', l_B^\lambda') = (-1)^{\lambda+\lambda'} \sqrt{\frac{1}{4\pi}} R^{-(\lambda+\lambda'+2)} \sum \sum \sum (-1)^{L+M} \times \\
\times d(l_A^\lambda, l_A^\lambda'; l_B^\lambda, l_B^\lambda; L) Y_{LM}^{(-\tilde{R})} \left[ \tilde{M}_{(l_A^\lambda, l_A^\lambda')} L_A \times \tilde{M}_{(l_B^\lambda, l_B^\lambda')} L_B \right]^{(L)}_M
\]

(30)

where:
\[
\frac{(2L_A + 1)(2L_B + 1)}{(2L + 1)} \times \left( \begin{array}{c}
\ell_A^0 \\
\ell_A^1 \\
L_A
\end{array} \right) \times \left( \begin{array}{c}
\ell_B^0 \\
\ell_B^1 \\
L_B
\end{array} \right) \\
\times (\lambda; 0; \lambda' 0 | L, 0)
\]

Substituting (30) into (18) and further using the fact that the coupled moments, defined in (27) and (28), are irreducible sets, we arrive finally at:

\[
\Delta B^{(2)}(\omega_A, \omega_B, \mathbf{R}) = (4\pi)^{5/2} \sum \sum (-1)^{\ell_A^0 + \ell_A^1} \times \left( \begin{array}{c}
\ell_A^0 \\
\ell_A^1 \\
L_A
\end{array} \right) \times \left( \begin{array}{c}
\ell_B^0 \\
\ell_B^1 \\
L_B
\end{array} \right)
\times A(\ell_A^0, \ell_A^1, \ell_B^0, \ell_B^1) \times \prod_{a,b=0}^{\infty} \%
\sum (\Delta_\epsilon_{a,b})^{-1} \sum (-1)^{M} \times \frac{1}{M} \times [\Delta_\epsilon_{a,b}] M \times \frac{1}{M} \times [(L_A) \cdot D_{\ell_A^0} (\omega_A^{-1})) \times (L_B) \cdot D_{\ell_B^0} (\omega_B^{-1}))]
\]

where:

\[
\ell_A, \ell_A^0 = 0, 1, 2, \ldots, \infty
\]

\[
\ell_B, \ell_B^0 = 0, 1, 2, \ldots, \infty
\]

\[
L_A = \left| \ell_A - \ell_A^0 \right|, \left| \ell_A - \ell_A^0 \right| + 1, \ldots, \ell_A + \ell_A^0
\]

\[
L_B = \left| \ell_B - \ell_B^0 \right|, \left| \ell_B - \ell_B^0 \right| + 1, \ldots, \ell_B + \ell_B^0
\]

\[
L = \left| L_A - L_B \right|, \left| L_A - L_B \right| + 1, \ldots, L_A + L_B
\]

\[
M = -L, -L + 1, \ldots, L
\]

and:

\[
A(\ell_A^0, \ell_A^1, \ell_B^0, \ell_B^1) = \left[ \frac{(2\ell_A + 2\ell_B + 1)! (2\ell_A + 2\ell_B + 1)!}{(2\ell_A + 1)! (2\ell_B + 1)! (2\ell_A + 1)! (2\ell_B + 1)!} \right]^2
\]

\[
B(\ell_A^0, \ell_A^1, \ell_B^0, \ell_B^1, L_A, L_B, L) = \left[ (2L_A + 1)(2L_B + 1) \right]^2 \times \left( \begin{array}{c}
\ell_A^0 + \ell_A^1 \\
\ell_A^0 + \ell_A^1 \\
L_A
\end{array} \right) \times \left( \begin{array}{c}
\ell_B^0 + \ell_B^1 \\
\ell_B^0 + \ell_B^1 \\
L_B
\end{array} \right) \times \left( \begin{array}{c}
\ell_A^0 + \ell_A^1 + \ell_B^0 + \ell_B^1 \\
L
\end{array} \right)
\]

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A term with fixed \( L_A \) and \( L_B \) in the second order interaction (32) represents the coupling of the tensor \( \mathcal{M}^{\text{oa}}_{(l_A' l'_A)} L_A \) centered on A with a tensor \( \mathcal{M}^{\text{ob}}_{(l_B' l'_B)} L_B \) centered on B. Hence the second order interaction is, just like the first order interaction, a tensor interaction [14], but contrary to the case of the first order interaction the two monomer tensors do not only couple to their maximal \( L \)-value \( (L = L_A + L_B) \), but to all their possible lower \( L \)-values as well. Note that the monomer tensor \( \mathcal{M}^{\text{oa}}_{(l_A' l'_A)} L_A \), which is of order \( L_A \), originates from the coupling of a 2 \( l_A \)-pole on A with a 2 \( l_A' \)-pole on A. In the same way the tensor \( \mathcal{M}^{\text{ob}}_{(l_B' l'_B)} L_B \) arises on monomer B from the coupling of two multipoles on B.

It is customary to distinguish three different contributions to the second order energy. To that end one splits the sum over the excited states of the dimer thus:

\[
\sum_{a,b=0}^{\infty} \sum_{a'=1}^{\infty} \sum_{b'=1}^{\infty} \sum_{\sigma} \sum_{\sigma'}
\]

(35)

The first term in the right hand side gives rise to interactions of the type:

\[
\Delta E^{A+B}_{(\text{ind})} \propto R \sum_{M} (-1)^M Y_{L,-M}(\hat{R}) \times \sum_{M} (-1)^M Y_{L,-M}(\hat{R}) \times \sum_{M} (-1)^M Y_{L,-M}(\hat{R}) \times
\]

(36)

\[
\sum_{\sigma} \sum_{\sigma'} (\Delta \varepsilon)_{\sigma \sigma'}^{-1} \mathcal{M}^{\text{ob}}_{(l_B' l'_B)} L_B
\]

(37)

is an irreducible polarizability tensor giving a 2 \( l_B' \)-pole and a 2 \( l'_B \)-pole on B, which in eq. (36) are interacting with a permanent 2 \( l_A \)-pole and 2 \( l_A' \)-pole on A. The interaction (36) has a classical counterpart in Debije's induction force [4]. Debije considered the special case \( l_A = l_A' = 2 \), \( l_B = l_B' = 1 \), that is, a permanent quadrupole on A inducing a dipole on B. This interaction has an \( R^{-8} \) dependence.

The second term in (35) gives a sum of interactions, all arising from the induction of multipoles on A by permanent moments on B.

The last term does not allow a classical interpretation, it gives
London's dispersion force [5]. London considered the special case \( \ell_A = \ell_A' = \ell_B = \ell_B' = 1 \), the induced-dipole-induced-dipole interaction. This interaction has an \( R^6 \) dependence.

When we average the second order energy (32) over all orientations of the monomers:

\[
\langle \Delta E^{(2)} (R) \rangle = \int \int \Delta E^{(2)}(\omega_A, \omega_B, R) \, d\omega_A \, d\omega_B
\]

and use (17), we obtain only a contribution for \( L_A = 0 \) and \( L_B = 0 \). And since:

\[
B(\ell_A \ell_A', \ell_B \ell_B', 0, 0) = \delta_{\ell_A \ell_A'} \delta_{\ell_B \ell_B'} (-1)^{\ell_A + \ell_B} (2\ell_A + 2\ell_B + 1)^{-1/2}
\]

we get:

\[
\langle \Delta E^{(2)} (R) \rangle = (4\pi)^2 \sum \frac{\ell_A + \ell_B}{2 \ell_A + 2 \ell_B} \epsilon_{\ell_A \ell_B} \epsilon_{\ell_A' \ell_B'}^{-1} \epsilon_{\ell_A' \ell_B'}^{-1} \epsilon_{\ell_A \ell_B} \times
\]

\[
R_{\ell_A \ell_B} \left( \frac{2 \ell_A + 2 \ell_B}{2 \ell_A} \right) ^{-2(\ell_A + \ell_B + 1)} \right)^{-1} \times
\]

\[
\sum \frac{m_A}{m_A} \langle 0 | \ell_A, m_A | a \rangle \langle a | \ell_A, -m_A | 0 \rangle \times
\]

\[
\sum \frac{m_B}{m_B} \langle 0 | \ell_B, m_B | b \rangle \langle b | \ell_B, -m_B | 0 \rangle.
\]

The matrix elements arising in this expression are defined in (9). For instance the average dipole-dipole interaction is:

\[
\langle \Delta E^{(2)}_{d-d} (R) \rangle = \frac{2}{3} R^6 \sum \epsilon_{\ell_A \ell_B}^{-1} \langle 0 | \ell_A, a \rangle \langle a | \ell_A, b \rangle \langle b | \ell_B, -m_B | 0 \rangle \times
\]

\[
\langle 0 | \ell_B, b \rangle \langle b | \ell_B, -m_B | 0 \rangle.
\]

where

\[
\langle 0 | \ell_A, a \rangle \langle a | \ell_A, b \rangle = \langle 0 | \ell_A, a \rangle \langle a | \ell_A, b \rangle
\]

\[
= \langle 0 | \ell_A, a \rangle \langle a | \ell_A, b \rangle \epsilon_{\ell_A \ell_B}^{-1} \epsilon_{\ell_A \ell_B}^{-1} \epsilon_{\ell_A \ell_B} \times
\]

\[
R_{\ell_A \ell_B} \left( \frac{2 \ell_A + 2 \ell_B}{2 \ell_A} \right) ^{-2(\ell_A + \ell_B + 1)} \right)^{-1} \times
\]

\[
\sum \frac{m_A}{m_A} \langle 0 | \ell_A, m_A | a \rangle \langle a | \ell_A, -m_A | 0 \rangle \times
\]

\[
\sum \frac{m_B}{m_B} \langle 0 | \ell_B, m_B | b \rangle \langle b | \ell_B, -m_B | 0 \rangle.
\]

and a similar definition holds for \( \langle 0 | \ell_B, b \rangle \langle b | \ell_B, -m_B | 0 \rangle \). This same formula (41) has been derived by London [5] for the case of two interacting atoms.
London averaged by summing over the degenerate states of the atoms. Note, however, that equation (40) is completely general, no assumption whatever has been made about the symmetry of $H^A$ and $H^B$, so the formula is valid for molecules of arbitrary symmetry.

**Notes.**

1. A formula similar to (40) has been derived by Riera and Meath [15]. These authors take the orientational average of the second order energy given in eq. (18). Since formula (18) is not simplified to the utmost with respect to its transformation properties, the final formula of ref. 15 is not as simple as our expression (40). Furthermore the result of Riera and Meath contains a small error; it seems that the authors have not divided by the volume of SO(3) and hence they present an un-normalized averaged interaction energy.

2. Contrary to the electrostatic (first order) interaction, neither the induction energy nor the dispersion energy vanishes upon orientational averaging. The leading contribution to the second virial coefficient arising from these forces is therefore proportional to $1/kT$ and hence is in general much larger than the electrostatic contribution, although the (non-averaged) electrostatic interaction is often larger than the (non-averaged) induction and (non-averaged) dispersion interaction.

The second order interaction energy computed above is always attractive, as can be seen from eq. (14). Nonetheless it is experimentally known that two closed-shell molecules repel each other at short distances, and so there is something lacking in the theory. Now, one of the basic assumptions we made in the beginning of this chapter was that intermolecular antisymmetrization is unnecessary, but, as we have already discussed in ch. II.1, intermolecular exchange causes repulsion and so we miss this effect. One can remedy this fault by including the intermolecular antisymmetrizer into the perturbation formulas. This approach has already been pursued by Eisenschitz and London [1]; more recently their results have been recast into a wave operator formalism by Van der Avoird [16]. Many other workers have also attempted to derive a practical exchange-perturbation theory [17], and several authors have applied such a theory to calculations on simple systems [18, 19]. The general experience is
that a second order energy which includes exchange is difficult to compute for any but the simplest systems. Moreover the practical exchange-perturbation calculations usually proceed by a variational approximation. Therefore, we decided rather to use the variational principle from the start.

The first of the following papers is based on a semi-empirical SCF method. This approach has the great advantage that relatively large complexes can be handled. However, as already has been discussed in the introduction (ch. II.1), the outcome of these calculations was not very promising. Therefore we turned to the ab initio multi-structure VB method. The paper on He₂ must be considered as a first test on this formalism; the work on the ethylene dimer is an application of the VB method to a chemically more interesting complex. The paper on He-H₂ has been an attempt to obtain an intermolecular potential of such quality that it could be of use in molecular beam scattering experiments. This attempt has proved to be successful [20].
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The TCNE-Benzene Complex: 
A CNDO Approach*

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CNDO/2 calculations on the TCNE-benzene complex are reported. A stable complex is found which exhibits a relatively large stabilization energy (0.2 a.u.) at a short interplanar separation (1.75 Å); the binding apparently arises solely through charge transfer. Mulliken population analyses were performed by reinterpreting the CNDO orbitals as Löwdin orbitals. Sample calculations on small organic molecules and first row diatomics indicate the procedure to be satisfactory. It is shown that generally only overlap populations that are summed over the orbitals of the atoms in question reflect the symmetry of the molecule.

Die Ergebnisse von CNDO/2-Rechnungen an Tetracyanaäthylbenzol-Komplexen werden mitgeteilt. Es wird ein stabiler Komplex gefunden, der eine relativ große Stabilisierungsentnergie (0,2 A.E.) bei geringem Abstand (1,75 Å) der Molekülebenen besitzt; die Bindung entsteht anscheinend nur durch Ladungsübertragung. Eine Populationsanalyse nach Mulliken wurde mit Hilfe der Interpretation der CNDO-Orbitale als Löwdin-Orbitale durchgeführt. Berechnungen an Beispielen wie kleinen organischen Molekülen und zweiatomigen Molekülen aus Elementen der ersten Reihe zeigen, daß die Methode befriedigende Ergebnisse liefert. Es wird gezeigt, daß im allgemeinen nur die Überlappungs-Populationen, die über die Orbitale der betrachteten Atome summiert werden, die Symmetrie des Moleküls widerspiegeln.

Calculs CNDO/2 sur le complexe TCNE-benzène. Un complexe stable apparaît pour une séparation interplan couette (1,75 Å) avec une énergie de stabilisation relativement forte (0,2 u.a.); la liaison provient apparemment du seul transfert de charge. Une analyse de population de Mulliken a été effectuée en réinterprétant les orbitales CNDO comme orbitales de Löwdin. Des calculs échantillonnés sur de petites molécules organiques et des molécules diatomiques de la première ligne montrent que le procédé s'avère satisfaisant. On montre qu'en général, seules les populations de recouvrement sommées sur les orbitales des atomes en question reflètent la symétrie de la molécule.

**Introduction**

$\pi-\pi$ molecular complexes pose an interesting study in bonding. The question of the prime effect in stabilizing such systems is not yet clear due mainly to the difficulty in adequately treating such large systems. For some time it was generally felt that charge transfer stabilization was mainly responsible for bonding, but spectroscopic measurements on some TCNE (tetracyanoethylene) complexes do not seem to support this idea [1]. Studies employing a $\pi$-only extended Hückel approach [2] have given indications of reproducing relative molecular geometries at chosen experimental interplanar intermolecular separations but in general fail to predict absolute binding. The advent of approximate self-consistent field
treatments introduced by Pople and coworkers [3] allows a more readily justifi-
fiable treatment of large systems and avoids many of the pitfalls of one-electron
methods. For example, several recent calculations [4, 5] using this method on
hydrogen bonded systems have yielded reasonable results. In the present paper
we present CNDO/2 calculations of the TCNE-benzene complex for a restricted
region of relative intermolecular geometry.

A basic purpose for initiating such a calculation is the elucidation of those
factors which dictate the observed relative intermolecular geometry characteristic
of the majority of both charge transfer and charge resonance complexes. Unfortu-
nately, the current calculations do not reveal any particular simplifying
feature; on the contrary, the issue is clouded a bit by our results which indicate
small and negative intermolecular overlap populations and a high degree of
charge transfer. It is worthwhile to discuss these results in light of the general
problems above. Too, since no previous CNDO calculations on systems of this
kind have been performed the present calculations may be taken as a model
study of the CNDO approach to a π-bonded bimolecular system.

**Choice of Model**

The dominant structural fragment seen in most π-π molecular complexes
consists of a bonds-over-bonds arrangement shown below,

![Diagram of bonds-over-bonds arrangement](image)

where the benzenoid moiety projects onto an ethylene-like fragment arising either
from a real ethylene group (case a, as, for example, the central portion of TCNE
itself) or from a fused benzenoid system (case b). Examples of such structures can
be seen in Chesnut and Moseley’s paper [2] and from the review paper of Prout
and Wright [6]. We wished to carry out calculations on a system that exhibits
such a characteristic projected structure and at the same time was small enough
to minimize computer time. The available program is limited to 80 orbitals
which severely restricts our selection. The TCNE-benzene system represents a
70-orbital problem and, although its structure is not known, one would expect
a behavior similar to the general class of materials. Indeed, the TCNE-naph-
thalene crystal structure is known [7], exhibiting the projection

![Diagram of TCNE-naphthalene crystal structure](image)
An interesting aspect of the TCNE-naphthalene structure is that as the TCNE and naphthalene molecules stack alternately with planes parallel to one another the TCNE molecules project onto one ring of the naphthalene below and the opposite ring of the naphthalene above.

Since we are interested in general trends we have concentrated on the above type of projected structure in the TCNE-benzene calculations. We have performed a few calculations on other geometries and, as discussed later, find that a rotated form of the complex exhibits greater binding according to the computational method we have employed. Aside from questioning the general integrity of the calculational approach, this raises the well-known problem of comparing calculations on an isolated molecular system (a gas-phase calculation) with experimental structural data obtained from studies of crystals.

Calculations and Method of Population Analysis

The calculations were performed on the IBM 360/75 computer at the Triangle Universities Computer Center, Research Triangle Park, North Carolina, using a modified version of the semiempirical self-consistent field CNINDO program supplied by the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. The semiempirical parameters used were the CNDO/2 parameters given by Pople et al. [3]. The internal geometries of TCNE and benzene were held fixed throughout the calculations. For TCNE, 120° angles plus the distances reported in Bekoe and Trueblood's crystal structure investigation [8] were used; for benzene, standard hexagonal symmetry was assumed with C–C and C–H distances of 1.40 Å and 1.08 Å, respectively. The molecular planes were always maintained parallel to each other.

Two modifications to the basic program were made. In its original form CNINDO showed diverging SCF cycles for TCNE and TCNE-benzene. To circumvent this difficulty the program was modified so that in the \((n+1)\)^{th} iterative SCF cycle the entered density matrix (charge and bond-order matrix), \(P^{(n)}\), used was taken to be

\[
P^{(n)} = P^{(n-1)} + \delta (P^{(n)^*} - P^{(n-1)}) ,
\]

where \(P^{(n-1)}\) is the density matrix entering the \(n\)^{th} cycle, \(P^{(n)^*}\) is the density matrix exiting the \(n\)^{th} cycle, and \(\delta\) is a damping factor. A value of 0.7 for \(\delta\) was found to yield optimum convergence for TCNE (convergence in 14 cycles) and proved satisfactory for the TCNE-benzene complex and another large cyanocarbon, TCNQ (tetracyanoquinodimethane). An average calculation on the TCNE-benzene complex took about 12.5 minutes.

The second modification involved the addition of a subroutine to perform a Mulliken population analysis [9] in terms of a transformed basis. One of the main points of interest of this work was the question of whether or not one can detect intermolecular bonding in the complex. One such measure has been simply to use the non-diagonal elements of the charge and bond-order matrix, the bond orders [10]. We are interested in the total measure of bonding between any two atoms and would thus want to sum individual bond orders of the various atom-
localized orbitals. This procedure, however, fails in general for an arbitrary choice of local atomic coordinate systems (to which the localized AO's are attached); physically equivalent (symmetry related) bonds can have different total summed bond orders (See Appendix). A simple example is to note that the π-bond order between a pair of $P_z-\pi$ orbitals in an aromatic system is changed in sign by inverting one of the local $z$-axes. The fact that the use of simple bond orders is justified in π-electron calculations depends upon the standard choice of parallel local axes normal to the π-plane.

A way of avoiding this problem is to use the sum of Mulliken orbital overlap populations. We show in the Appendix that these summed populations reflect the symmetry of the molecules. The CNDO orbitals, however, are orthogonal in the zero-differential-overlap approximation so that there are no non-vanishing overlap populations. We choose, however, to consider the CNDO orbital as Löwdin orbitals [11], that is, semi-localized orbitals which resemble localized atomic orbitals as closely as possible [12] and yet are mutually orthogonal. Thus, the CNDO orbital set $\{\phi_n\}$ is taken to be related to a localized, non-orthogonal set $\{\phi'_n\}$ by the transformation

$$\phi' = \phi S^{1/2},$$

where $S$ is the overlap matrix in the basis $\{\phi'_n\}$ and was constructed from the overlap integrals of the Slater orbitals used in the CNDO program. Expressing our CNDO wave functions in the $\{\phi'_n\}$ basis then allows one to perform a

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond</th>
<th>$\sigma$</th>
<th>$\pi$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A Li$_2$</strong></td>
<td>—</td>
<td>0.872 (0.962)</td>
<td>0.0 (0.0)</td>
<td>0.872 (0.962)</td>
</tr>
<tr>
<td><strong>N$_2$</strong></td>
<td>—</td>
<td>0.431 (0.220)</td>
<td>0.880 (0.880)</td>
<td>1.311 (1.100)</td>
</tr>
<tr>
<td><strong>F$_2$</strong></td>
<td>—</td>
<td>0.256 (0.297)</td>
<td>0.017 (0.001)</td>
<td>0.239 (0.296)</td>
</tr>
<tr>
<td><strong>LiF</strong></td>
<td>—</td>
<td>0.155 (0.190)</td>
<td>0.322 (0.208)</td>
<td>0.477 (0.398)</td>
</tr>
<tr>
<td><strong>LiH</strong></td>
<td>—</td>
<td>0.757 (0.691)</td>
<td>0.0 (0.0)</td>
<td>0.757 (0.691)</td>
</tr>
<tr>
<td><strong>B benzene</strong></td>
<td>C–C</td>
<td>0.876 (0.82)</td>
<td>0.240 (0.240)</td>
<td>1.116 (1.06)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.768 (0.78)</td>
</tr>
<tr>
<td></td>
<td>C=C</td>
<td>0.916 (0.791)</td>
<td>0.428 (0.420)</td>
<td>1.344 (1.211)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.778 (0.812)</td>
</tr>
<tr>
<td></td>
<td>C–C</td>
<td>—</td>
<td>—</td>
<td>0.856 (0.710)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.766 (0.785)</td>
</tr>
<tr>
<td></td>
<td>acetylene</td>
<td>C–C</td>
<td>0.390 (0.544)</td>
<td>0.920 (0.918)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.810 (0.800)</td>
</tr>
<tr>
<td></td>
<td>cis-butadiene</td>
<td>C=C</td>
<td>0.910 (0.77)</td>
<td>0.412 (0.39)</td>
</tr>
<tr>
<td></td>
<td>C–C</td>
<td>0.832 (0.81)</td>
<td>0.050 (0.09)</td>
<td>0.882 (0.92)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.764, 0.780, 0.798 (0.78)</td>
</tr>
<tr>
<td></td>
<td>HCN</td>
<td>C≡N</td>
<td>0.390 (0.544)</td>
<td>0.920 (0.918)</td>
</tr>
<tr>
<td></td>
<td>C–H</td>
<td>—</td>
<td>—</td>
<td>0.810 (0.800)</td>
</tr>
<tr>
<td></td>
<td>TCNE</td>
<td>C=C</td>
<td>0.818</td>
<td>0.376</td>
</tr>
<tr>
<td></td>
<td>C–C</td>
<td>0.844</td>
<td>0.052</td>
<td>0.896</td>
</tr>
<tr>
<td></td>
<td>C≡N</td>
<td>0.824*</td>
<td>0.448b</td>
<td>1.272</td>
</tr>
</tbody>
</table>

* Includes the equivalent of one (in plane) π-bond.

b The “pure” π-bond.
Mulliken population analysis in terms of net atomic charges and total bond overlap populations and this is the procedure we have followed. Recently, Brown and Roby [13] have shown that this interpretation of zero-differential-overlap theories can be justified from first principles.

To test this procedure we calculated total bond orders for a series of first row diatomics and small organic molecules and compared our results with literature values. The agreement is quite adequate; the comparisons for some representative systems are shown in Table 1, where the present results are compared with the calculations of Fraga and Ransil [14] for the diatomics and with the calculations of Lipscomb and coworkers [15] for the polyatomics. We used the same diatomic distances as Fraga and Ransil; for the organic systems we employed values from the "Tables of Interatomic Distance and Configurations in Molecules and Ions" (The Chemical Society, London, 1965) which differ very slightly in a few instances with the values of Newton, Boer, and Lipscomb.

**Results and Discussion**

Although no experimental gas phase data are available for the stabilization energy, the dipole moment and the intermolecular of the TCNE-benzene complex, one can get a rough idea of the order of magnitude of these quantities by comparison with similar complexes. In Table 2 some illustrative experimental data for complexes in which TCNE acts as the acceptor are presented.

To date no calculations, except those of Chesnut and Moseley [2] on the TCNE-anthracene complex, have been performed that vary the interplanar distance. Lippert, Hanna, and Trotter [18] take the fixed interplanar distance 3.50 Å and calculate by means of Morrell’s perturbation theory [16] a dipole moment of 0.54 D and a stabilization energy of $-6.21$ kcal/mole. Their method is especially devised for charge transfer complexes and they use some parameters that are determined for the ease under consideration. Herndon and Feuer [20] take a fixed distance as well (3.20 Å). They apply a perturbational method using as first-order functions for the separate molecules CNDO/2 functions and find a $-3.54$ kcal/mole stabilization energy. Mantione [21] calculated Van der Waals – London interactions in TCNE complexes with $p$-xylene, $o$-xylene, mesitylene and durene. His results agree remarkably well with the experimental results. Again the distance was fixed (3.30 Å).

The current calculations represent an attempt at a somewhat more general approach in which the relative geometry is determined by the calculation. Even

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\Delta E$ (kcal/mole)</th>
<th>$\mu$ (Debye)</th>
<th>$R$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>3.34$^a$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>durene</td>
<td>-10.1$^b$</td>
<td>1.26$^c$</td>
<td>—</td>
</tr>
<tr>
<td>naphthalene</td>
<td>-4.06$^d$</td>
<td>1.28$^e$</td>
<td>3.30$^f$</td>
</tr>
</tbody>
</table>

$^a$ In CCl$_4$ (Ref. [16]).  
$^b$ In gas phase (Ref. [17]).  
$^c$ In CCl$_4$ (Ref. [16]).  
$^d$ In CCl$_4$ (Ref. [16]).  
$^e$ In CCl$_4$ (Ref. [15]).  
$^f$ In solid state (Ref. [7]).
Fig. 1. $\Delta E = E - E_\infty$ (in a.u.) as a function of the interplanar separation, $R$ (in Å), for the relative geometries studied. $\mu$, the dipole moment (in Debyes) is also shown for the non-rotated structure. The structure projections are approximately to scale and illustrate the two relative geometries studied

so, finite computer time and funds necessitated a limitation on the possible geometries to be studied. Most of the calculations refer to that situation in which the two molecules are brought together directly on top of each other with the projected TCNE double bond direction colinear with the 1,4-carbon atoms on the benzene ring (the non-rotated form); a few points for the geometry in which the TCNE was rotated by $30^\circ$ about the axis normal to its plane (the rotated forms) were also calculated. The non-rotated and $30^\circ$ rotated geometries are shown in projection as part of Fig. 1. One must note that the optimum procedure in calculations of this kind would be to vary all distances to find the minimum energy; this would require very extensive calculations for the present case, calculations which we don't believe are warranted. Thus, in all our calculations the internal geometries of the component molecules are held fixed as the distance between them, $R$, was varied.

Fig. 1 shows the calculated energy versus the interplanar separation for both the rotated and non-rotated structures; in Table 3 the electronic and nuclear energy components are listed along with the total energy. While the non-rotated structure is the one for which most calculations were carried out, the rotated form ($30^\circ$) at $R = 1.75$ Å actually exhibits a lower minimum ($E_{30^\circ} < E_{15^\circ} < E_0$ at 1.75 Å). Relative to one's a priori prejudices, the energy curve shows too deep a minimum at too short an interplanar separation with an extremely steep variation
Table 3. Relative energies (in a.u.) as a function of $R$

$E_N =$ nuclear repulsions, $E_{el} =$ electronic energy $= E - E_N$, $E =$ total energy $= E_N + E_{el}$

<table>
<thead>
<tr>
<th>$R$ (Å)</th>
<th>$E_N - E_{N, \infty}$</th>
<th>$E_{el} - E_{el, \infty}$</th>
<th>$\Delta E = E - E_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>271.401</td>
<td>$-270.925$</td>
<td>0.476</td>
</tr>
<tr>
<td>1.375</td>
<td>262.258</td>
<td>$-262.206$</td>
<td>0.052</td>
</tr>
<tr>
<td>1.50</td>
<td>253.567</td>
<td>$-253.700$</td>
<td>0.133</td>
</tr>
<tr>
<td>1.64</td>
<td>244.349</td>
<td>$-244.543$</td>
<td>0.194</td>
</tr>
<tr>
<td>1.75*</td>
<td>237.471</td>
<td>$-237.670$</td>
<td>$-0.199$</td>
</tr>
<tr>
<td>1.75 b</td>
<td>237.417</td>
<td>$-237.629$</td>
<td>$-0.212$</td>
</tr>
<tr>
<td>1.75 c</td>
<td>237.358</td>
<td>$-237.586$</td>
<td>$-0.228$</td>
</tr>
<tr>
<td>2.00</td>
<td>222.948</td>
<td>$-223.099$</td>
<td>$-0.151$</td>
</tr>
<tr>
<td>2.25</td>
<td>209.827</td>
<td>$-209.915$</td>
<td>$-0.088$</td>
</tr>
<tr>
<td>2.50</td>
<td>197.945</td>
<td>$-197.990$</td>
<td>$-0.045$</td>
</tr>
<tr>
<td>3.00</td>
<td>177.339</td>
<td>$-177.348$</td>
<td>$-0.009$</td>
</tr>
<tr>
<td>3.50</td>
<td>160.180</td>
<td>$-160.181$</td>
<td>$-0.001$</td>
</tr>
</tbody>
</table>

* 0° rotation. − b 15° rotation. − c 30° rotation.

of the energy at both small and large values of $R$. Whereas stabilization energies of the order of 2 to 5 kcal/mole might be expected, an energy minimum here is calculated to be approximately 125 kcal/mole. Whereas interplanar separations in crystals are from 3.2 to 3.5 Å, the minimum here occurs at approximately 1.75 Å. The energy curve at large $R$ approaches an $R^{-14}$ behavior with no hint of the London $R^{-6}$ dispersion force behavior. The absence of the London forces in our results need not be surprising since it is generally held that these forces cannot be reproduced in a self-consistent field calculation without configuration interaction.

The large value of $\Delta E$, the energy of stabilization, is somewhat characteristic of the CNDO method which tends to overemphasize binding. This property may well also explain why the minimum in $\Delta E$ occurs at too short a distance. To improve usefulness of these calculations a detailed study of what parameters or integrals led to this effect should be made and the necessary reparameterization be made. As alluded to above, the importance of configuration interaction must also be ascertained. The lowering of $\Delta E_{\text{min}}$ that occurs in going to the rotated complex occurs through a lowering of the nuclear repulsion terms which overcome an increase in the electronic energy (see Table 3). It is clear that the detailed geometry may well be very sensitive to the specific input parameters in systems as large and complicated as the present one. Jesaitis and Streitwieser [22] point out that because the CNDO method uses $s$-orbitals to calculate the coulomb repulsion, the electron-electron repulsive energy may be underestimated in systems where the charge can be highly delocalized. This effect may be quite significant in the present case since transfer of charge from benzene to TCNE allows the transferred electron greater delocalization. Thus, the underestimation of coulomb repulsion would promote such charge transfer.
Also plotted in Fig. 1 is the dipole moment, \( \mu \), which was calculated directly in the CNDO approximation. Here again the value at the calculated equilibrium separation (about 3.5 debyes) is larger than the generally expected moments (of the order of 1 to 1.5 debyes). The large dipole moments is attributed to the large degree of charge transfer found in the calculations. The behavior of the dipole moment and also the charge populations shown in Fig. 2 as one approaches the equilibrium separation and proceeds to shorter distances indicates clearly the onset of the repulsive interactions which have clearly changed the behavior of the electrons in the complex. Although \( \mu \) tends to drop ultimately, \( \Delta q \), the amount of charge transfer, continues to increase as shorter distances are approached. Were we to take our interpolated results at, say, 3.25 Å, we obtain at \( \Delta E \) of \(-3.3\) kcal/mole and a dipole moment of about 0.1 Debye. Clearly one must be cautious in handling results obtained from a single geometry.

The search for possible intermolecular bonding was one of the initial reasons for initiating this study and was the reason for performing the Mulliken population...
analyses. For $R \geq 1.75 \text{Å}$ no positive intermolecular overlap populations (OP's) are found; indeed, all values are in the range generally expected for non-bonded atoms.

At $R = 1.75 \text{Å}$ the $C_2-C_5$ OP is $-0.078$, the largest magnitude observed, while the $C_1-C_4$ OP is $-0.018$. One might have expected this latter OP to be most indicative of bonding; perhaps the fact that it is the least negative of the significant OP's does hint at this fact. All of the atoms “near” each other exhibit similar negative OP's and this includes the hydrogen interactions (which would indeed normally be expected to show repulsive effects).

To indicate some general trends in the charge populations we have plotted certain sums for the non-rotated structure in Fig. 2. $P_{T-T}$ and $P_{Bz-Bz}$ represent the sums of OP's between atoms (all atoms) on TCNE and, separately, on benzene, respectively; $P_{T-Bz}$ represents the summed OP's between all atoms on the two different molecules. $Q_T^{\text{net}}$ and $Q_{Bz}^{\text{net}}$ are the net Mulliken charges summed for the separate molecules and $\Delta q$ represents the total charge transferred from benzene to TCNE; a value of $+1$ for $\Delta q$ would represent the system (TCNE)$^{-1}$ (benzene)$^{+1}$. $\Delta q$ is calculated by dividing $P_{T-Bz}$ equally between the two molecules and represents the increase in the total Mulliken gross charge on TCNE.

The energy curve is indicated in the background for reference. There are several interesting aspects. The $P_{T-T}$ and $P_{Bz-Bz}$ sums hardly change (slight increase) as $R$ decreases, indicating that the net intramolecular binding is not being much affected by those forces which are stabilizing the complex. The total OP ($P_{T-T} + P_{Bz-Bz} + P_{T-Bz}$) does show a uniform decrease throughout the range of decreasing $R$ while both net charge sums increase. We interpret this to indicate that the stabilization arises essentially solely from charge transfer. Nearly all the individual atomic net charges increase, except for the hydrogen atoms which show a decrease.

Decreasing overlap populations are indicative of the increase of anti-bonding MO's in the total wave function. Such anti-bonding orbitals will tend to pile charge up on atoms as net charges at the expense of bond populations. This is apparently what is happening in our present calculation. The intermolecular OP's are being driven negative causing the net atomic charges to increase on both molecules. The distribution is such as to favor the more electron-accepting TCNE molecule giving rise to a finite $\Delta q$ and dipole moment. The parallel nature of $-P_{T-Bz}$ and $\Delta q$ would seem to indicate that it is basically only the intermolecular coupling which is anti-bonding (in the sense of negative OP's) and that the MO's of the whole complex are the MO's of the individual molecules weighted (polarized) toward the TCNE molecule. This fits in with the essentially constant behavior of $P_{T-T}$ and $P_{Bz-Bz}$ (down to $R = 1.75 \text{Å}$, at least) which indicates that molecular integrity is maintained for each molecular component. Although the calculated energy and equilibrium distance might indicate the formation of one “super molecule”, the Mulliken population analysis shows clearly that this is not what
is happening; rather, the two component molecules remain easily recognizable as such, down to the shortest distance calculated (1.25 Å).

Obviously a careful study of the dominant parameters in the CNDO approach should be made in order to make a proper evaluation of the method as applied to these systems. If London forces are indeed the significant factor perhaps more than a simple SCF approach will be necessary. However, if one is to accept both the present method of calculation and the premise that SCF wavefunctions are “reasonably good” one must conclude that charge transfer may yet prove to be a significant factor in the stability of molecular complexes.

Acknowledgement. We are indebted to Duke University and the Duke University Computational Center for partial support of our computer calculations and for technical assistance.

Appendix

In this appendix we will show that equivalent bonds in a molecule are not necessarily characterized by identical bond orders but that summed overlap populations do reflect the physical equivalence of symmetry-related bonds. The latter summed, or total, overlap populations are thus better suited to characterize chemical bonds within a molecule.

In most computer work the localized atomic orbitals (AO's) are determined by the local coordinate system whereas at other times one often employs equivalent AO's (characterized by the fact that symmetry operations induce essentially permutations of the equivalent AO's among themselves). We consider initially an arbitrary set of AO's.

The charge and bond order matrix, $P$, for a single determinantal wave function constructed from orthonormal molecular orbitals is invariant under transformations of the subspace spanned by the occupied MO's. A symmetry operation $g$ mixes only MO's of equal energy; thus, for a closed-shell system, symmetry operators transform only occupied MO's among themselves and therefore leave $P$ invariant.

$$gP = P' = P.$$  \hfill (1)

To describe the symmetry operation $g$ with respect to the AO's let $|\alpha i\rangle$ be the $i^{th}$ AO on center $x$; then in general

$$g|\alpha i\rangle = \sum_{\beta j} |\beta j\rangle D(g)_{\beta j; \alpha i}.$$  \hfill (2)

Since $g$ is a one-to-one mapping of the set of nuclei onto itself, we can write

$$D(g)_{\beta j; \alpha i} = \delta_{\beta x'} D(\alpha i)(g)_{ji}$$  \hfill (3)

in which $x'$ is the $g$-image of $x$. If the atomic orbitals span representations of the full rotation group, then the matrix $D(\alpha i)(g)$ will represent the rotation of the local axes on $x'$ relative to the $g$-image of the $\alpha$-coordinate system. We will assume that this is the case, and furthermore that the representation is orthogonal.
Consider next how the filled MO's \{ |s> \} transform under \( g \); let \( |s> \) be the MO

\[
|s> = \sum_{ai} C_{ai,s} |\alpha i> .
\]

Then

\[
g |s> = \sum_{ai} C_{ai,s} g |\alpha i> = \sum_{ai} \sum_{\beta j} C_{ai,s} D(g)_{\beta j; ai} |\beta j> \]

\[
= \sum_{\beta j} C'_{\beta j,s} |\beta j>. \tag{4}
\]

Where the second and third lines of Eq. (4) define the quantity \( C'_{\beta j,s} \). Thus, assuming for simplicity real coefficients,

\[
P'_{ai; \beta j} = \sum_s C'_{ai,s} C'_{\beta j,s}
\]

\[
= \sum_{\gamma k} \sum_{\delta p} D(g)_{ai; \gamma k} D(g)_{\beta j; \delta p} C_{\gamma k,s} C_{\delta p,s}. \tag{5}
\]

Where, from the definition of the set \{ |s> \}, the sum over \( s \) implies a sum over the occupied MO's of the system.

The matrix representation \( D(g) \) of \( g \) is orthogonal, that is:

\[
D(g)_{ai; \gamma k} = D(g^{-1})_{\gamma k; ai}. \tag{6}
\]

Put \( h = g^{-1} \) and define \( \alpha'' \) by \( h: \alpha \rightarrow \alpha'' \).

\[
D(g)_{ai; \gamma k} = D(h)_{\gamma k; ai} = \delta_{\gamma \alpha''} D^{(\alpha)}(h)_{ki}. \tag{7}
\]

Eq. (1) indicates that \( P = g P = P' \), so

\[
P'_{ai; \beta j} = \sum_{\gamma k} \sum_{\delta p} \delta_{\gamma \alpha''} D^{(\alpha)}(h)_{ki} \delta_{\delta \beta''} D^{(\beta)}(h)_{pj} P_{\gamma k; \delta p}
\]

\[
= \sum_{k,p} D^{(\alpha)}(h)_{ki} D^{(\beta)}(h)_{pj} P_{\alpha''k; \beta''p}. \tag{8}
\]

We conclude that \( P_{ai; \beta j} \) is in general not equal to \( P'_{ai;j} \) in which \( \alpha'' \) and \( \beta'' \) denote atoms equivalent to, respectively, \( \alpha \) and \( \beta \). If we sum over \( i \) and \( j \) in order to obtain the total bond order, we will get different answer for the bond orders of the \( \alpha-\beta \) and the \( \alpha''-\beta'' \) bond; [unless, of course, \( D^{(\alpha)}(h) \) and \( D^{(\beta)}(h) \) are identity matrices, meaning that the local coordinate systems transform into one another under \( h \)].

We now prove the validity of the following relation between summed Mulliken overlap populations:

\[
\sum_{i \text{ on } \alpha} \sum_{j \text{ on } \beta} P_{ai; \beta j} S_{ai; \beta j} = \sum_{i \text{ on } \alpha''} \sum_{j \text{ on } \beta''} P_{\alpha''i; \beta''j} S_{\alpha''i; \beta''j}. \tag{9}
\]
First we transform $S$ with $h$; since $S$ is invariant under a unitary transformation:

\[
S'_{\beta j; \alpha i} = S''_{\beta j; \alpha i} = \sum_{y_k} \sum_{\delta p} D(h)_{y_k; \beta j} D(h)_{\delta p; \alpha i} S_{y_k; \delta p}
\]

\[
= \sum_{k, p} D^{(\beta)}(h)_{kj} D^{(\alpha)}(h)_{pl} S_{\beta''; k; \alpha''; p}
\]

\[
= \sum_{k, p} D^{(\beta)}(h)_{jk}^{-1} D^{(\alpha)}(h)_{lp}^{-1} S_{\beta''; k; \alpha''; p}.
\]  

(10)

Substituting the results (8) and (10) in the l. h. s. of (9) and using the fact that $S$ is symmetric we obtain:

\[
\sum_{i,j} P_{\alpha i; \beta j} S_{\alpha i; \beta j} = \sum_{i,j} \sum_{k, p, q, r} D^{(\alpha)}(h)_{ki} D^{(\alpha)}(h)_{ir}^{-1} D^{(\beta)}(h)_{pq} D^{(\beta)}(h)_{jq}^{-1} P_{\alpha''; k; \beta''; p} S_{\alpha''; r; \beta''; q}
\]

\[
= \sum_{k, p} P_{\alpha''; k; \beta''; p} S_{\alpha''; k; \beta''; p}.
\]  

(11)

This result indicates that the overlap population between two atoms summed over the atomic orbitals of the atoms is identical for equivalent pairs of atoms.

If one is dealing with equivalent atomic orbitals, the matrix $D^{(\alpha)}(g)$ takes a simple form. Suppose $g$ transforms $|\alpha i\rangle$ into $E_{ii'} |\alpha' i'\rangle$, in which $E_{ii'} = \pm 1$ (if we use real AO’s). $D^{(\alpha)}(g)$ takes the form:

\[
D^{(\alpha)}(g)_{ij} = \delta_{ji'} E_{ii'}.
\]  

(12)

Substituting this in (8):

\[
P_{\alpha i; \beta j} = E_{ii'} E_{jj'} P_{\alpha' i'; \beta' j'}
\]  

(13)

and in (10):

\[
S_{\alpha i; \beta j} = E_{ii'} E_{jj'} S_{\alpha' i'; \beta' j'}.
\]  

(14)

From this we see that symmetry related elements of $P$ and $S$ differ at most in sign; further the product equality

\[
P_{\alpha i; \beta j} S_{\alpha i; \beta j} = P_{\alpha' i'; \beta' j'} S_{\alpha' i'; \beta' j'}
\]  

(15)

will hold.

References


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Ab-initio valence bond calculations on the He–He potential curve using small bases†

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In studying methods for the ab-initio calculation of Van der Waals interactions which can be extended to larger molecules, we have tested the Valence Bond scheme on the He₂ system. This method looks promising, as it appears to yield in one consistent formalism both the attractive dipole–dipole terms and the repulsive exchange terms with reasonable accuracy, using only a simple orbital basis and a very small number of VB structures.

1. Introduction

The interaction between two ⁰S ground-state He atoms has been investigated by many people with methods of varying degrees of accuracy and sophistication. The older approaches (e.g. reference [1]) use perturbation formalisms which account for the long-range Van der Waals attraction, and superpose empirical repulsive potentials in an ad hoc manner, in order to give good fits to the depth and position of the Van der Waals minimum. Later workers [2–4] concentrated on the exchange interaction, mainly using an MO scheme. These investigators were not able to obtain minima in the potential curves, so one started to realize that the computation within a uniform model of a complete interaction curve for He₂ poses a real problem. Even the 64-term Configuration Interaction wave function of Phillipson [5] did not predict the correct depth of the Van der Waals minimum. One still had to obtain the repulsive and attractive contributions to the energy by separate calculations [6]. This situation remained unaltered all through the sixties [7–10], which led to the now common conviction that a single configuration potential curve for two closed-shell atoms must be entirely repulsive [11].

In 1970 two independent simultaneous publications [12, 13] presented high quality potential curves, each calculated by a single consistent computational technique. Although these results prove beyond doubt that the Van der Waals potential well can be computed with an accuracy comparable to that of experiment, it will be difficult to apply these methods to larger systems.

The purpose of this communication is to point out that reasonable results can be obtained by very simple calculations; that is, simple with regard to the size of the basis sets and the computer time spent on the whole curve. Only if one is

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able to predict with minimal effort the Van der Waals energy of a small system like He–He will it be possible to hope for positive results in computations on larger systems.

2. Method

The Valence Bond (VB) method is similar to a perturbation treatment in the sense that it is based on the states of the unperturbed atoms. In VB theory, one solves a secular problem in which an element of the Hamiltonian matrix has the general form

\[ H_{i,j} = \langle \mathcal{A} P_S \psi^A_{\mu} \psi^B_{\nu} | H | \mathcal{A} P_S \psi^A_{\mu'} \psi^B_{\nu'} \rangle. \]  \hspace{1cm} (1)

Here \( \mathcal{A} \) is the antisymmetrizer for the total system, \( P_S \) a spin-adapting projection operator and \( \psi^A_{\mu}, \psi^B_{\nu} \) are unperturbed states of the atoms A and B respectively.

The two main problems in the computation of \( H_{i,j} \) are the effect of \( P_S \) and the non-orthogonality between the orbitals on the atoms A and B. The matrix elements (1) are constructed by Reeves’ algorithm [14] which is based on a Young projector [15].

This algorithm expects orthonormal spatial orbitals, and so we orthonormalize a chosen set of atomic orbitals by means of a matrix \( t \). Then the full \( H \)-matrix \( H \) with elements defined by (1) is constructed on the basis of all states (with a certain spin multiplicity) which arise from the orthonormalized AO set. The effect of the orbital transformation \( t^{-1} \) on the \( N \)-electron wave functions is given by an \( N \)th-order tensor representation [16] \( T(t^{-1}) \) which undoes the effect of \( t \) after performance of the transformations

\[ O = H'C' - S'C'E = T^1(t^{-1})HT(t^{-1})T(t)C - T^1(t^{-1})ST(t^{-1})T(t)CE. \]  \hspace{1cm} (2)

Specific VB structures can be selected by considering only certain columns of \( T(t^{-1}) \) and so the dimension of the primed secular equation, which is on the basis of the original non-orthogonal AO’s, is generally smaller than the dimension of the \( H \)-matrix defined by (1). Solution of the transformed equation in the usual manner gives the desired VB states and energies.

In this procedure, which we intend to elaborate in a future publication, one avoids tedious derivations of matrix elements on basis of non-orthogonal orbitals§.

The exact form chosen for the matrix \( t \) is unimportant if the effect of the orthonormalization is annihilated according to equation (2). However, for large problems this is not feasible and in that case the choice of a good orthonormalization procedure [17] becomes important. We have promising experiences with the following three-step process:

(i) Löwdin-orthonormalize the orbitals occupied in the free atoms.

(ii) Perform a Gram–Schmidt orthonormalization of the remaining orbitals onto the occupied ones.

(iii) Löwdin-orthonormalize the orbitals obtained in step (ii) among each other.

§ We thank the referee for drawing our attention to two papers [25, 26] which treat the non-orthogonality problem in a similar way. In these references the secular matrices are defined on the basis of Slater determinants instead of Young projected functions. Although the use of Slater determinants facilitates the construction of \( T(t^{-1}) \), it requires a much larger dimension of the secular problem, since one does not work with eigenfunctions of \( S^2 \).
Programmes based on the outlined ideas have been written for an IBM 370/158 computer, taking as integral input the output from the IBMOL–5 programme [18].

3. Results

On each He atom the four orbitals: 1s, 2p, 2p, 2p, are placed. The 1s orbitals (SCF orbitals from Huizinaga [19]) are represented by a contracted set of six primitive gaussians. Also six primitives are contracted to represent a single-ζ Slater-type p orbital. The exponent ζ of this STO can be optimized in four different ways, see table 1.

<table>
<thead>
<tr>
<th>Energy minimized</th>
<th>𝛽</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlated atomic 1S energy</td>
<td>2.45</td>
</tr>
<tr>
<td>Excited state SCF 3P energy</td>
<td>0.58</td>
</tr>
<tr>
<td>Excited state SCF 1P energy</td>
<td>0.47</td>
</tr>
<tr>
<td>Van der Waals energy He–He at R = 5.6 bohr</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 1. Optimized STO exponents ζ of the 2p orbital.

The value ζ = 1.3 compares well with the value ζ = 1.378 found from an analytic optimization of the Van der Waals attraction [20]; the other values in table 1 agree with those given in reference [12]. In all subsequent calculations the value of ζ is held fixed on 1.3. The first calculations are based on the four σ-type AO’s only. Although the usual perturbation approach [11] starts from purely co-valent states, yet we started with a set of ‘full’ VB calculations. Since four AO’s give rise to at most 20 singlet structures, full VB implies a 20-dimensional secular problem. The results are shown in figure 1.

Compared to the experimental values [21]: \( E_m/k = 11.0 \text{ K} \) and \( R_m = 5.6 \text{ bohr} \), the minimum is much too deep. Inspection of the wave function \( \Psi \) at the minimum, while retaining only the dominant terms

\[
\Psi = 0.999 \left[ s_A^2, s_B^2 \right] - 0.034 \left[ s_A^2, p_B^2 \right] + \left[ p_A^2, s_B^2 \right] \\
- 0.005 \left[ s_A, p_B, s_B \right] + 0.004 \left[ s_A, p_A, s_B, p_B \right]
\]

shows that the leading structure represents the Hartree-Fock uncorrelated ground state in the separated atom limit. The last term in \( \Psi \) is the one predicted by perturbation theory to be responsible for the induced dipole-induced dipole part of the dispersion energy [11]. The second structure \( s_A^2, p_B^2 \) is known to contribute considerably to the intra-atomic correlation energy of atom B, and \( p_A^2, s_B^2 \) does the same for atom A. But we expect a more or less constant shift of the potential curve from these latter terms, as the intra-atomic correlation energy does not depend heavily on \( R \) [22]. This is confirmed by the coefficients of the first three structures which are practically independent of \( R \) up to the separated atom limit.

Unexpected is the presence of the excited CT (charge transfer) structures \( s_A^2, p_A, p_B \) and \( p_A, p_B, s_B^2 \) while the CT states \( s_A^2, p_A, s_B \) and \( s_A, p_A, s_B^2 \) are

\[ k = 1.38054 \times 10^{-23} \text{ J/K (Boltzmann’s constant).} \]

1 bohr = 5.29167 × 10⁻¹¹ m.
Figure 1. Interaction energy in He₂ calculated by full VB (20 structures) on four σ orbitals.

absent. After a moment of thought the relative importance of these terms can be explained as follows. Making the formal expansion of \( p_A(r_A) \) in a set of atomic functions centred on B:

\[
p_A(r_A) = \sum_{n,l} C_{n,l}(R) f_{n,l}(r_B)
\]

we write

\[
[s_A^2, p_A, s_B] = \sum_{n,l} C_{n,l}(R) [s_A^2, f_{n,l}(r_B), s_B(r_B)].
\]

The right-hand side of this equation is an expansion in singly excited states on atom B, which, \( s_B(r_B) \) being an SCF orbital, does not contribute to the ground-state via intra-atomic terms in the hamiltonian operator. (Even in the case of non-orthogonal orbitals [27] it can be proved easily, by invoking Brillouin's theorem, that the admixture of singly excited states leaves the ground state of atom B a pure \( s_B^2 \) state.) This explains the unimportance of CT terms without simultaneous excitation.

In the same way the excited CT structure becomes

\[
[s_A^2, p_A, p_B] = \sum_{n,l} C_{n,l}(R) [s_A^2, f_{n,l}(r_B), p_B(r_B)],
\]
from which we deduce immediately that this structure yields a contribution to the intra-atomic correlation energy of atom B. Because of the $R$-dependent expansion coefficient $C_{nJ}(R)$ this contribution is distance dependent. To get a better grasp of this distance-dependent improvement of the intra-atomic correlation energy we performed VB calculations on the free He atom A, with a basis of structures on the 'empty' (no electrons, no nucleus) centre B approaching A. The results are plotted in figure 2. The influence of the basis on B is seen to grow drastically with decreasing distance. It is important to note that the He atom is physically unperturbed, and that this artificial energy lowering is a mathematical effect due to the enlargement of the structure basis. Around 5.5

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2}
\caption{Distance dependency of the energy of the He atom A in the structure basis of A+B, multiplied by 2. Only the structures with non-negligible contribution are indicated.}
\end{figure}
\end{center}

bohr this energy lowering is of the same order of magnitude as the physical interaction between two He atoms, but together with the physical interaction this energy does not fully add up to the well depth of the full VB calculation. So we must conclude that the effect of the basis set enlargement is not an additive one and, therefore, to eliminate this phenomenon we omit all structures that contribute to the intra-atomic correlation, in accordance with the purpose of this investigation\footnote{After completion of this work a paper on the He–He interaction\cite{28} appeared which also considers in detail the effect of basis enlargement. The authors use a larger atomic orbital and configuration basis. They perform a large Configuration Interaction calculation and correct for the distance-dependent basis-set effect by subtracting the result of an atomic calculation with a vacant basis on the other centre, thus assuming additivity.}. In figure 3 three computed potential curves are exhibited. The
upper two are calculated with $\sigma$-type AO's, taking into account the two co-valent structures $[s_{A}^2, s_{B}^2]$ and $[s_{A}, p_{A}, s_{B}, p_{B}]$ only. The lower of these two is obtained from pure, non-orthogonal AO's, and the higher one from AO's that are orthogonalized by the three-step process described in the previous section. Notice that because of the careful orthogonalization the curves almost coincide.

We have tried several other ways of orthonormalization, for instance SCF followed by localization, but they all give results that are definitely inferior to the ones shown.

![Graph](image)

**Figure 3.** Van der Waals energy calculated by VB on the basis of four $\sigma$ orbitals (two structures) or eight $\sigma + \pi$ orbitals (four structures).

The lowest of the three curves in figure 3 has been computed by inclusion of two $\pi$ AO's on each atom and the four structures:

$[s_{A}^2, s_{B}^2], [s_{A}, p_{xA}, s_{B}, p_{xB}], [s_{A}, p_{yA}, s_{B}, p_{yB}], [s_{A}, p_{xA}, s_{B}, p_{xB}]$.

Here the AO's are orthogonalized, again following the described three-step scheme.

All doubly-excited configurations give rise to two linearly independent singlet VB structures. One of these structures corresponds to the coupling of
two excited singlet He atoms, the other one to the coupling of two excited triplet atoms [15]. It appears that the contributions of the latter structures to the interaction energy are negligible.

4. DISCUSSION

In figure 3 is shown how a very simple calculation based on two $\sigma$-type AO’s per atom and only two VB structures is capable of giving already an important part of the experimental Van der Waals energy (upper two curves). One cannot expect much more, of course, since in effect only the $\sigma$-dependent part of the dipole–dipole interaction [11] is taken into account.

Including the $\pi$ contributions to the dispersion energy by adding just two more structures it can be concluded that a very simple computation suffices to give a major part of the Van der Waals energy. Here the theoretical limit is the total induced dipole-induced dipole ($R^{-6}$) contribution to the dispersion energy. Kestner [11] estimated this to give a minimum of $5.68$ K, but this agrees neither with the results of Schaefer et al. [12, 23], nor with ours.

In table 2 our results are compared with those of Schaefer et al.; the agreement, especially in the outer region, is striking, since these authors based their $\sigma + \pi$ calculations on five s and p$\sigma$ orbitals and four p$\pi$ orbitals per atom, yielding 72 $\sigma$ configurations and 16 $\pi$ configurations.

| SCF | $\langle s_A^{s_B} | H | s_A^{s_B} \rangle$ | $\sigma(s+p)$ | $\sigma + \pi(s+p)$ |
|-----|---------------------------------|-------------|-----------------|
| R bohr | Ref. [23] | This work | Ref. [23] | This work | Ref. [23] | This work |
| 5.2 | 24.45 | 23.43 | +7.7 | +8.08 | -0.6 | +0.57 |
| 5.4 | 15.03 | 14.11 | +1.7 | +1.64 | -5.0 | |
| 5.6 | 9.24 | 8.46 | -1.6 | -1.71 | -7.0 | -6.63 |
| 5.8 | 5.66 | 5.05 | -3.08 | -3.25 | -7.46 | -7.26 |
| 6.0 | 3.45 | 3.00 | -3.64 | -3.82 | -7.17 | -7.14 |
| 6.2 | 1.77 | 1.64 | -3.85 | -3.60 | -5.90 | |
| 6.4 | 1.00 | -3.38 | -5.56 | |
| 6.6 | 0.63 | -3.25 | |
| 6.8 | 0.32 | -2.87 | -4.48 | |
| 7.0 | 0.287 | 0.22 | -2.51 | -2.49 | -3.90 | |
| 8.0 | 0.023 | 0.03 | -1.23 | -1.17 | -1.85 | -1.83 |
| 9.0 | 0.002 | 0.00 | -0.61 | -0.57 | -0.92 | |
| 10.0 | 0.000 | 0.00 | -0.33 | -0.28 | -0.49 | |
| 12.0 | 0.00 | -0.09 | |
| 14.0 | 0.00 | 0.00 | -0.06 | |

Table 2. Interaction energies in units of degrees Kelvin. The SCF energy for two isolated He atoms is $-5.722\,232.8$ hartree.

Concluding, it can be stated that the VB method performs very well for weakly interacting systems such as two He atoms. It constitutes a single consistent model capable of giving a good prediction of the entire Van der Waals well.

Of course, in this work the intra-atomic correlation correction is neglected by using a Hartree–Fock atom as the reference system. At the Van der Waals minimum, however, this correction differs only 1.23 K from the correlation energy.
in the free atoms [23]. Although this difference increases for shorter interatomic distances [24], it remains rather small relative to the repulsion energy. Moreover, the VB scheme can only be expected to perform well if the atoms do not deviate too much from their electronic structure at infinite distance. If one is interested in the repulsive region at smaller distances, an approach based on the Hartree–Fock molecule as the reference system seems more appropriate, unless one is prepared to include substantially larger numbers of VB structures than we did in this paper.

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Ab initio valence-bond calculations of the van der Waals interactions between $\pi$ systems: The ethylene dimer

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A multistructure valence-bond method for the calculation of van der Waals forces is presented which includes in one consistent formalism the electrostatic, induction, and dispersion forces and takes exchange correctly into account. The application of this method to the ethylene dimer leads to the following main conclusions: (1) The "first order" electrostatic forces are comparable in magnitude to the "second order" forces even though the molecules possess no permanent dipole moments. Dispersion forces are much larger than induction. Second order interactions are more isotropic than first order forces. (2) In the multipole expansions of the long range forces, the inclusion of the first term only is not sufficient for a good approximation to the interaction. (3) Exchange effects become nonnegligible at approximately 12 bohr, while the van der Waals minimum between two perpendicular molecules is at 9.4 bohr. At about 6 bohr, penetration effects make the multipole expansion meaningless. Possible simplifications for future calculations are suggested. A seemingly good van der Waals minimum which is calculated by the ab initio SCF method is shown to be caused in part by the (mathematical) effect of basis set enlargement. CNDO results disagree completely with the ab initio calculations.

1. INTRODUCTION

Van der Waals forces between $\pi$-electron systems are of great importance in accounting for the conformation of many of the biopolymers. Together with hydrogen bonding, these forces play a decisive role in the secondary structure of the nucleic acids and proteins. Many authors have discussed the interaction between the $\pi$ electrons in the stacked bases of the double stranded DNA molecule.

Similar stacks of molecules are found in all solid CT (charge transfer) complexes of the $\pi-\pi$ type. In CT complexes, as well as in the majority of the molecular crystals, van der Waals forces can be held responsible for the stabilization energy.

Most of the calculations on the long and intermediate range interactions between organic molecules are based on the ideas of London, who applied Rayleigh-Schrödinger first and second order perturbation theory. In his earlier work, London proposed a multipole expansion of the interaction operator, whereas later he suggested rather to approximate the charge distributions on the monomers. Both London schemes neglect intermolecular exchange and hence lack completely the Pauli exchange interactions. These are repulsive for closed-shell monomers and very dominant at shorter distances. Since the long range London forces are mostly attractive, inclusion of the Pauli repulsion is necessary in order to account for a van der Waals minimum. Several ways of dealing with the exchange have been proposed. On the one hand, perturbation formalisms have been derived which take exchange into account in all orders of perturbation, but in general these methods are not practical for larger systems unless extra approximations are introduced. On the other hand, simpler and less rigorous ways of dealing with the exchange have been discussed, all of which include parameters that are to be fitted to experiment.

Although the semiempirical methods of computing intermolecular forces contain questionable approximations and assumptions, they have been extremely useful in deepening the insight in the structure of biopolymers and molecular crystals; moreover, once the ambiguities in the approximations are removed, they are likely to remain the most fruitful approach in this field, since the more rigorous ab initio methods will in all probability stay too expensive to be applied to large systems in the foreseeable future.

Still, ab initio methods can be of great help in clearing up unsettled questions, as for instance the convergence of the multipole expansion, the correctness of the segment monopole approximation, or the nature of the exchange repulsion.

Unlike the situation a decade or so ago, the approximations proposed by London for computing the matrix elements occurring in a description of the van der Waals forces are no longer a necessity. Since the advent of high speed computers and sophisticated program packages (e.g., Ref. 28), one is not only able to produce good quality wavefunctions for the monomers, but also to calculate exactly all the intermolecular Coulomb and exchange integrals. Of course, this does not solve some of the more formal problems: how to account for the exchange and how to approximate the infinite sum in the second order perturbation.

The first efforts made into the direction of ab initio calculations for intermolecular forces stayed within the SCF framework. However, it soon became clear that the Hartree-Fock method does not yield dispersion energies, but only electrostatic, induction, and exchange energies. So, a realistic calculation must include at least intermolecular correlation energy.

In earlier work, we have shown that it is feasible to calculate in the consistent formalism of the multistructure valence-bond method both the attractive dispersion and the repulsive exchange contribution to the total interaction energy. The valence-bond method is an ap-
pealing formalism in this respect, as it converges into London’s theory for increasing intermolecular distances. Furthermore, a judicious choice of VB structures yields a quantitative description of the intermolecular correlation.

We have chosen to study the ethylene dimer because it is the simplest organic π-π complex. As such, and also in its own right, it has received much attention.

II. THEORY

A. The valence-bond method and its connection with perturbation theory

In valence-bond theory, one calculates the energy of a system by solving a secular problem over "VB structures," which are antisymmetric many-electron eigenfunctions of the spin operator $S^2$. Spin-free VB structures may conveniently be constructed by acting with a Young operator $Y$ on simple orbital products. In this paper, where we are concerned with the interaction between two molecules A and B, the dimer VB structures are denoted by $Y(\phi_A^a \phi_B^b)$. Here $\phi_A^a$ and $\phi_B^b$ are monomer structures obtained from products of molecular orbitals localized on A and B, respectively, by projection with monomer Young operators. The monomer MO's used in this work are obtained from LCAO–SCF calculations on the separate monomers. It can be proved that the dimer VB structures may also be constructed by acting directly with $Y$ on simple products consisting of the same MO's as contained in $\phi_A^a$ and $\phi_B^b$. In practice, we apply this latter procedure.

The monomer structures included in our calculations are the ground states $\phi_A^a$ and $\phi_B^b$ and singly excited states $\phi_A^a \phi_B^b$ and $\phi_A^b \phi_B^a$. We expect the dimer structure $Y(\phi_A^a \phi_B^b)$ to account for the interactions between the unpolaredized molecules, the structures $Y(\phi_A^a \phi_B^b)$ and $Y(\phi_A^b \phi_B^a)$ for the mutual induction effects and the doubly excited structures $Y(\phi_A^a \phi_B^b)$ for dispersion forces. This is clarified by the following discussion of the long range asymptotic behaviour of the valence-bond results.

It may be shown that the contributions of the intermolecular permutations in $Y$ to the Hamiltonian and overlap matrix elements start vanishing if the intermolecular distance $R$ is increased. The VB structures $Y(\phi_A^a \phi_B^b)$ then become effectively equal to the products $\phi_A^a \phi_B^b$. These products form an orthonormal basis and the VB total energy for large $R$ can be obtained by diagonalization of the total Hamiltonian on this basis. The relation with Rayleigh–Schrödinger perturbation theory is shown if we write

$$H = H^A + H^B + V_{AB}$$  \hspace{1cm} (1)

and imagine the diagonalization of $H$ to be performed in two steps. First, diagonalize $H^A$ in the basis $\{\phi_A^a\}$ by a linear transformation to $\{\phi_A^a\}$ so that

$$\langle \phi_A^a | H^A | \phi_A^a \rangle = \delta_{i\mu}E_A^a, \text{ } i = 0, 1, 2, \ldots$$  \hspace{1cm} (2)

and analogously on monomer B:

$$\langle \phi_B^a | H^B | \phi_B^a \rangle = \delta_{j\mu}E_B^a, \text{ } j = 0, 1, 2, \ldots$$  \hspace{1cm} (3)

Because of Brillouin's theorem, also valid in a finite LCAO model, the SCF ground state $\phi^0_A$ does not interact with the singly excited structures $\phi_A^a$, $i \neq 0$, under $H^A$, and therefore

$$\phi^0_A = \phi_A^0,$$

and the same on B:

$$\phi^0_B = \phi_B^0.$$  \hspace{1cm} (4)

After this first diagonalization step, we have the matrix elements

$$\langle \phi_A^a | H | \phi_A^0 \rangle = \delta_{i\mu}E_A^a, \text{ } \langle \phi_B^a | H | \phi_B^0 \rangle = \delta_{j\mu}E_B^a,$$

where $\delta_{i\mu}$ and $\delta_{j\mu}$ are Kronecker delta functions.

The second step, which actually calculates the VB energy by completing the diagonalization of $H$, has to annihilate all the nondiagonal elements over $V_{AB}$. Assuming that the matrix elements over this operator are small, we can use the following expansion for the lowest eigenvalue of $H$:

$$E_{VB} = E_A^0 + E_B^0 + \langle \phi_A^a | \phi_B^a \rangle V_{AB} + \text{higher order terms}$$  \hspace{1cm} (5)

Because $\phi_A^a$ and $\phi_B^a$ are identical to the ground state $\phi_A^0$, and the excited states can be regarded as the eigenstates of $H^{(1)} = H^A + H^B$ in the finite structure basis $\{\phi_A^0\}$, this formula shows an explicit relation between perturbation theory and the valence-bond energy, valid for large intermolecular distances. We define for all distances

$$E^{(1)}_{VB} = \langle Y \phi_A^a \phi_B^b | H | Y \phi_A^a \phi_B^b \rangle,$$

the expectation value of the total Hamiltonian over the dimer ground state VB structure, and

$$E_{VB}^{(1)} = E_{VB} - E^{(1)}_{VB},$$

the energy lowering due to the inclusion of excited structures, and obtain expressions for the interaction energies,

$$\Delta E_{VB}^{(1)} = E_{VB}^{(1)} - E_A^0 - E_B^0,$$

$$\Delta E_{VB}^{(2)} = E_{VB}^{(2)} - E_V^{(1)}$$

which go asymptotically over into the first and second order perturbation energies. (The assumption that higher-order terms are small is confirmed by our calculations.) Note finally that these valence-bond expressions take into account in a correct manner, because of the action of the projector $Y$.

B. Valence bond and the multipole expansion

Besides invoking the Rayleigh–Schrödinger second-order perturbation theory, London and many workers after him also introduced an approximation to the interaction operator $V_{AB}$ by expanding $V_{AB}$ in a multipole series and then truncating this series after the first few terms. Although we did not follow this procedure, but rather worked with the full interaction operator, we can still compare our results with those obtained in a multipole approximation by virtue of the high symmetry.
where R is the intermolecular distance, \( x_1^2 \), \( y_1^2 \), and \( z_1^2 \) are components of a 2\( p \)-pole operator on A, \( (n = n_1 + n_2 + n_3) \), and \( x_2^2 \), \( y_2^2 \), and \( z_2^2 \) are components of a 2\( p \)-pole operator on B, \( (m = m_1 + m_2 + m_3) \). Because the ground state of the ethylene monomer possesses \( A_{1g} \) symmetry, only locally excited states on A with the same symmetry as \( x_1^2 \), \( y_1^2 \), and \( z_1^2 \), and locally excited states on B with the symmetry of \( x_1^2 \), \( y_1^2 \), and \( z_1^2 \), will mix with this ground state. The symmetry of these operators is determined by their exponents \( n_1 \), \( n_2 \), \( n_3 \), and \( m_1 \), \( m_2 \), \( m_3 \) being even or odd. See Table I.

Conversely, using an untruncated operator \( V^{AB} \), as we do in our calculations, and mixing only states of certain local symmetry with the ground state, Table I will tell us which terms of the multipole expansion are therewith implicitly taken into account. It is easy to see that the consecutive terms of \( V^{AB} \), included by selecting the excited states of a certain symmetry, form a power series in \( 1/R^3 \), in which the first term is the most important (around 10 bohr). Thus, by performing VB calculations on basis of states of well-defined local symmetry, we have a means of comparing the exact results with those obtained from the multipole approximation. Furthermore, the analysis of the energy in terms of multipole interactions will guide us through the difficult process of selecting suitable states to be included in a multistructure VB calculation.

C. The nonorthogonality and spin problem

Although the valence-bond method has obvious conceptual advantages, its applications have not been very frequent. The main reason is the difficulty in the computation of the matrix elements

\[
H_{ij} = \langle \psi_i^A | V^{AB} | \psi_j^B \rangle
\]

(11)

These matrix elements are hard to evaluate because of (1) the occurrence of the operator \( Y \), (2) the nonvanishing overlap between the monomer states \( \psi_i^A \) and \( \psi_j^B \).

Much effort has been put into the elaboration of the first

| TABLE I. Symmetry of multipole component under \( D_{3h} \): \( n_1, n_2, n_3 \) |
|------------------|------------------|
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( A_{1g} \) |
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( B_{1g} \) |
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( B_{2g} \) |
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( A_u \) |
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( B_{1u} \) |
| \( x_1^{2n_1} y_1^{2n_2} z_1^{2n_3} \) | \( B_{2u} \) |

To study the effect of orthonormalization, we proceed by constructing the matrix \( T(t) \) explicitly for the case of four open-shell electrons coupled to a singlet. The matrix \( t \) is obtained by a Gram-Schmidt orthonormalization of the open-shell orbitals among themselves, all of which were first Gram-Schmidt orthonormalized onto the closed-shell orbitals, which themselves were already Löwdin orthonormalized among each other. Having obtained \( T(t) \), the secular problem is transformed to the original nonorthogonal orbital basis as described in Ref. 34. The results for a typical case with and without orthonormalization using the same VB structures are given in Table II.

As can be concluded from this table, the interaction
energy is slightly larger in the orthogonal case, which must probably be ascribed to the admixture of ionic VB structures by the orthogonalization. This contributes to the intramolecular correlation energy. The effect of orthogonalization being very small indeed in the region of interest to us, we conclude that the calculation of van der Waals forces, in contrast to chemical bonding, the use of orthogonalized monomer orbitals seems fully justified. In the actual calculation only the lowest two monomer MO's originating from the carbon is orbitals are kept doubly occupied. We have decided on the following orthonormalization procedure, which leaves the first order energy unaltered, and the excited orbitals as close as possible to the original ones: (1) Löwdin orthonormalize among each other all the orbitals that are occupied in the free monomers (seven \(\sigma\)-MO's and one \(\pi\)-MO); (2) Gram–Schmidt orthonormalize the excited orbitals onto all the thus obtained monomer orbitals; (3) Löwdin orthonormalize among each other the orthonormalized excited orbitals.

III. COMPUTATIONAL ASPECTS

A. Computer programs

The calculations were performed by the following chain of six programs:

(i) the integral program of IBMOL–5,\textsuperscript{76} producing one and two electron integrals over contracted Cartesian Gaussian functions.\textsuperscript{35} This program has been modified so that storage requirements are reduced by a factor of 2, 6 and run times by a factor of 4 (for cases without symmetry). Still, this program is about 5 times slower than a later version of IBMOL.\textsuperscript{71} implemented after this work was finished;

(ii) the SCF program of IBMOL–5, which is essentially the same as that of ALCHEMY;\textsuperscript{72}

(iii) an orthonormalization program performing all the orthonormalizations described in this paper;

(iv) a transformation program\textsuperscript{77} yielding integrals over \(\sigma\)-MO's and based on an \(n^6\) algorithm;\textsuperscript{72,74}

(v) the first part of the VB program, which generates and sorts coefficients that do only depend on the spin, the number of orbitals, and the VB structures to be specified as input. Usually, these choices are kept unaltered in a series of related calculations (e.g., exponent or geometry variation), and in that case this step needs to be executed only once. The coefficients are generated by a FORTRAN translation of Reeves’ algorithm,\textsuperscript{83} published in ALCHEMY. Besides the coefficients occurring in the one electron part of the \(H\) matrix, the subroutine also calculates coefficients arising in the following expansion of the two electron part of the \(H\)-matrix elements:

\[
\langle \psi_f | \sum_{\mu \nu} \frac{1}{r_{\mu\nu}} | \psi_i \rangle = \sum_{ij} \sum_{jk} \sum_{kl} C(i,j; i,j,k,l) \langle ij | kl \rangle. \tag{12}
\]

This matrix element is based on VB structures constructed from orthonormal orbitals. It is one of the strong points of Reeves’ algorithm that it does not put any constraints on the spin quantum number or on the number of singly occupied orbitals that can be handled. The summation in the right-hand side of Eq. (12) is restricted to a “canonical” order in \(i, j, k, l\). The coefficients \(C(i,j; i,j,k,l)\) permit the following factorization:\textsuperscript{78}

\[
C(i,j; i,j,k,l) = C_1(i,j) C_2(i,j, k,l), \tag{13}
\]

where \(C_1(i,j)\) is independent of \(i,j,k,l\) and \(C_2(i,j,k,l)\) can take on only 11 different values.\textsuperscript{76} These properties of the \(C\) coefficients can be made useful to limit the input/output and main storage requirements of the VB program by the following procedure. Store \(C_1(I,J)\) in canonical order of \(I\) and \(J\) discarding labels. Pack the value of \(C_2(I,J; i,j,k,l)\) together with its six labels into one eight-byte word and perform all the ensuing processing on the \(C_2(I,J; i,j,k,l)\) alone. After the construction of the \(H\) matrix is completed, the coefficients \(C(I,J)\) are retrieved to multiply each \(H\)-matrix element.

The coefficients \(C_2(I,J; i,j,k,l)\) are generated by Reeves’ algorithm in a sequential order of \(I\) and \(J\), with \(I \geq J\), and in a rather arbitrary order of \(i, j, k, l\). The four index transformation program, however, produces a canonically ordered list of integrals. In order to avoid enormous data transports at the execution of Eq. (12), the generation of the \(C_2(I,J; i,j,k,l)\) is followed by a sorting procedure which brings the coefficients in canonical order of \(i,j,k,l\). Because we followed closely an idea of Yoshimine\textsuperscript{77} to minimize the number of I/O operations, here as well as in the construction of the \(H\) matrix, we refer to that author for more details.\textsuperscript{76}

(vi) The second part of the VB program constructs the \(S\) and \(H\) matrix [Eq. (11)] and transforms these matrices optionally to nonorthogonal orbitals by means of a matrix \(T(I)\). We intend to give more details about the actual construction of \(T(I)\) in a later paper. As the last step the secular problem is solved, employing fully the blocked structure of \(S\) (only structures with the same orbital occupancy give an overlap). The present version of the program contains a diagonalization subroutine based on the Givens–Householder–QR scheme,\textsuperscript{79,80} demanding core space for one full matrix and a few columns. At the moment this is the only, but easily removable, bound to the maximum number of structures.

We conclude by quoting a few representative figures, all regarding double precision arithmetic on an IBM 370/158 computer: The computation of the integrals for the ethylene dimer in the 84-dimensional primitive basis specified below took on the average 54.4 min. The transformation of a list of integrals derived from 52 AO’s to one on basis of 28 MO’s needed 32 min. The generation of a list of 70,606 coefficients deriving from 183 singlet structures, 28 orbitals, and 32 electrons takes 79 sec. The reordering of this list takes 19 sec. The construction of the corresponding 183-dimensional \(H\) matrix takes 24 sec and the solution of the secular problem 263 sec.
TABLE III. AO basis for ethylene.

<table>
<thead>
<tr>
<th></th>
<th>Coefficientsa</th>
<th>Exponentsb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.026916</td>
<td>10.9710</td>
</tr>
<tr>
<td>s</td>
<td>0.197505</td>
<td>15.3607</td>
</tr>
<tr>
<td></td>
<td>0.845777</td>
<td>37.4090</td>
</tr>
<tr>
<td>s</td>
<td>0.574338</td>
<td>10.5181</td>
</tr>
<tr>
<td>s</td>
<td>0.482412</td>
<td>3.32078</td>
</tr>
<tr>
<td>s</td>
<td>0.12696</td>
<td>0.231436</td>
</tr>
<tr>
<td>s</td>
<td>1.0</td>
<td>4.20169</td>
</tr>
<tr>
<td>s</td>
<td>0.572790</td>
<td>0.585491</td>
</tr>
<tr>
<td>s</td>
<td>0.202063</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>1.0</td>
<td>6.4805</td>
</tr>
<tr>
<td>s</td>
<td>0.63902</td>
<td>0.08104</td>
</tr>
<tr>
<td>s</td>
<td>1.0</td>
<td>0.31708</td>
</tr>
</tbody>
</table>

This work. References 81 and 82.

B. Atomic and molecular orbitals

For reasons of economy, a rather small basis of contracted GTO's was employed: a C(6,3/3,2) set on the carbons and a H(3/2) set on the hydrogens. See Table III. The hydrogen exponents taken from Ref. 81 were scaled by a factor 1.2. The contraction coefficients of all AO's were obtained from a calculation on the free ethylene in an uncontracted basis, applying the rules of Dunning. In accordance with the findings of Moskowitz and co-workers, an isotropic basis of p orbitals was observed to give good results, so we used the same exponents and contractions for the three p orbitals. Several degrees of contraction have been tried, with the rather loose scheme which was finally decided on (Table III) yielding the most acceptable deviation from the uncontracted computation. For comparison’s sake, several SCF results of ethylene are listed in Table IV.

Quadropole moments are given in Table V. No atomic polarization functions (carbon 3d, hydrogen 2p) were included because this would have lead to prohibitive calculation times. Using the faster integral program available now, some tests are underway to study the effect of such functions. The AO basis used gives rise to molecular orbitals on each monomer, of which only the lowest 8 are doubly occupied in the ground state, the virtual ones playing the role of molecular polarization functions. To keep the VB calculations tractable, we were forced to make a selection of the virtual orbitals to participate in the dimer VB calculations. From

TABLE IV. Ethylene calculations in different basis sets.

<table>
<thead>
<tr>
<th>Basis</th>
<th>Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-4G</td>
<td>-77.65810</td>
</tr>
<tr>
<td>C(6,3/3,2), H(3/2)</td>
<td>-77.900063</td>
</tr>
<tr>
<td>C(6,3), H(3)</td>
<td>-77.901246</td>
</tr>
<tr>
<td>s + p limit</td>
<td>-78.0062</td>
</tr>
<tr>
<td>Hartree–Fock limit</td>
<td>-78.0023</td>
</tr>
</tbody>
</table>

*Reference 84.
*This work, atomic coordinates from Ref. 85.
*Reference 86.
*Reference 87.

TABLE V. Quadrupole moments, ethylene (a.u.).

<table>
<thead>
<tr>
<th></th>
<th>Qxx</th>
<th>Qyy</th>
<th>Qzz</th>
<th>Qxy</th>
<th>Qxz</th>
<th>Qyz</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(6,3/3,2), H(3/2)</td>
<td>1.1533</td>
<td>1.5875</td>
<td>-2.7408</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double zeta</td>
<td>1.4842</td>
<td>1.4982</td>
<td>-2.9624</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimentalb,c</td>
<td>...</td>
<td>...</td>
<td>-2.98d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.75e</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*This work, coordinates of monomer A, Fig. 1.
*Reference 88.
*Reference 89.
*Reference 90.

earlier work, it could be inferred that an optimization of the virtual orbitals is important for the correct estimate of induction and dispersion energy. Therefore, it was decided not to proceed simply with the virtual orbitals originating from a ground state Hartree-Fock calculation, but to determine individually each MO to be included in the pool of excited MO’s. To this end a π-electron was consecutively promoted to the lowest orbital of each occurring symmetry: b, b, b, b, b, b, and b, whereupon these six orbitals were one by one optimized through open-shell SCF procedures on the respective excited states. The orbitals obtained this way are orthogonal neither on each other nor on the ground state orbitals (except perhaps for symmetry reasons), which is why we performed a preliminary Gram-Schmidt orthonormalization on the separate set of monomer orbitals, preserving the energy order of the orbitals. The orbital energies and symmetries are shown in Table VI.

C. VB structures

As was pointed out in the foregoing section, only those VB structures are to be taken into account that mix under the first few multipole operators resulting from the expansion of the interaction operator. Only single excitations on each of the monomers have to be included to calculate a substantial part of the London-van der Waals

TABLE VI. Ethylene orbitals included in VB calculations, 1–8 from closed-shell SCF on ground state, 9–14 from open-shell SCF on singly excited states.

<table>
<thead>
<tr>
<th>nr</th>
<th>Symmetriesa</th>
<th>Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>-11.267616</td>
</tr>
<tr>
<td>2</td>
<td>b</td>
<td>-11.266116</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>-1.025331</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>-0.783823</td>
</tr>
<tr>
<td>5</td>
<td>b</td>
<td>-0.641625</td>
</tr>
<tr>
<td>6</td>
<td>a</td>
<td>-0.582044</td>
</tr>
<tr>
<td>7</td>
<td>b</td>
<td>-0.499021</td>
</tr>
<tr>
<td>8</td>
<td>b</td>
<td>-0.375118</td>
</tr>
<tr>
<td>9</td>
<td>b</td>
<td>0.007255</td>
</tr>
<tr>
<td>10</td>
<td>b</td>
<td>0.060831</td>
</tr>
<tr>
<td>11</td>
<td>a</td>
<td>0.682727</td>
</tr>
<tr>
<td>12</td>
<td>b</td>
<td>0.132136</td>
</tr>
<tr>
<td>13</td>
<td>b</td>
<td>0.225397</td>
</tr>
<tr>
<td>14</td>
<td>b</td>
<td>1.003311</td>
</tr>
</tbody>
</table>

*Point group D_{1h}.
TABLE VII. Contributions of local excitations to the lowest multipole operators of certain symmetry.

<table>
<thead>
<tr>
<th>Multipole operator</th>
<th>Dipole moment</th>
<th>Quadrupole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1u}$</td>
<td>$3 \rightarrow 12^b$</td>
<td>$3 \rightarrow 11$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$6 \rightarrow 14$</td>
<td>$6 \rightarrow 11$</td>
</tr>
<tr>
<td></td>
<td>$8 \rightarrow 11$</td>
<td>$7 \rightarrow 13$</td>
</tr>
<tr>
<td></td>
<td>$4 \rightarrow 9$</td>
<td>$8 \rightarrow 14$</td>
</tr>
<tr>
<td></td>
<td>$3 \rightarrow 12$</td>
<td>$4 \rightarrow 12$</td>
</tr>
<tr>
<td></td>
<td>$6 \rightarrow 12$</td>
<td>$5 \rightarrow 10$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$4 \rightarrow 11$</td>
<td>$3 \rightarrow 13$</td>
</tr>
<tr>
<td></td>
<td>$8 \rightarrow 9$</td>
<td>$6 \rightarrow 13$</td>
</tr>
<tr>
<td></td>
<td>$7 \rightarrow 10$</td>
<td>$B_{1g}$</td>
</tr>
<tr>
<td></td>
<td>$5 \rightarrow 13$</td>
<td>$7 \rightarrow 11$</td>
</tr>
<tr>
<td></td>
<td>$3 \rightarrow 10$</td>
<td>$4 \rightarrow 10$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$6 \rightarrow 10$</td>
<td>$5 \rightarrow 12$</td>
</tr>
<tr>
<td></td>
<td>$5 \rightarrow 11$</td>
<td>$7 \rightarrow 9$</td>
</tr>
<tr>
<td></td>
<td>$7 \rightarrow 12$</td>
<td>$3 \rightarrow 14$</td>
</tr>
<tr>
<td></td>
<td>$4 \rightarrow 13$</td>
<td>$8 \rightarrow 16$</td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$</td>
<td>$5 \rightarrow 9$</td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$</td>
<td>$8 \rightarrow 9$</td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$</td>
<td>$3 \rightarrow 9$</td>
</tr>
<tr>
<td></td>
<td>$B_{1g}$</td>
<td>$8 \rightarrow 16$</td>
</tr>
</tbody>
</table>

*aTable relates to monomer A in Fig. 1. For monomer B in geometry II, the y and z coordinates must be interchanged.

*bOrbital numbers from Table VI.

energy. Induction energy is obtained by exciting one molecule only, whereas the simultaneous excitations of both monomers yield dispersion forces. The subsystems can be excited to a singlet or a triplet state, and since two singlets as well as two triplets can couple to a singlet dimer state, each pair of local excitations will yield two linearly independent structures. In Table VII the excitations are given which admix to the ground state under the various components of the dipole and the quadrupole operator. In this table, as in the calculations, the assumption is made that the carbon 1s electrons do not contribute to the induction and dispersion energy, and consequently the lowest two monomer MO’s are kept doubly occupied. From Table VII one derives Table VIII, where the numbers of VB structures are exhibited which must be included to get a full description of the following second order interactions: induced dipole-induced dipole, induced dipole-induced quadrupole, induced quadrupole-induced quadrupole, and permanent quadrupole-induced dipole. At this point it must be stressed again that by using a nontruncated interaction operator, symmetry arguments can not completely separate the higher multipole interactions from the lower ones. For instance, the result to be presented as “z-component part of dipole/dipole dispersion energy” includes in fact also the z-component part of dipole/octupole, octupole/octupole, etc. dispersion energy. From Tables I and VII it can immediately be deduced which of the higher multipole interactions are also included under the different choices of local symmetry. From these tables it can also be concluded, even though we did not include atomic polarization functions, that all symmetries are represented except one: $A_u$. The lowest order operator with $A_u$ symmetry is the $xyz$ component of the octupole operator which couples with the $xy$ component of the quadrupole operator on the other

center, giving rise to a $R^{-12}$-dependent contribution to the dispersion energy.

No ionic structures were added because the included covalent VB structures should account for the electrostatic, induction, and dispersion forces (Sec. II A). The covalent structures are also expected to describe exchange forces rather well although we use orthogonalized orbitals, because the first order interaction between closed-shell monomers is invariant under orthogonalization (Sec. II C). So, the first order exchange forces are accounted for exactly: only for short distances are ionic structures expected to improve the exchange energy (in second order). Moreover, the inclusion of ionic structures would greatly complicate the formalism, since they are known to yield a distance dependent contribution to the intramolecular correlation energy, implying that we would have to take the fully correlated monomers as the reference system.

IV. RESULTS

To date, almost all semiempirical calculations on the conformation of biopolymers and molecular crystals apply the pair approximation neglecting three and more body interactions. A recent study looked into the pair approximation for the case of the ethylene crystal and concluded that three body forces are indeed negligible. So, in accordance with the purpose of this work, we restrict the attention to the dimer.

The interaction energy as a function of distance has

TABLE VIII. Number of VB structures contributing to the components of second order multipole interactions.

<table>
<thead>
<tr>
<th>Multipole interaction</th>
<th>Geometry I</th>
<th>Geometry II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_1^+ - \mu_2^-$</td>
<td>32</td>
<td>48</td>
</tr>
<tr>
<td>$\mu_1^- - \mu_2^+$</td>
<td>72</td>
<td>48</td>
</tr>
<tr>
<td>$\mu_1^- - \mu_2^-$</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Total dipole–dipole</td>
<td>154</td>
<td>146</td>
</tr>
<tr>
<td>(dispersion)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_1^+ - Q_2^0 + Q_2^+ - \mu_2^-$</td>
<td>96</td>
<td>120</td>
</tr>
<tr>
<td>$\mu_1^- - Q_2^0 + Q_2^- - \mu_2^+$</td>
<td>96</td>
<td>80</td>
</tr>
<tr>
<td>$\mu_1^+ - Q_2^- + Q_2^+ - \mu_2^+$</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Total dipole–quadrupole</td>
<td>232</td>
<td>280</td>
</tr>
<tr>
<td>(dispersion)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_1^+ - Q_2^-$</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>$Q_1^- - Q_2^+$</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>$Q_1^+ - Q_2^+$</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>$Q_1^- - Q_2^-$</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Total quadrupole–quadrupole</td>
<td>172</td>
<td>164</td>
</tr>
<tr>
<td>(dispersion)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permanent quadrupole–induced dipole (induction)</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Total multipole interaction (up to quadrupole–quadrupole)</td>
<td>586</td>
<td>600</td>
</tr>
</tbody>
</table>
been computed for two relative orientations of the ethylene molecules (Fig. 1):

(i) Geometry I is the structure occurring in the stacks of \(\pi\)-electron systems mentioned in the introduction. This structure also constitutes the simplest possible model exhibiting all the basic features of transannular interaction, such as it appears for instance in the \((m,n)\)-paracyclophanes or bicyclooctatriene.\(^{50}\)

(ii) Geometry II is the structure yielding the maximum electrostatic quadrupole–quadrupole attraction.\(^{50}\) [Note that the quadrupole moment of ethylene is close to that of a linear molecule (Table V), with the axis perpendicular to the molecular plane.]

The importance of quadrupole–quadrupole interaction for determining the spatial arrangement of molecular crystals has often been emphasized,\(^{93-95}\) whereas in other work\(^{12,13}\) the significance of this interaction in solids is cast into doubt. So it is a point of interest to compute the size of this term.

In Table IX, the total first- and second order interaction energies defined in Sec. II are given: the same results are graphically presented in Figs. 2 and 3. The first order energy consists in general of short range exchange and penetration effects on the one hand, and long range electrostatic interactions on the other. In Table

<table>
<thead>
<tr>
<th>Geometry I</th>
<th>Geometry II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E^{(1)}_{\text{vb}})</td>
<td>(\Delta E^{(1)}_{\text{vb}})</td>
</tr>
<tr>
<td>(\Delta E^{(2)}_{\text{vb}})</td>
<td>(\Delta E^{(2)}_{\text{vb}})</td>
</tr>
<tr>
<td>(\Delta E_{\text{vb}})</td>
<td>(\Delta E_{\text{vb}})</td>
</tr>
</tbody>
</table>

TABLE IX. First order, second order, and total interaction energies. Energy units: \(10^{-3}\) hartree.\(^{16}\) Distance \(R\) between the centers of mass in bohr.\(^{94}\) Geometries given in Fig. 1. Definitions of interaction energies given by Eqs. (8) and (9). Zero point of energy: \(-155,8801231\) hartree.

<table>
<thead>
<tr>
<th>(R) (bohr)</th>
<th>(\Delta E^{(1)}_{\text{vb}})</th>
<th>(\Delta E^{(2)}_{\text{vb}})</th>
<th>(\Delta E_{\text{vb}})</th>
<th>(\Delta E^{(1)}_{\text{vb}})</th>
<th>(\Delta E^{(2)}_{\text{vb}})</th>
<th>(\Delta E_{\text{vb}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>180.14, 59</td>
<td>-102.2, 58</td>
<td>170.01, 101</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>5.0</td>
<td>424.9, 56</td>
<td>-365.86</td>
<td>366.13, 173</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
<td>(\ldots)</td>
</tr>
<tr>
<td>6.0</td>
<td>1023.2, 57</td>
<td>-161.25</td>
<td>163.31, 31</td>
<td>467.46, 33</td>
<td>-236.45</td>
<td>457.1, 64</td>
</tr>
<tr>
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<tr>
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<td>3.25, 2</td>
<td>-4.14</td>
<td>0.57</td>
<td>-2.71</td>
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</table>
TABLE X. Decomposition first order energy into electrostatic quadrupole—quadrupole: $\Delta E_{Q-Q}^{(1)}$; quadrupole—hexadecupole: $\Delta E_{Q-H_{16}}^{(1)}$; hexadecupole—hexadecupole: $\Delta E_{H_{16}-H_{16}}^{(1)}$ interaction energy and short range exchange and penetration effects. Units: $10^{-5}$ hartree.

<table>
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<th>Geometry II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (bohr)</td>
<td>$\Delta E_{Q-Q}^{(1)}$</td>
</tr>
<tr>
<td>4.0</td>
<td>44.079.69</td>
</tr>
<tr>
<td>5.0</td>
<td>1444.31</td>
</tr>
<tr>
<td>6.0</td>
<td>580.74</td>
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<tr>
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<tr>
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<td>12.16</td>
</tr>
<tr>
<td>16.0</td>
<td>4.30</td>
</tr>
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</table>

X and Figs. 4 and 5, these long and short range contributions to the first order energy are separated. The electrostatic force has been split as follows; the classical quadrupole—quadrupole interaction $\Delta E_{Q-Q}^{(1)}$ has been computed using our own quadrupole moments shown in Table V; Lacking a computer program generating fourth moments, we took hexadecupole values from Ref. 88, which are of double-$\epsilon$ quality. We employed these for the hexadecupole—quadrupole interaction $\Delta E_{Q-H_{16}}^{(1)}$ and hexadecupole—hexadecupole interaction $\Delta E_{H_{16}-H_{16}}^{(1)}$. Invoking Rose’s formula, 49 one easily derives the values given in Table X. The difference between the quantum mechanical first order energy and the classical electrostatic interaction (up to hexadecupole—hexadecupole) is also given in Table X under the heading “exchange and penetration energy.” Besides the real exchange and penetration effects, these values also contain the deviations caused by the use of hexadecupole moments that are not derived from our monomer wave function and the contribution of higher multipole interactions. Work is in progress to refine the analysis on these points.

In Table XI, the second order energy is decomposed into the various components of the multipole moments, a decomposition that is not obtained by expanding the interaction operator but is induced by the use of local symmetry, as described in Sec. II. Making this decomposition, one implicitly assumes that the contributions to the second order in our definition (7) are...

<table>
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<tr>
<th>R</th>
<th>z–z</th>
<th>y–y</th>
<th>x–x</th>
<th>$z^2–r^2$</th>
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<th>yz–yz</th>
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<td>$-168.92$</td>
<td>$-2.14$</td>
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<td>$-2.33$</td>
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Geometry I

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<th>$z^2–r^2$</th>
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<td>$-0.00$</td>
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</tr>
</tbody>
</table>

Geometry II

The ratios of the different terms in the multipole expansion to the second order energy are plotted in Figs. 6 and 7, clearly exhibiting the convergence of the multipole series. In Fig. 6, the corresponding ratio of the contribution of the $\pi–\pi^*$ excitation has also been drawn. Note that this part of the dipole–dipole dispersion is obtained from a three-structure VB calculation on the basis of only the ground state and the two states representing the intermolecular coupling of the $T(\pi^*)$ and $V(\pi^*)$ states, respectively, whereas Table VIII tells us that the total second order energy is obtained from as many as 600 VB structures. The effect of the $\pi–\pi^*$ transition is not shown in Fig. 7, because no special contribution is noticeable in the case of Geometry II. In neither of the two geometries does any other structure yield a dominant contribution.

Wondering if possibly the first order and induction energy could be accounted for by the SCF formalism, we performed two sets of LC-DA–MO–SCF calculations on the dimer, treating it as if it were one “supermolecule.” One set was done with the CNDO/2 program, using the original parameter setting, and the other calculations were of the $ab$ initio type, employing the GTO basis given in Table III. The results are given in Figs. 8 and 9.

---

FIG. 6. Relative contributions to second order energy for Geometry I. Absolute values given in Table XI.
V. DISCUSSION

A. Long range interactions and their multipole expansions

The difference between the interaction of two parallel (Fig. 2) and two perpendicular (Fig. 3) ethylene molecules, one being repulsive and the other attractive, is seen from Tables IX and X to be mainly due to the first order electrostatic interaction. At large and intermediate distances, the \( Q^{-Q} \) (quadrupole-quadrupole) interaction is the dominant term in this first order energy, but at smaller distances the higher multipoles become important as well. Note that the multipole expansion in first order diverges completely at \( R \approx 5 \) bohr, with even \( \Delta E^{11}_{Q^{-Q}} < \Delta E^{11}_{n^{-m}} \) for Geometry I. Clearly, penetration effects have rendered the expansion invalid in this region. Note also that the three term expansion ceases to be an adequate representation of the intermolecular potential much earlier: for distances smaller than 10 bohr, the interaction between higher moments than hexadecupoles must be included. The decisive role of the \( Q^{-Q} \) interaction in determining the energy difference between the two geometries considered suggests that these interactions are also important in determining the structure of molecular crystals. 93-96 In a crystallographic environment, the effect of the surrounding quadrupoles on a molecule may average out though. 12,13 Still, our calculations show that first order electrostatic forces cannot be neglected a priori. If the \( Q^{-Q} \) interaction is calculated, higher multipoles cannot consistently be omitted.

As far as the second order forces are concerned, they are always attractive and, therefore, they will certainly contribute to the cohesion energy of the crystal. The attraction is slightly larger for the perpendicular geometry than for the parallel one. Comparing Figs. 6 and 7, we note that the dipole–dipole dispersion has relatively more weight in the parallel geometry. In Table XI, the source of this phenomenon can readily be located: it is the \( \pi-\pi \) component of the dispersion, which in Geometry I receives a considerable contribution from the \( \pi-\pi^* \) transition on both monomers. In Geometry II, these \( \pi-\pi^* \) transitions contribute to different dipole–dipole components, and it appears that they play no particular role in this geometry. In the second order energy, as in the first order, we find that the leading term in the multipole expansion does not suffice for a good description of the interaction energy, so that we should also take higher multipoles into account. The induction energy is not very large, which is not a widely accepted fact. A point of criticism could here be that the induction of a quadrupole by the permanent quadrupole on the other monomer has not been calculated. But since the corresponding energy has a \( R^{-10} \) dependence and since the quadrupole-induced dipole \( (R^{-4}) \) term is already quite small, we felt safe in neglecting it.

B. Penetration and exchange effects

Although we have not calculated these effects directly, their occurrence can easily be recognized from our results. Figure 6 shows a sudden drop in the relative dipole–dipole contribution originating from a steep rise in the induction energy, which we ascribe to the same penetration of the charge distribution that also causes the divergence of the expanded first order energy. If this assignment is correct, the exponential increase of the first order repulsion at about 7 and 8 bohr for Geometry I and II, respectively, must be caused by exchange

FIG. 7. Relative contributions to second order energy for Geometry II. Absolute values given in Table XI.

FIG. 8. Interaction energies from CNDO calculations on the supermolecule.
effects. Actually, the difference of about 1 bohr in the "hard core" diameters for Geometry I and II, together with a scattering diameter \( \sigma \) of 8.3 bohr for Geometry II (Fig. 3) matches a geometrical model that attributes a van der Waals radius of 3.7 bohr to a spherical methylene group. Pauling\(^{99} \) suggests 3.8 bohr for this radius, a number which is also in accordance with the C \( \cdots \) C and C \( \cdots \) H contact distances proposed by Kitaigorodski\(^{12} \).

The over-all repulsive interaction between two parallel ethylene molecules is also in agreement with the well-known fact that a strong steric hindrance exists between two transannular ethylenic moieties. This has been discussed earlier in connection with the influence on the \( \pi \)-\( \pi^* \) transitions localized in the double bonds\(^{100} \) and it has been investigated by means of extended Hückel calculations\(^{99} \).

C. Comparison with experiment

Figure 3, relating to the perpendicular geometry, shows a van der Waals well depth \( \epsilon \) of 33.5 \( \times 10^{-5} \) hartree at \( R_0 = 9.4 \) bohr and a scattering diameter \( \sigma \) of about 8.3 bohr. The first order contribution to \( \epsilon \) is 12.5 \( \times 10^{-5} \) hartree.

Experimental values for the van der Waals well of the ethylene dimer are as follows; \( \epsilon = 72.9 \times 10^{-5} \) hartree, \( \sigma = 7.7 \) bohr\(^{101} \); or \( \epsilon = 65.0 \times 10^{-5} \) hartree, \( \sigma = 8.0 \) bohr\(^{101} \). While our scattering diameter agrees reasonably with both values, the discrepancy between the measured and computed values of \( \epsilon \) is considerable. Since the experimental values have been obtained from viscosity data in which a certain rotational averaging is included, the difference may be even larger. Two points are relevant in this respect. Earlier calculations\(^{99} \) on \( \text{H}_2 \) pointed to a need for the optimization of the excited monomer orbitals and also showed that the excited state SCF method is not an adequate tool to this end. (The behavior of virtual SCF orbitals is worse.) So, not having employed excited orbitals which are fully optimized for a description of the long range interaction, and not having included atomic polarization functions, we feel that our results may underestimate the dispersion energy. Also, the question whether Rydberg orbitals should have been included seems appropriate, since the ethylene spectrum shows several Rydberg series and there is even some doubt if the \( \pi^* \) orbital may not be Rydberg-like.\(^{103} \) One must realize, however, that the \( \text{ab initio} \) calculation of van der Waals forces between molecules of this size is not an easy matter and requires very time-consuming computations. In view of this, we feel that our results are promising. Further work on the optimization of excited orbitals, including atomic polarization functions, is in progress.

Another reason for the disagreement with the experimental results may lie on the experimental side. The viscosity data were interpreted in an isotropic 6-12 potential, which is not very realistic for this case. To give an impression how sensitively the \( \epsilon \) values depend on the measured viscosities, we quote Flynn and Thodos,\(^{101} \) who call the difference "plausible" between viscosity \( \epsilon/k \) values of 410 \(^{\circ} \text{K} \) and 208 \(^{\circ} \text{K} \) found for \( n \)-butane by themselves and Hirschfelder \textit{et al.},\(^{102} \) respectively.

This underlines the unreliability of the few experimental data available to gauge the parametrization of semi-empirical calculations.

Even though the second order energy may be underestimated, we still feel that the ratios of the different contributions (Figs. 6 and 7) are of correct magnitude, because they are computed in a single consistent manner without introduction of any \textit{a priori} prejudices about their importance.

D. Interactions between stacked \( \pi \) systems

The repulsive interaction calculated between two parallel ethylene molecules may seem in contradiction to the opinion\(^{14} \) that the stabilization of the helical conformation of DNA is mainly caused by attractive vertical interactions between the bases, and, equally, to the idea that \( \pi-\pi \) charge transfer complexes are stabilized by van der Waals interactions. Although the ethylene dimer evidently falls short in exhibiting all the properties of interactions between DNA bases or large charge transfer complexes, we can still offer a possible explanation on the basis of Fig. 6. Here a very pronounced contribution of the \( \tau \) electrons to the dispersion energy is observed, and we may therefore, not without justification, speculate that in the case of large, very polarizable \( \tau \) systems, the second order energy is able to surmount the first order repulsion, that is, of course, in the region where the Pauli repulsion is still negligible. This
outstanding contribution of the π−π∗ excitations is only found for parallel π systems.

E. Local symmetry, additivity, and perturbation theory

Two important conclusions concerning the method of calculation of the second order energy can be drawn. The triplet–triplet VB structures hardly mixing with the ground state, it appears that local spin selection rules, forbidding the mixing of triplet–triplet and singlet–singlet structures, are very well preserved upon formation of the dimer. So, VB calculations on the weak interactions considered in this work can be drastically simplified by omitting all the structures representing the triplet–triplet coupling. There is a small exception though: for the short distances of the parallel geometry, 11 triplet–triplet structures, all belonging to the y−y dispersion component, contribute slightly to second order energy (3.09×10⁻² and 1.66×10⁻³ hartree for R equal to 4.0 and 5.0 bohr, respectively). The most noticeable among these 11 functions is the one representing the coupling of the T(ππ*) states. Subsequent inclusion of all triplet–triplet structures gave no further improvement, and it can thus be concluded that down to 4.0 bohr the triplet–triplet couplings give rise to negligible contributions to the ground state.

Another important conclusion to be drawn regards the possibility of approximating the lowest eigenvalue of the secular problem over VB structures by a perturbation-like formula. Recall that each component of the second order energy has been computed on a basis of VB structures which are adapted to the local symmetry. In this case characterized by D₂h and D₂. The off-diagonal H-matrix elements connecting blocks of different local symmetry contain only terms arising from the interaction operator VAB. The high degree of additivity in the multipole components of the second order energy shows these elements to be so small that the higher order terms in formula (5) can be neglected between structures of different local symmetry, thus enabling a componentwise construction and diagonalization of H. This in itself is already a great help in keeping the method tractable for large complexes, but it also points to a further potential simplification. Although from our present calculations it cannot be inferred with absolute certainty that the VAB terms within the symmetry blocks are equally small, there is no reason why they should not be. This additivity even holds in the region where the Pauli repulsion has become large, and we may therefore tentatively conclude that a perturbation-like second order formula may be applicable to the lowest eigenvalue of the H matrix including exchange for the whole range of the potential curve. It should be said that the H matrix in this conclusion is assumed to be over a basis of the eigenvectors of H^A and H^B, as described in Sec. II of this paper, because otherwise H contains nondiagonal terms originating from H^A or H^B.

F. SCF Results

Let us finish this section by making a few comments on the SCF results presented in Figs. 8 and 9. It is noteworthy that the CNDO calculations predict the parallel geometry to be the more stable one, whereas the ab initio results fall in line with the VB predictions in this respect. A similar disagreement of CNDO with ab initio SCF has been noted before for (HCN)$_2$ and has there been ascribed to the neglect of three and four center repulsions causing CNDO to favor a cyclic structure. This explanation being very plausible, it makes the CNDO results for this complex meaningless.

The ab initio results on the other hand, seem surprisingly good, with a σ value of 8.0 bohr and ε = 57.6×10⁻⁵ hartree, which may be compared with the experimental values $\sigma = 8.0$ bohr, $\epsilon = 65.0 \times 10^{-5}$ hartree. However, as a check on the usefulness of these results, we performed an SCF computation on the free monomer A in its own AO basis augmented by the vacant AO basis of monomer B placed at a distance 9.0 bohr, assuming Geometry II. This basis set enlargement gave an energy improvement of 56.09×10⁻⁵ hartree, which might become somewhat smaller by accounting for the filling of the orbitals on monomer B. Still, this proves that the splendid SCF curve is partly due to the mathematical artifact of distance dependent basis set enlargement, and has little physical significance. It is difficult to separate the physical interaction energy from these SCF results, since the energy lowering by the basis set enlargement is a nonadditive effect. This pitfall, threatening those who apply small basis SCF to the computation of intermolecular forces, was first noted by Kestner in a discussion of early ab initio SCF calculations on He$_2$. Our results bear witness again to the fact that calculations on van der Waals interactions employing the SCF "super-molecule" approach must necessarily be looked upon with mistrust as long as the monomer bases do not approach the Hartree–Fock limit.

ACKNOWLEDGMENT

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three-body long-range interactions only start appearing in third order of perturbation theory, while the corresponding pair forces occur in second order. This statement is only strictly true for the interaction between neutral atoms in an S state, since its proof as given in Ref. 31, Chap. 5, requires the vanishing of $\langle \chi \psi \psi \phi \phi \phi \phi \rangle$. Still, the three-body forces are expected to be much smaller than the pair forces.

361 hartree = 27.21 eV = 627.49 kcal/mol = 2.625 x 10^8 J/mol, 1 bohr = 0.529177 x 10^{-10} m. Quadrupole units: 1 a.u. = 1.344 x 10^{-28} esu cm^2.
37CHINO Molecular Orbital Program by P. A. Dobosh, distributed by Q. C. P. E., Indiana University, Bloomington, IN.
INTERACTION POTENTIAL FOR He–H₂ IN THE REGION OF THE VAN DER WAALS MINIMUM

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Received 4 July 1975

Interaction energies for the He–H₂ system have been computed by a VB method for the intermolecular distances 5.2 ≤ R ≤ 20.0 bohr and two different orientations of the H₂ molecule (θ = 0°, 90°). The results, especially for the anisotropy, are in good agreement with experiment. The dispersion constants C₆ and C₈ and the corresponding anisotropy constants a₆ and a₈ are presented.

1. Introduction

As one of the simplest systems with a multi-dimensional potential surface, the He–H₂ complex is of experimental as well as theoretical interest. Integral total collision cross sections [1], spin–lattice relaxation times [2] and Raman line shapes [3] have yielded experimental information on the He–H₂ potential surface, and not long ago an analytic intermolecular potential has been proposed by Shafer and Gordon [4] (from here on referred to as SG) which accurately fits all these experimental data.

Theoretical investigations have concentrated either on the short range (repulsive) potential [5–7] or on the long range dispersion forces [8]. Tsapline and Kutzelnigg [9] (henceforth referred to as TK) were the first to calculate van der Waals minima for He–H₂. Their minima are close to the experimental results. However, TK predict the linear configuration of the He–H₂ system to be favoured by 2.35 × 10⁻⁵ hartree above the perpendicular geometry, whereas the empirical results of SG show the linear geometry to be slightly less stable than the perpendicular one (by an amount of 0.3 × 10⁻⁵ hartree). Also the theoretical and experimental van der Waals radii are not in complete agreement.

It could be supposed that this discrepancy is caused by the neglect of intra-monomer correlation in the calculations and more specifically by the coupling of intra- with inter-monomer correlation [9,10]. However, as it seems hard to accept that this correlation effect could be responsible for such a relatively large error in the anisotropy, we thought it worthwhile to perform some of the calculations as well, using another formalism [11–13] and another basis of atomic orbitals, but also neglecting the effects of intra-monomer correlation. Interaction curves for two different geometries are presented:

(i) the perpendicular geometry with an angle θ = 90° between the molecular axis of H₂ and the vector $\mathbf{R}$ connecting the midpoint of H₂ with He and
(ii) the linear geometry with θ = 0°.

The distance R has been varied from 5.2 to 20.0 bohr, the H–H distance has been kept constant (1.40 bohr).

2. Method

The method employed in this work is essentially a multistucture valence-bond method based on VB structures containing AO’s on He and MO’s on H₂. In this formalism it is possible, by using local symmetry, to separate the different terms in the multipole expansion of the dispersion energy [11], although the complete unexpanded form of the interaction operator is used in our calculations. To obtain the contribution from a certain component of the multipole operator the basis must include at least one VB structure representing a locally excited state that combines with the monomer ground state under this multipole component.
Table 1
Atomic orbital basis

<table>
<thead>
<tr>
<th></th>
<th>(N_{\text{contr}}) (^a)</th>
<th>(\xi) (^b)</th>
<th>Optimization method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>6</td>
<td>(-)</td>
<td>SCF calculation He</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.30</td>
<td>van der Waals int. in He(_2)</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.45 (^c)</td>
<td>van der Waals int. in He(_2)</td>
<td>[13]</td>
</tr>
<tr>
<td>H</td>
<td>6</td>
<td>1.2</td>
<td>SCF calculation in H(_2) (^d)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.0</td>
<td>SCF calculation in H(_2)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.1</td>
<td>van der Waals int. in H--H(_2)</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.1 (^c)</td>
<td>van der Waals int. in H--H(_2)</td>
<td>this work</td>
</tr>
</tbody>
</table>

\(^{a}\) Number of primitive GTO’s in contracted set.
\(^{b}\) Contracted set represents STO with exponent \(\xi\) (bohr\(^{-1}\)).
\(^{c}\) Exponent GTO: \(\alpha = 0.2738\) (bohr\(^{-2}\)).
\(^{d}\) Contraction coefficients optimized.
\(^{e}\) Exponent GTO: \(\alpha = 0.1576\) (bohr\(^{-2}\)).

Within the VB framework one can define two quantities \(\Delta E^{(1)}\) and \(\Delta E^{(2)}\) resembling first- and second-order perturbation energies, respectively. \(\Delta E^{(1)}\) is the expectation value of the total Hamiltonian over the dimer ground state minus the SCF energies of the free monomers. \(\Delta E^{(2)}\) is the difference between the VB multi-structure interaction energy and the just defined first-order energy. This difference is asymptotically equal to London’s well-known second-order energy expression [11].

The orbitals on the different monomers do of course overlap, but since we have found previously that a well-chosen orthogonalization does not influence the results to a significant extent, we have orthogonalized the basis, while meeting the following requirements:

- the ground state VB structure, and with it \(\Delta E^{(1)}\), is left invariant;
- the orbitals remain as localized as possible on the respective monomers; consequently they reflect the symmetry of the subsystems.

A careful orthogonalization is of the utmost importance. If, for instance, one allows all orbitals in the dual space to mix among each other, as is done in the method of bi-orthogonal orbitals [14], one finds first-order energies which are very sensitive to the basis set and which sometimes are negative in regions of the potential surface where strong repulsions are expected [14].

3. Basis

The selection of an orbital basis needs special care in the study of van der Waals interactions, because these are usually very small. It has been found [13], for instance, that the orbitals constituting the excited states must be optimized by maximizing the dispersion energy. Good ground state orbitals are also required: for a reliable estimate of dispersion energies [13] as well as for correct exchange repulsions [15]. Thus, we have included in the AO basis two p-orbitals on each hydrogen: one rather diffuse orbital to obtain the corresponding parts of the dispersion energy and another more compact orbital necessary for the description of the exchange repulsion between He and H\(_2\). The need for at least two p-orbitals in cases such as this has sometimes been overlooked [16]. Contrary to the case of the p-orbitals, one d-orbital per hydrogen atom appears to be sufficient, mainly because the orbital exponent required for getting a good ground state energy of H\(_2\) very nearly optimizes the dispersion energy of H\(_2\)--H\(_2\). One must realize, in this connection, that the dispersion energy is not very sensitive to variations of this exponent in the neighbourhood of the optimum.

The inclusion of an optimized p-orbital on He is necessary to account for the dipole excitations on this atom; one optimized d-orbital on He takes care of the quadrupole excitations.

The AO's used in this work are contracted GTO's with tesseral harmonics as their angular parts. Except for the 1s-orbitals on He and H\(_2\), they have been fitted to STO's with exponents \(\xi\). The \(\xi\)-values have subsequently been optimized. See Table 1 for a summary of the basis. We have also experimented with larger contractions of the He and H\(_2\) p-orbitals, but this hardly affected the results.

The MO's of \(\sigma\)-symmetry on H\(_2\) are obtained from
Table 2

<table>
<thead>
<tr>
<th></th>
<th>Present work TK [9]</th>
<th>11F limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF energy He a)</td>
<td>-2.8611163</td>
<td>-2.86168</td>
</tr>
<tr>
<td>SCF energy H2 b)</td>
<td>-1.1330237</td>
<td>-1.133629</td>
</tr>
<tr>
<td>quadrupole H2 d)</td>
<td>0.4931</td>
<td>0.4933 b)</td>
</tr>
</tbody>
</table>

a) Hartree.

b) Ref. [18].

c) Ref. [17].

d) \(\frac{1}{2}(\epsilon^2 - \sigma^2)\) in au.

Table 3

First-order, second-order and total interaction energies. Distance in bohr, energy in \(10^{-5}\) hartree

<table>
<thead>
<tr>
<th>(\Delta E^{(1)})</th>
<th>(\Delta E^{(2)})</th>
<th>(\Delta E_{\text{tot}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta E^{(1)})</td>
<td>(\Delta E^{(2)})</td>
<td>(\Delta E_{\text{tot}})</td>
</tr>
<tr>
<td>(R)</td>
<td>(\text{bohr})</td>
<td>(\text{bohr})</td>
</tr>
<tr>
<td>5.2</td>
<td>56.50</td>
<td>28.32</td>
</tr>
<tr>
<td>5.6</td>
<td>24.40</td>
<td>-18.71</td>
</tr>
<tr>
<td>6.0</td>
<td>10.41</td>
<td>-12.59</td>
</tr>
<tr>
<td>6.3</td>
<td>5.45</td>
<td>-9.49</td>
</tr>
<tr>
<td>6.5</td>
<td>3.52</td>
<td>-7.91</td>
</tr>
<tr>
<td>6.6</td>
<td>2.83</td>
<td>-7.23</td>
</tr>
<tr>
<td>7.0</td>
<td>1.16</td>
<td>-5.10</td>
</tr>
<tr>
<td>8.0</td>
<td>0.11</td>
<td>-2.26</td>
</tr>
<tr>
<td>9.0</td>
<td>0.00</td>
<td>-1.08</td>
</tr>
<tr>
<td>10.0</td>
<td>0.00</td>
<td>-0.56</td>
</tr>
<tr>
<td>11.0</td>
<td>0.00</td>
<td>-0.32</td>
</tr>
<tr>
<td>12.0</td>
<td>0.00</td>
<td>-0.18</td>
</tr>
<tr>
<td>20.0</td>
<td>0.00</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Fig. 1. Perpendicular geometry. Total interaction energy \(\Delta E_{\text{tot}}\) of TK [9], SG [4] and this work. First-order energy \(\Delta E^{(1)}\) of this work, SCF-interaction energy \(\Delta E_{\text{SCF}}\) of TK [9]. From \(1 \times 10^{-5}\) hartree upwards the energy scale is logarithmic.

0.26 for He, 0.16 and 0.08 for H2 in the case of the linear and the perpendicular geometry, respectively. If we had obtained the first-order interaction from SCF calculations on the dimer, we would have had to correct for these small effects, but because we calculate \(\Delta E^{(1)}\) directly from the monomer orbitals, the fact that the basis set is not completely saturated does not concern us.

an SCF calculation on the free molecule, and those of \(\pi\) and \(\delta\)-symmetry are simply symmetric and antisymmetric combinations of equivalent orbitals on the atoms.

As in earlier work [11–13] we have found again that VB structures representing the coupling of triplet excited monomers can be omitted. This halves the number of VB structures contributing to the dispersion energy. In total, about 50 of such singlet—singlet structures can be derived from the given orbital basis; all of these have been taken into account in this work.

The quality of the atomic orbital basis may be judged from the values in table 2. Another criterion for the adequacy of the basis is the "saturation test" [19], which is a computation of the SCF energy of each of the single subsystems in the dimer basis. We have found the following small energy improvements at \(R = 6.5\) bohr, expressed in \(10^{-5}\) hartree: 0.34 and...
4. Results and discussions

In table 3 the first-order, second-order and total interaction energies are given for the two configurations considered in this work. Figs. 1 and 2 give some of these results graphically, showing also a comparison with the total interaction energies of SG [4] and the SCF and total interaction energies of TK [9].

4.1. First-order energy

For the perpendicular geometry one notes that our first-order energies are very similar to the SCF energies of TK: the hardly significant difference can probably be explained by the differences in the basis sets. In the case of the linear geometry, our first-order results differ a little more from the SCF curve of TK, which is lying lower. The induction part (mainly permanent quadrupole on $\text{H}_2$, induced dipole on He) of the interaction energy could be a source of this discrepancy, because it is contained in the dimer SCF energy but not in our first-order energy. We have therefore computed the induction energy explicitly, by the VB method, as well as classically using the quadrupole moment of $\text{H}_2$ from table 2 and the polarizability $\alpha = 1.393$ (bohr)$^3$ of He [13]. We find that the two methods agree in all significant figures, which are not many in this case because the effect is very small indeed: $0.05 \times 10^{-5}$ hartree at 6.5 bohr (linear geometry). In any event this value is too small to explain the difference between TK's and our results. Possibly TK have improved the SCF energies of the subsystems somewhat in the dimer basis, due to a non-saturated monomer basis, and have not subsequently corrected for this effect. This allegation is supported by the occurrence of a minimum in their curve which, although very weak, is still too deep to be caused by induction. Also, our first-order energy at 5.2 bohr compares quite well with the best SCF value of ref. [5] after correction for the induction energy: $56.5 \times 10^{-5}$ hartree versus $56.3 \times 10^{-5}$ hartree [5], whereas TK find about $51 \times 10^{-5}$ hartree (interpolated) for the same value. (For the perpendicular case with the same distance these values are 38.9 (this work), 39.6 [5] and about 37 (TK).)

The first-order repulsion can be fitted quite satisfactorily by the following potential, valid for $R \geq 5.2$ bohr. (The $\theta$-dependency is given by a second-order Legendre polynomial.)

$$
\gamma^{(1)}(R, \theta) = A e^{-\beta R} [1 + \gamma P_2(\cos\theta)].
$$

The optimal parameters are:

$A = 34.5$ hartree, $\beta = 2.16$ (bohr)$^{-1}$, $\gamma = 0.267$.

The $\beta$-value is somewhat larger than any of the values proposed in ref. [5] for $3.8 \leq R \leq 5.2$ (bohr), a range which is different from ours, though. Since a
small deviation in $\beta$ gives a considerable effect on $A$, it is not surprising that our $A$-value differs by a factor of about 3 from the values of ref. [5].

4.2. Total energy

With regard to the total energy, we see from table 4 that for the perpendicular geometry TK’s calculations agree better with the experimental results than ours, although our values do not deviate too much either. We have observed before that our method has a tendency to underestimate the dispersion energy to some extent. Using a comparable basis set we have found for He-He [13] a dispersion energy $\Delta E^{(2)}$ which is 90% of the value computed in a much larger basis including f-orbitals [20].

As to the linear geometry, the results of this work are in full agreement with the experimental $R_m$-value and, again, underestimate the experimental well depth somewhat, whereas TK find too deep a minimum at too short a distance (table 4)*.

So, although the anisotropy found in this work is much less pronounced than that of TK [9], we still predict the wrong geometry to be more stable, that is, comparing with SG [4]. To explain this discrepancy one may point out several inaccuracies in this work, such as the neglect of intra-monomer correlation or a possible geometry-dependent underestimate of the dispersion, but it must also be noted that SG’s potential lacks some flexibility in the long-range part. The following discussion may clarify this remark. Within the VB formalism one can calculate the dispersion coefficients $C_6$, $C_8$, etc., directly. Thus computing $C_6$ and $C_8$ for the linear and perpendicular geometry, one may extract averaged $C_6$- and $C_8$-values plus the corresponding anisotropy constants $\alpha_6$ and $\alpha_8$. In this manner we have computed the following long range potential:

$$V^{(2)}(R,\theta) = -C_6 \frac{1}{R^6} \left[ 1 + \alpha_6 P_2(\cos\theta) \right]$$

$$- C_8 \frac{1}{R^8} \left[ 1 + \alpha_8 P_2(\cos\theta) \right],$$

with

$$C_6 = 4.34 \text{ au}, \quad C_8 = 49 \text{ au}, \quad \alpha_6 = 0.149, \quad \alpha_8 = 0.23.$$  

The values of $C_6$, $C_8$ and $\alpha_8$ are in fair agreement with the values $C_6 = 4.01 \text{ au}, C_8 = 41 \text{ au}, \alpha_6 = 0.105$ quoted by SG. This potential gives an excellent fit to the second-order energies of table 3 for $R > 7.0$ bohr. Now, SG assume $\alpha_6$ and $\alpha_8$ to be identical, thus overestimating $C_8$ for the perpendicular geometry, while underestimating $C_8$ for the linear case. So, by this lack of flexibility in their long range anisotropy they favour the perpendicular geometry somewhat above the linear one, but because of the way they fit the potential, it is difficult to see how this affects the minima.

It could be presumed that the superposition, $V^{(1)} + V^{(2)}$, of the short and the long range potential can yield a reasonable fit for the whole range. This is not so, mainly because of the inadequacy of $V^{(2)}$ to represent charge-penetration effects. A better fit would require some extra (exponential) terms to account for charge penetration.

Since scattering experiments are often interpreted by the use of Lennard-Jones potentials [21], we have computed the following analytic form from the positions and the depths of the minima:

$$V_{LJ}(R,\theta) = -2\epsilon(R_0/R)^6 \left[ 1 + \delta_{2,6} P_2(\cos\theta) \right]$$

$$+ \epsilon(R_0/R)^{12} \left[ 1 + \delta_{2,12} P_2(\cos\theta) \right],$$

---

* When informed about our results Professor Kutzelnigg has communicated that their potential curves become very similar to ours when they extended their formalism in order to account for the coupling between inter- and intra-monomer correlations. In comparing these results it must be remembered, though, that the relative contributions from inter- and intra-monomer terms depend on the degree of localization of the orbitals on the subsystems.
with

\[ e = 4.13 \times 10^{-5} \text{ hartree}, \quad R_0 = 6.48 \text{ bohr}, \]
\[ q_{2,6} = 0.164, \quad q_{2,12} = 0.271. \]

The L-J potential gives a good description of the computed van der Waals well, but overestimates both the repulsion and the long range attraction in the region considered. The anisotropy constants \( q_{2,12} \) and \( q_{2,6} \) are not very different from our corresponding asymptotic values \( \gamma = 0.267 \) and \( \alpha_6 = 0.149 \). Furthermore, they are in good agreement with experimental results [22] obtained from the scattering of molecular \( \text{H}_2 \) beams with several of the noble gases.

Acknowledgement

We thank Dr. J. Reuss for suggesting the problem, and him and Drs. L. Zandee, T. van Berkel and F. Mulder for valuable discussions.

References

SUMMARY

The most important part of this dissertation consists of reprints of papers published earlier. Two subjects are treated in these papers:

I. Application of the representation theory of $GL(n)$ and $S_N$ to the many-body problem.

II. Calculations on intermolecular forces.

Many of the techniques discussed under I are applied in II.

I. In the chapters I.1. through I.6. of this dissertation the close connection is discussed which exists between spin, permutation symmetry and transformation properties of N-electron wave functions. This mathematical connection is treated in detail, mainly because this theory is not yet very well-known among chemists. In two of the reprinted papers the results of the theory are applied to the transformation properties of N-electron wave functions with respect to "blocked" orbital mixings.

The other two group theoretically oriented papers treat respectively the group theoretical classification of atomic Russell-Saunders states and the classification of more-particle interactions with respect to permutation symmetry.

II. The goal of these investigations has been the development of a practical method for the computation of intermolecular potentials in the region of the Van der Waals minimum. The first article on this subject presents the results of calculations by means of a simple semi-empirical method (the CNDO method). The results were such that we looked for a more reliable method. This was found in the multi-structure valence bond formalism. The first paper based on this formalism (calculations on He$_2$) presents a test on the reliability and the tractability of the method. The second article is an attempt to furnish more insight into the bonding of a chemically more interesting complex (the ethylene dimer). In the third valence bond paper we have attempted to calculate a potential of good quality for He-He$_2$. An important reason for the choice of the He-H$_2$ complex was the fact that experimental work on this complex was under way in the atomic and molecular spectroscopy group of this university. So the computed potential could be compared directly with the experiment.

Because the VB calculations were guided by London's theory of intermolecular forces, the papers are preceded by a presentation of this theory in terms of irreducible tensor operators.
SAMENVATTING

Dit proefschrift bestaat voor het voornaamste gedeelte uit herdrukken van reeds eerder verschenen artikelen. Deze artikelen betreffen twee onderwerpen:

I. Toepassing van de representatie-theorie van $GL(n)$ en $S_N$ op het veel-deeltjes probleem.

II. Berekeningen aan intermoleculaire wisselwerkingen.

Veel van de technieken besproken onder I zijn toegepast in II.

I. Zoals uiteengezet wordt in de hoofdstukken I.1 t/m I.6 van deze dissertatie, bestaat er een nauw verband tussen spin, permutatie-symmetrie en transformatie-eigenschappen van N-elektron golffuncties. Dit wiskundig verband wordt in detail behandeld, voornamelijk omdat deze theorie voor een groot gedeelte nog nauwelijks bekend is onder chemici. In twee van de herdrukte artikelen worden de resultaten van de theorie toegepast op de transformatie-eigenschappen van N-elektron golffuncties onder "geblokte" orbital mengingen.

De andere twee groepentheoretisch georiënteerde artikelen betreffen respectievelijk de groepentheoretische klassificatie van atomaire Russell-Saunders toestanden en de klassificatie van meer-deeltjes interacties met betrekking tot permutatie-symmetrie.

II. Doel van dit onderzoek was te komen tot een bruikbare methode voor de berekening van intermoleculaire potentialen in het gebied van het Van der Waals minimum. Het eerste artikel over dit onderwerp geeft de resultaten van berekeningen met een eenvoudige semi-empirische methode (de CNDO methode). Deze resultaten waren zodanig dat gezocht werd naar een meer betrouwbare methode. Deze werd gevonden in het "multi-structure valence bond" formalisme. Het eerste artikel dat gebaseerd is op dit formalisme (berekeningen aan $He_2$) presenteert een test op de betrouwbaarheid en handelbaarheid van de methode. Het tweede artikel is een poging meer inzicht te verschaffen in de binding van een chemisch interessanter complex (het eteen dimer). In het derde valence bond artikel is geprobeerd een potentiaal voor $He-H_2$ van goede kwaliteit te berekenen. Een voornamde reden voor de keuze van het complex $He-H_2$ was dat hieraan experimenteel werk werd verricht op de afdeling atoom- en moleculenspectroscopie van deze universiteit, en dat de berekende potentiaal dus
direct aan het experiment getoetst kon worden.

Omdat de VB berekeningen London's theorie voor intermoleculaire krachten als leidraad hadden, worden de artikelen voorafgegaan door een presentatie van deze theorie in termen van niet-reduceerbare tensoroperatoren.
ACKNOWLEDGEMENTS

I thank Dr. M. Boon for many enlightening discussions about the theory described in the first part of this thesis and Prof. F.A. Matsen for his stimulating lectures on the same subject.

Many people have been of great help to the calculations reported on in the second part of this thesis. Among those not already properly thanked in the acknowledgements of the reprinted papers, I must especially mention Prof. D.B. Chesnut, who made my stay at Duke University pleasant and worthwhile, the staff of the computing center in Nijmegen, particularly Chris Meijer, who taught me how to operate the computer and was always ready to help when problems arose, and many students, especially Ton van Berkel and Petro Geurts, who collaborated on two of the papers reprinted in this work.

Finally I thank Jenny Wormer for the enormous task of typing all the parts of this thesis that are not in the form of reprinted articles, and Ine van Berkel and the offset department for typing the manuscripts of the papers reprinted in this work.

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CURRICULUM

De schrijver van dit proefschrift bezocht de Technische Hogeschool te Delft, Duke University te Durham N.C., V.S. (gedurende een jaar), en is sinds 15 september 1970 werkzaam aan het Instituut voor Theoretische Chemie van de Universiteit van Nijmegen.