NOTE ON

AB INITIO VALENCE BOND CALCULATIONS
OF THE VAN DER WAALS INTERACTIONS
BETWEEN TWO ETHYLENE MOLECULES

by

P. E. S. WORMER and A. VAN DER AVOIRD
Institute for Theoretical Chemistry
University of Nijmegen. The Netherlands

SUMMARY

Until about 1970 the calculation of Van der Waals forces between molecules at intermediate distances, i.e. the region where exchange becomes non-negligible, had to be carried out in two separate parts. The long range attractive forces, induction and dispersion, were usually calculated by second order perturbation theory, applied in a more or less empirical manner, but always neglecting exchange and penetration effects. The short range exchange interactions were estimated semi-empirically or calculated by a Hartree-Fock treatment of the « supermolecule », which besides exchange also includes electrostatic and polarization forces, but no dispersion interactions.

A single consistent theory for the intermediate range can be obtained either by extending the perturbation approach to include exchange or by adding those correlation terms to the Hartree-Fock interaction energy that account for the dispersion forces. For somewhat larger systems the latter approach seems the more practical. It appeared from calculations on He₂ by Schaefer, McLaughlin, Harris, Alder and by Bertoncini, Wahl (who were the first to perform a single ab initio calculation of the complete Van der Waals well) that localized orbitals must be used in order to separate the intermolecular correlations, which are the main contributions
to dispersion forces, from the much larger intramolecular correlation effects. We have chosen the multistructure Valence Bond method, because it works with orbitals which are completely localized on the separate molecules.

The ground state VB structure consists of a product of ground state Hartree-Fock wave functions of the separate (closed-shell) molecules, antisymmetrized with respect to all intermolecular exchange permutations. The expectation value of the total Hamiltonian minus the expectation values of the separate molecular Hamiltonians over their ground state wave functions, includes (first order) electrostatic and exchange forces between the non-polarized molecules. Induction and dispersion effects are taken into account by admixture of excited structures. Just as in second order perturbation theory we account for polarization of a given molecule A by including single excitations on A, for dispersion forces between two molecules A and B by allowing simultaneous excitations on A and B. The difference with the perturbation treatment is that we antisymmetrize and spin-project the product wave functions, in order to take also higher order exchange effects into account, and determine the mixing coefficients of VB structures variationally. It can be shown that the Valence Bond interaction energy converges to the usual first and second order energy for increasing intermolecular distances.

Comparison of some test calculations on \( \text{He}_2 \) with the more extensive calculations on this system show that with a very small number of VB structures a good approximation to the Van der Waals well can be obtained when the excited orbitals are suitably chosen.

We have applied this method to the calculation of Van der Waals forces between two ethylene molecules in particular to obtain some information about interactions between \( \pi \)-systems which have been subject to many semi-empirical studies because of their practical importance in biopolymers and molecular crystals. The results for two conformations, one with parallel \( \text{C}_2\text{H}_4 \) planes and one with perpendicular planes, for a range of intermolecular distances from 4 to 16\( \text{\AA} \), having been calculated by including up to 600 VB structures, were presented in the lecture. The interactions consist of electrostatic, polarization, dispersion and exchange forces between the \( \sigma \) and \( \pi \) electrons of the ethylene molecules. The relative import-
ance of these contributions and their respective multipole expansions was discussed.

Three of the most important conclusions are:

1) the first and second order interactions are comparable in magnitude, the latter, which are always attractive, being much more isotropic than the first, which change sign upon rotation.

2) if one would wish to make multipole expansions one should, both for first and second order interaction energies, include at least the terms up to $R^{-10}$ in the region considered.

3) exchange effects become non-negligible at $12 a_0$ approximately, the Van der Waals minimum distance being $9.4 a_0$.

The formalism and the computational procedure is described in more detail in Molecular Physics (in press) and in J. Chem. Phys., April 15 (1975), where also the numerical results and their analysis can be found.