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

Paul E. S. Wormer and Ad van der Avoird

Institute of Theoretical Chemistry, University of Nijmegen, The Netherlands
(Received 3 December 1974)

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.

I. 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-
peeling formalism in this respect, as it converges into
London’s theory for increasing intermolecular dis­
tances. 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.35–44

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 struc­
tures,” which are antisymmetric many-electron eigen­
fuctions of the spin operator $S^2$. Spin-free VB struc­
tures may conveniently be constructed by acting with a
Young operator $Y$ on simple orbital products.43 In this
paper, where we are concerned with the interaction be­
tween two molecules $A$ and $B$, the dimer VB struc­
tures are denoted by $Y(\phi_A^L\phi_B^A)$. Here $\phi_A^L$ and $\phi_B^A$ 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 simple products consisting of the same MO’s as con­
tained in $\phi_A^L$ and $\phi_B^A$. In practice, we apply
this latter procedure.

The monomer structures included in our calculations
are the ground states $\phi^A_0$ and $\phi^B_0$ and singly excited states
$\phi^A_i$ and $\phi^B_i$. We expect the dimer structure $Y(\phi^A_0\phi^B_0)$
to account for the interactions between the unpolarized
molecules, the structures $Y(\phi^A_0\phi^B_i)$ and $Y(\phi^A_i\phi^B_0)$ for the
mutual induction effects and the doubly excited struc­
tures $Y(\phi^A_i\phi^B_j)$ for dispersion forces. This is clarified by
the following discussion of the long range asymptotic
behaviour of the valence-bond results.

It may be shown46 that the contributions of the inter­
molecular permutations in $Y$ to the Hamiltonian and
overlap matrix elements start vanishing if the intermole­
cular distance $R$ is increased. The VB structures
$Y(\phi^A_i\phi^B_j)$ then become effectively equal to the
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 $\{|\phi^A_i|\}$ by a
linear transformation to $\{|\phi^A_i|\}$ so that

$$\langle \phi^A_i | H^A | \phi^A_j \rangle = \delta_{ij} E^A_i, \quad i = 0, 1, 2, \ldots$$  \hspace{1cm} (2)

and analogously on monomer $B$:

$$\langle \phi^B_i | H^B | \phi^B_j \rangle = \delta_{ij} E^B_j, \quad j = 0, 1, 2, \ldots$$  \hspace{1cm} (3)

Because of Brillouin’s theorem, also valid in a finite

LCAO model,47 the SCF ground state $\phi^A_0$ does not inter­
act with the singly excited structures $\phi^A_i$, $i \neq 0$, under
$H^A$, and therefore

$$\phi^A_0 \psi^A = \phi^A_0 \psi^A$$

and the same on $B$:

$$\phi^B_0 \psi^B = \phi^B_0 \psi^B$$

After this first diagonalization step, we have the matrix elements

$$\langle \phi^A_i \phi^B_j | H | \phi^A_k \phi^B_l \rangle = \delta_{il} \delta_{jk} (E^A_i + E^B_j)$$

$$\quad + \langle \phi^A_i \phi^B_j | V^{AB} | \phi^A_k \phi^B_l \rangle$$  \hspace{1cm} (4)

The second step, which actually calculates the VB ener­
gy by completing the diagonalization of $H$, has to anni­
hilate all the nondiagonal elements over $V^{AB}$. Assuming
that the matrix elements over this operator are small, we can use the following expansion48 for the lowest
eigenvalue of $H$:

$$E^{VB}_0 = E^{VB}_0 + E^{VB}_0 \langle \phi^A_0 \phi^B_0 | V^{AB} | \phi^A_0 \phi^B_0 \rangle$$

$$+ \sum_{i,j} \left| \langle \phi^A_i \phi^B_j | V^{AB} | \phi^A_0 \phi^B_0 \rangle \right|^2 + \text{higher order terms}.$$  \hspace{1cm} (5)

Because $\phi^A_0 \phi^B_0$ is identical to the ground state $\phi^A_0 \phi^B_0$, and
the excited states can be regarded as the eigenstates of
$H^{(1)} = H^A + H^B$ in the finite structure basis $\{|\phi^A_i|\}$, this
formula shows an explicit relation between perturbation
theory and the valence-bond energy, valid for large
intermolecular distances. We define for all distances

$$E^{(1)}_{VB} = \langle Y \phi^A_0 \phi^B_0 | H | Y \phi^A_0 \phi^B_0 \rangle,$$  \hspace{1cm} (6)

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

$$E^{(2)}_{VB} = E^{(1)}_{VB} - E^{(1)}_{VB},$$  \hspace{1cm} (7)

the energy lowering due to the inclusion of excited struc­
tures, and obtain expressions for the interaction ener­
gies,

$$\Delta E^{(1)}_{VB} = E^{(1)}_{VB} - E^{(1)}_{VB} - E^B_0,$$  \hspace{1cm} (8)

$$\Delta E^{(2)}_{VB} = E^{(2)}_{VB} - E^{(1)}_{VB},$$  \hspace{1cm} (9)

which go asymptotically over into the first and second
order perturbation energies. (The assumption that
higher-order terms are small is confirmed by our cal­
culations.) Note finally that these valence-bond expres­
sions take exchange 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, London16 and many workers
after him also introduced an approximation to the inter­
action operator $V^{AB}$ by expanding $V^{AB}$ in a multipole
series 54,55 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
still compare our results with those obtained in a
multipole approximation by virtue of the high symmetry

where $R$ is the intermolecular distance, $x^{(n)}_i y^{(n)}_j z^{(n)}_k$ is a component of a $2^n$-pole operator on $A$, $(n = n_1 + n_2 + n_3)$, and $x^{(n)}_i y^{(n)}_j z^{(n)}_k$ is a component of a $2^n$-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 $x^{(n)}_i y^{(n)}_j z^{(n)}_k$, and locally excited states on $B$ with the symmetry of $x^{(n)}_i y^{(n)}_j z^{(n)}_k$, 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 $1/R^2$ 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

$$H_{ij} = \langle Y \psi_i^A \psi_j^B | H | Y \psi_i^A \psi_j^B \rangle$$  \hspace{1cm} (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 $D_{3h}$, $n_1$, $n_2$, $n_3$

\begin{tabular}{|c|c|}
\hline
Component & Symbol \\
\hline
$x^{2n_1} y^{2n_2} z^{2n_3}$ & $A_{1g}$ \\
$x^{2n_1+1} y^{2n_2+1} z^{2n_3}$ & $B_{1u}$ \\
$x^{2n_1+1} y^{2n_2} z^{2n_3+1}$ & $B_{2g}$ \\
$x^{2n_1} y^{2n_2+1} z^{2n_3+1}$ & $B_{2u}$ \\
$x^{2n_1+1} y^{2n_2+1} z^{2n_3}$ & $A_d$ \\
$x^{2n_1+1} y^{2n_2} z^{2n_3}$ & $B_{1g}$ \\
$x^{2n_1} y^{2n_2} z^{2n_3}$ & $B_{3g}$ \\
\hline
\end{tabular}

### TABLE II. Effect of orthonormalization on second order energy.

<table>
<thead>
<tr>
<th>Distance$^a$</th>
<th>Nonorthogonal orbitals$^a$</th>
<th>Orthogonal orbitals$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>-337.10</td>
<td>-398.49</td>
</tr>
<tr>
<td>5.0</td>
<td>-166.73</td>
<td>-187.58</td>
</tr>
<tr>
<td>6.0</td>
<td>-71.57</td>
<td>-74.46</td>
</tr>
<tr>
<td>7.0</td>
<td>-28.13</td>
<td>-28.35</td>
</tr>
<tr>
<td>8.0</td>
<td>-11.62</td>
<td>-11.63</td>
</tr>
<tr>
<td>9.0</td>
<td>-2.64</td>
<td>-2.64</td>
</tr>
<tr>
<td>10.0</td>
<td>-0.49</td>
<td>-0.49</td>
</tr>
<tr>
<td>11.0</td>
<td>-0.13</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

$^a$Energy in $10^{-5}$ hartree.

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 re-
region of interest to us, we conclude that for the calculation
of van der Waals forces, in contrast to chemical bond-
ing, 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 or-
bitals are kept doubly occupied. We have decided on the
fully justified. In the actual calculation only the lowest
following orthonormalization procedure, which leaves
the intramolecular correlation energy.3 4  The effect
of van der Waals forces, in contrast to chemical bond-
ing, the use of orthogonalized monomer orbitals seems
must probably be ascribed to the admixture of ionic VB
unaltered in a series of related calculations (e.g., ex-
amples and sorting coefficients that do only depend on the
spin, the number of orbitals, and the VB structures to
ates and sorts coefficients that do only depend on the
symmetry). Still, this program is about 5 times slower
so that storage requirements are reduced by a factor of
2. 6 and run times by a factor of 4 (for cases without
movable, bound to the maximum number of structures.

III. COMPUTATIONAL ASPECTS

A. Computer programs

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

(i) the integral program of IBMOL-5,70 producing one
and two electron integrals over contracted Cartesian
Gaussian functions.28 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.71 implemented after this
work was finished;

(ii) the SCF program of IBMOL-5, which is essentially
the same as that of ALCHM72;

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

(iv) a transformation program73 yielding integrals
over MO's and based on an n4 algorithm; 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., ex-
ponent 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' al-
gorithm,63 published in ALGOL. 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:

\[
\langle \psi_f | \sum_{p=q} \frac{1}{|p_q|} | \psi_i \rangle \\
= \sum_{i} \sum_{j} \sum_{k} \sum_{l} C(I,J;i,j,k,l)(ij | kl).
\]  (12)

This matrix element is based on VB structures con-
structed from orthonormal orbitals. It is one of the strong
points of Reeves' algorithm that it does not put any con-
straints 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 restrict-
ed to a "canonical" order in i, j, k, l.75 The coefficients
\(C(I,J;i,j,k,l)\) permit the following factorization76:

\[
C(I,J;i,j,k,l) = C_1(I,J) C_2(I,J;i,j,k,l),
\]  (13)

where \(C_1(I,J)\) is independent of \(i,j,k,l\) and \(C_2(I,J;i,j,k,l)\) can take on only 11 different values.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 en-
suing processing on the \(C_2(I,J;i,j,k,l)\) alone. After
the construction of the \(H\) matrix is completed, the coeffi-
cients \(C_1(I,J)\) are retrieved to multiply each \(H\)-ma-
trix 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
\(I > J\), 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 Yoshimine77 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.78

(vi) The second part of the VB program constructs
the \(S\) and \(H\) matrix [Eq. (11)] and transforms these ma-
trices optionally to nonorthogonal orbitals by means of
a matrix \(T(t)\). We intend to give more details about the
actual construction of \(T(t)\) 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,79,80
demanding core space for one full matrix and a few col-
umns. At the moment this is the only, but easily re-
moveable, bound to the maximum number of structures.

We conclude by quoting a few representative figures,
all regarding double precision arithmetic on an IBM
S370/158 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>Coefficients</th>
<th>Exponents</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.026916</td>
<td>1087.10</td>
</tr>
<tr>
<td>0.197505</td>
<td>163.867</td>
</tr>
<tr>
<td>0.845777</td>
<td>37.4090</td>
</tr>
<tr>
<td>0.574338</td>
<td>10.5181</td>
</tr>
<tr>
<td>1.024212</td>
<td>3.32078</td>
</tr>
<tr>
<td>1.0</td>
<td>0.293436</td>
</tr>
<tr>
<td>0.212696</td>
<td>4.20169</td>
</tr>
<tr>
<td>0.878780</td>
<td>0.858491</td>
</tr>
<tr>
<td>1.0</td>
<td>0.202063</td>
</tr>
<tr>
<td>0.143689</td>
<td>6.4805</td>
</tr>
<tr>
<td>1.0</td>
<td>0.98104</td>
</tr>
<tr>
<td>1.0</td>
<td>0.21798</td>
</tr>
</tbody>
</table>

*aThis work.  
*bReferences 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, 3/2, 2) set on the carbons and a H(3/2) set on the hydrogens. See Table III. The hydrogen exponents taken from Ref. 81 and 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.83 In accordance with the findings of Moskowitz and co-workers,84 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. Quadrupole 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 26 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 earlier work,84 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 $\pi$-electron was consecutively promoted to the lowest orbital of each occurring symmetry: $b_3$, $b_2$, $a_1$, $a_2$, $b_1$, and $b_3$, 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 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>-77.85810</td>
</tr>
<tr>
<td>C(6, 3/2, 2), H(3/2)</td>
<td>-77.900063</td>
</tr>
<tr>
<td>C(6, 3), H(3)P</td>
<td>-77.901246</td>
</tr>
<tr>
<td>$s + p$ limit</td>
<td>-76.0062</td>
</tr>
<tr>
<td>Hartree–Fock limit</td>
<td>-78.0623</td>
</tr>
</tbody>
</table>

*aReference 84.  
*bThis work, atomic coordinates from Ref. 85.  
*cReference 86.  
*dReference 87.

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

<table>
<thead>
<tr>
<th>$Q_{xx}$</th>
<th>$Q_{yy}$</th>
<th>$Q_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1533</td>
<td>1.5875</td>
<td>-2.7408</td>
</tr>
<tr>
<td>Double zeta</td>
<td>1.4642</td>
<td>1.4982</td>
</tr>
<tr>
<td>Experimental</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

$Q_{xx}^a = \langle \rho^2 \rangle - (\rho^2)/2$.

*aThis work, coordinates of monomer A, Fig. 1.  
*bReference 88.  
*cReference 89.  
*dReference 90.

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>Symmetries</th>
<th>Energy (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$a_1$</td>
<td>-11.267616</td>
</tr>
<tr>
<td>2</td>
<td>$b_2$</td>
<td>-11.266116</td>
</tr>
<tr>
<td>3</td>
<td>$a_1$</td>
<td>-1.025231</td>
</tr>
<tr>
<td>4</td>
<td>$b_2$</td>
<td>-0.783838</td>
</tr>
<tr>
<td>5</td>
<td>$b_3$</td>
<td>-0.641625</td>
</tr>
<tr>
<td>6</td>
<td>$a_1$</td>
<td>-0.58206</td>
</tr>
<tr>
<td>7</td>
<td>$b_1$</td>
<td>-0.499021</td>
</tr>
<tr>
<td>8</td>
<td>$b_1$</td>
<td>-0.375118</td>
</tr>
<tr>
<td>9</td>
<td>$b_1$</td>
<td>-0.007255</td>
</tr>
<tr>
<td>10</td>
<td>$b_3$</td>
<td>-0.060831</td>
</tr>
<tr>
<td>11</td>
<td>$a_1$</td>
<td>0.082727</td>
</tr>
<tr>
<td>12</td>
<td>$b_2$</td>
<td>0.132136</td>
</tr>
<tr>
<td>13</td>
<td>$b_1$</td>
<td>0.225237</td>
</tr>
<tr>
<td>14</td>
<td>$b_3$</td>
<td>1.062311</td>
</tr>
</tbody>
</table>

*aPoint group $D_{2h}$.  
*bReference 84.
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 Is 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.1 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 VII.** Contributions of local excitations to the lowest multipole operators of certain symmetry.

<table>
<thead>
<tr>
<th>Dipole moment</th>
<th>Quadrupole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{1u}$</td>
<td>$A_y$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$B_{1u}$</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>$B_{2u}$</td>
</tr>
</tbody>
</table>

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

*Orbital numbers from Table VI.

---

**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>$\mu_x - \mu_y$</td>
<td>32</td>
<td>48</td>
</tr>
<tr>
<td>$\mu_y - \mu_z$</td>
<td>72</td>
<td>48</td>
</tr>
<tr>
<td>$\mu_z - \mu_x$</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>$\mu_x - Q_x + Q_x - \mu_y$</td>
<td>96</td>
<td>120</td>
</tr>
<tr>
<td>$\mu_y - Q_y + Q_y - \mu_z$</td>
<td>96</td>
<td>80</td>
</tr>
<tr>
<td>$\mu_z - Q_z + Q_z - \mu_x$</td>
<td>60</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>$Q_x - Q_x$</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>$Q_y - Q_y$</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>$Q_z - Q_z$</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>$Q_x - Q_y$</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</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.

(ii) Geometry II is the structure yielding the maximum electrostatic quadrupole-quadrupole attraction. [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, whereas in other work 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>$R$ (Bohr)</th>
<th>$\Delta E_{VB}^{(1)}$</th>
<th>$\Delta E_{VB}^{(2)}$</th>
<th>$\Delta E_{VB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>-1023.58</td>
<td>17081.01</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>-1056.85</td>
<td>3856.13</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>-161.26</td>
<td>891.31</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>-30.88</td>
<td>71.76</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>-94.71</td>
<td>58.70</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>-10.70</td>
<td>26.50</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>-5.97</td>
<td>16.99</td>
<td></td>
</tr>
<tr>
<td>11.0</td>
<td>-2.14</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>-0.53</td>
<td>-7.55</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>-2.14</td>
<td>-0.57</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1. Geometries of the ethylene dimer considered in this work.

FIG. 2. First order and total valence-bond interaction energies for Geometry I (Table IX).

FIG. 3. First order and total valence-bond interaction energies for Geometry II (Table IX).
TABLE X. Decomposition first order energy into electrostatic quadrupole-quadrupole: \( \Delta E_{Q-Q}^{(1)} \); quadrupole-hexadecupole: \( \Delta E_{Q-H}^{(1)} \); hexadecupole-hexadecupole: \( \Delta E_{H-H}^{(1)} \) interaction energy and short range exchange and penetration effects. Units: \( 10^{-5} \) hartree.

| R (bohr) | \( \Delta E_{Q-Q}^{(1)} \) | \( \Delta E_{Q-H}^{(1)} \) | \( \Delta E_{H-H}^{(1)} \) | Exchange + penetration | \( \Delta E_{Q-Q}^{(1)} \) | \( \Delta E_{Q-H}^{(1)} \) | \( \Delta E_{H-H}^{(1)} \) | Exchange + penetration |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 4.0      | 4407.69         | -10312.75       | 11843.05        | 12166.60        | -2604.47        | 6198.12         | -5030.01        | ...             | ...             | ...             | ...             |
| 5.0      | 1444.31         | -2162.74        | 1589.55         | 3374.69         | -853.43         | 1299.84         | -675.12         | ...             | ...             | ...             | ...             |
| 6.0      | 580.44          | -603.57         | 306.06          | 767.64          | -342.97         | 362.76          | -130.84         | 4918.51         | ...             | ...             | 932.27          |
| 7.0      | 268.55          | -205.17         | 76.93           | 145.24          | -158.68         | 123.31          | -32.68          | 19.28           | ...             | ...             | ...             |
| 8.0      | 137.74          | -80.57          | 23.12           | 22.34           | -81.39          | 48.42           | -9.82           | 147.50          | ...             | ...             | ...             |
| 9.0      | 76.44           | -35.33          | 8.01            | ...             | -45.16          | 21.23           | -3.40           | 19.28           | ...             | ...             | ...             |
| 10.0     | 45.13           | -16.89          | 3.10            | 1.33            | -26.67          | 10.15           | -1.32           | 2.40            | ...             | ...             | ...             |
| 11.0     | 28.03           | -8.67           | 1.32            | ...             | -16.56          | 5.21            | -0.56           | 1.79            | ...             | ...             | ...             |
| 12.0     | 12.16           | -2.69           | 0.29            | 0.16            | -7.18           | 1.62            | -0.12           | 0.15            | ...             | ...             | ...             |
| 13.0     | 4.30            | -0.63           | 0.05            | 0.02            | -2.54           | 0.38            | -0.02           | 0.04            | ...             | ...             | ...             |

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-\( \zeta \) quality. We employed these for the hexadecupole-quadrupole interaction \( \Delta E_{Q-H}^{(1)} \) and hexadecupole-hexadecupole interaction \( \Delta E_{H-H}^{(1)} \). Invoking Rose's formula, 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 wavefunction 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 XI. Decomposition of second order energy into components of dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole dispersion and permanent quadrupole-induced dipole induction. Energy in $10^{-5}$ hartree, $96$ distance in bohr. $96$

<table>
<thead>
<tr>
<th>R</th>
<th>x-y</th>
<th>y-z</th>
<th>z-x</th>
<th>$r^2$</th>
<th>y-zy</th>
<th>x-xz</th>
<th>$r^2$</th>
<th>xy-xy</th>
<th>xz-xz</th>
<th>yz-yz</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>-0.20,31</td>
<td>-469.59</td>
<td>-95.64</td>
<td>-47.05</td>
<td>-125.09</td>
<td>-71.91</td>
<td>-165.76</td>
<td>-2.32</td>
<td>-14.21</td>
<td>-168.92</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>-0.30,33</td>
<td>-225.82</td>
<td>-225.43</td>
<td>-61.20</td>
<td>-5.83</td>
<td>-16.12</td>
<td>-5.29</td>
<td>-6.63</td>
<td>-4.72</td>
<td>-9.80</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>-2.34,36</td>
<td>-46.31</td>
<td>-10.64</td>
<td>-2.96</td>
<td>-6.27</td>
<td>-1.92</td>
<td>-0.58</td>
<td>-0.06</td>
<td>-0.38</td>
<td>-1.63</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>-1.20,38</td>
<td>-18,29</td>
<td>-5.68</td>
<td>-1.30</td>
<td>-2.33</td>
<td>-0.69</td>
<td>-0.21</td>
<td>-0.02</td>
<td>-0.12</td>
<td>-0.69</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>-0.37,48</td>
<td>-8.48</td>
<td>-1.87</td>
<td>-0.29</td>
<td>-0.63</td>
<td>-0.10</td>
<td>-0.03</td>
<td>-0.00</td>
<td>-0.01</td>
<td>-0.15</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>-0.09,47</td>
<td>-1.05</td>
<td>-0.47</td>
<td>-0.04</td>
<td>-0.06</td>
<td>-0.01</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.02</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>-0.02,47</td>
<td>-0.30</td>
<td>-0.15</td>
<td>-0.00</td>
<td>-0.01</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td></td>
</tr>
</tbody>
</table>

Geometry I

<table>
<thead>
<tr>
<th>R</th>
<th>x-y</th>
<th>y-z</th>
<th>z-x</th>
<th>$r^2$</th>
<th>y-zy</th>
<th>x-xz</th>
<th>$r^2$</th>
<th>xy-xy</th>
<th>xz-xz</th>
<th>yz-yz</th>
<th>Induction</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>-0.28,15</td>
<td>-32.62</td>
<td>-56.00</td>
<td>-30.16</td>
<td>-21.91</td>
<td>-32.45</td>
<td>-5.09</td>
<td>-0.44</td>
<td>-3.81</td>
<td>-2.73</td>
<td>-24.36</td>
</tr>
<tr>
<td>7.0</td>
<td>-0.15,18</td>
<td>-13.03</td>
<td>-27.12</td>
<td>-12.53</td>
<td>-7.70</td>
<td>-14.57</td>
<td>-1.29</td>
<td>-0.14</td>
<td>-1.60</td>
<td>-0.25</td>
<td>-2.64</td>
</tr>
<tr>
<td>8.0</td>
<td>-0.81,26</td>
<td>-6.13</td>
<td>-5.50</td>
<td>-2.60</td>
<td>-6.19</td>
<td>-0.38</td>
<td>-0.04</td>
<td>-0.01</td>
<td>-0.25</td>
<td>-3.93</td>
<td></td>
</tr>
<tr>
<td>9.0</td>
<td>-0.49,33</td>
<td>-2.33</td>
<td>-6.64</td>
<td>-2.48</td>
<td>-0.94</td>
<td>-0.14</td>
<td>-0.20</td>
<td>-0.38</td>
<td>-0.18</td>
<td>-0.07</td>
<td>-1.74</td>
</tr>
<tr>
<td>10.0</td>
<td>-0.37,15</td>
<td>-1.15</td>
<td>-3.55</td>
<td>-1.18</td>
<td>-0.39</td>
<td>-1.26</td>
<td>-0.16</td>
<td>-0.01</td>
<td>-0.07</td>
<td>-0.03</td>
<td>-0.82</td>
</tr>
<tr>
<td>11.0</td>
<td>-1.50,36</td>
<td>-2.28</td>
<td>-0.58</td>
<td>-0.15</td>
<td>-0.62</td>
<td>-0.36</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
</tr>
<tr>
<td>13.0</td>
<td>-0.59,20</td>
<td>-0.72</td>
<td>-0.17</td>
<td>-0.04</td>
<td>-0.17</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
</tr>
<tr>
<td>16.0</td>
<td>-0.19,06</td>
<td>-0.21</td>
<td>-0.04</td>
<td>-0.01</td>
<td>-0.04</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
<td>-0.00</td>
</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 $\pi(\pi^*)$ and $\pi(\pi^*)$ 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.

FIG. 6. Relative contributions to second order energy for Geometry I. Absolute values given in Table XI.
P. E. S. Wormer and A. van der Avoird: van der Waals interactions between $\pi$ systems

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 5 bohr, with even $\Delta E_{QQ}^{(1)} < \Delta E_{QQ}^{(1)}$ 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. 92-95 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 {	extit{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 $y-y$ 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 ($R^{-8}$) 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
P. E. S. Wormer and A. van der Avoird: van der Waals interactions between π systems

FIG. 9. Interaction energies from ab initio LCAO–SCF 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 suggests 3.8 bohr for this radius, a number which is also in accordance with the C...C and C...H contact distances proposed by Kitaigorodski. 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, and it has been investigated by means of extended Hückel calculations.

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, or \( \epsilon = 65.0 \times 10^{-5} \) hartree, \( \sigma = 8.0 \) bohr. 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 on He\(_2\) 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. One must realize, however, that the 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, who call the difference "plausible" between viscosity values of 410 °K and 208 °K found for \( n \)-butane by themselves and Hirschfelder et al., respectively. This underlines the unreliability of the few experimental data available to gauge the parametrization of semiempirical 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 a priori prejudices about their importance.

D. Interactions between stacked π systems

The repulsive interaction calculated between two parallel ethylene molecules may seem in contradiction to the opinion 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 \( \pi \) electrons to the dispersion energy is observed, and we may therefore, not without justification, speculate that in the case of large, very polarizable \( \pi \) 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 \( \pi - \pi^* \) excitations is only found for parallel \( \pi \) 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 \( \gamma - \gamma \) dispersion component, contribute slightly to second order energy. The most noticeable among these 11 functions is the one representing the coupling of the \( T(\pi^*) \) 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 \( D_{nm} \). The off-diagonal \( H \)-matrix elements connecting blocks of different local symmetry contain only terms arising from the interaction operator \( V^{AB} \). 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 \( V^{AB} \) 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 \textit{ab initio} results fall in line with the VB predictions in this respect. A similar disagreement of CNDO with \textit{ab initio} results fall in line with the VB predictions in this respect. A similar disagreement of CNDO with \textit{ab initio} SCF results for the \( (HCN)_2 \) 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 \textit{ab initio} results on the other hand, seem surprisingly good, with a \( \sigma \) value of 8.0 bohr and \( \epsilon = 57,6 \times 10^{-5} \) 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 expansion gave an energy improvement of \( 56.09 \times 10^{-5} \) 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 \textit{ab initio} SCF calculations on \( H_2 \). 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

We would like to thank Dr. C. Moser for his hospitality at CECAM, where part of the programs have been developed, A. van Berkel for his help in writing the program for nonorthogonal orbitals, and Dr. F. B. van Duijneveldt and Dr. M. van Hemert for valuable discussions.

*Supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).


\(^3\) H. de Voe and I. Tinoco, Jr., J. Mol. Biol. 4, 500 (1962).


Trans. II 1, 115 (1973).


P. Claverie, in Ref. 1.


H. Margenau and N. R. Kestner, Theory of Intermolecular Forces (Pergamon, Oxford, 1969); Appendix A.


E. Clementi, Proc. Natl. Acad. Sci. USA 69, 2942 (1972); we thank Dr. E. Clementi and Dr. M. van Hemert for making available the ibmol –5a program.


The authors thank Dr. M. van Hemert at Leiden University for his four-index transformation program.


Recently, a description of a computer program written by G. H. F. Diercksen and B. T. Sutcliffe [Theor. Chim. Acta 34, 105 (1974)] appeared, which incorporates Reeves' algorithm53 with a sorting procedure similar to that of Yoshimine.74


It is often found stated in the literature (e.g., Ref. 31) that...
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 \( \langle \phi \phi^\dagger \phi \phi^\dagger \phi \rangle \). Still, the three-body forces are expected to be much smaller than the pair forces.

96. 1 hartree = 27.21 eV = 627.49 kcal/mol = 2.625 \times 10^6 J/mol,
1 bohr = 0.529167 \times 10^{-10} m. Quadrupole units: 1 a.u. = 1.344 \times 10^{-30} esu cm^2.
97. CND0 Molecular Orbital Program by P. A. Dobosh, distributed by Q. C. P. E., Indiana University, Bloomington, IN.