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CONTRIBUTIONS TO ATOMIC AND MOLECULAR INTERACTIONS

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PREVIEW

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**Contributions to Atomic and Molecular  
Interactions**

by

**Jackie Ray Collins, Ph.D.**

**A DISSERTATION**

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The Graduate College in the University of Nebraska  
In Partial Fulfillment of Requirements  
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**Under the Supervision of Professor Gordon A Gallup**

**Lincoln, Nebraska**

**August, 1986**

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**BY**

Jackie Ray Collins

**APPROVED**

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Contributions to Atomic and Molecular  
Interactions

Jackie Ray Collins, Ph.D.

University of Nebraska, 1986

Advisor: Gordon A. Gallup

This dissertation examines several molecular systems by the *ab initio* multiconfigurational valence bond (MCVB) method. Four major topics are addressed: 1) contributions to intermolecular forces, 2) the nature of basis set superposition error (BSSE) and a comparison of two methods to estimate its magnitude, 3) the photoelectron spectrum of cyclopropane and its relationship to recent mass spectral experiments, 4) a generalized superposition of resonance structures (GSRS) method for ranking the importance of different resonance structures in conjugated pi systems in model molecules.

The interaction energies of  $\text{He}_2$  and  $\text{Be}_n$  were calculated and partitioned into dispersion, induction, charge transfer, and electrostatic plus Pauli repulsion components. The general conclusions drawn from these studies suggest that charge transfer effects may be smaller than previously thought.

The estimation of BSSE is examined by using both full functional and virtual counterpoise methods. The results of each method are compared to "frozen core" calculations.

It was found that the full counterpoise method overcorrects in some cases whereas the virtual did not.

The first two electronic states of the cyclopropane radical cation were calculated and the potential energy surface for each characterized. The origin of the double hump in the first peak in the photoelectron spectrum is explained and the energy surfaces are used to rationalize observations from mass spectral studies such as the randomization of the three carbon atoms upon ionization and the propene-like behavior upon increasing internal energy of the radical cation.

The theoretical basis for traditional resonance theory of organic molecules is investigated by calculating the separate contributions of resonance structures to the total energy of the pi system of several model systems within an *ab initio* framework. Six molecules were calculated benzene, fulvene, 3,4-dimethylenecyclobutene, and trimethylenecyclopropane, butadiene, and hexatriene. The results suggest that the traditional Kekulé structures are indeed the most important, with respect to energy, in this model.

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## INTRODUCTION

This dissertation is partitioned in to four major projects, chapters 1-4, in the area of atomic and molecular interactions. We have used the multiconfigurational valence bond method developed in this laboratory by Professor G.A. Gallup and coworkers in all of the studies presented here. The major goal behind each of these investigations is the use of theory to gain physical insight into the mechanism of atomic and molecular interactions. Each chapter presents material which is essentially self-contained and separate from the rest. We give a brief synopsis of each chapter below.

Chapter 1 is concerned with the physical effects important in describing intermolecular forces and specifically examines the  $\text{He}_2$ ,  $\text{Be}_2$ ,  $\text{Be}_3$ , and  $\text{Be}_4$  systems. It is suggested that charge transfer effects may not be as large as previously believed in these systems and the role of inter-atomic vs intra-atomic correlation is discussed.

Chapter 2 focuses on the problem of basis set superposition error (BSSE), briefly discussed in chapter 1, in greater detail. We investigated the full functional counterpoise and virtual counterpoise methods, currently used by theorists to correct for the

spurious lowering of the energy due to BSSE, to determine which one more correctly compensates in the cases of  $\text{He}_2$ ,  $\text{H}_2\text{-H}_2$ , and  $(\text{H}_2\text{O})_2$ . We conclude that the full counterpoise method overcorrects in some cases whereas the virtual did not.

Chapter 3 presents the results of calculations on the cyclopropane radical cation. We calculated the first two  $A'$  states of the system and use the potential energy surfaces to explain the first peak in the photoelectron spectrum of the parent molecule and the observations of several mass spectral experiments.

Chapter 4 discusses a generalized superposition of resonance structures formalism as applied via *ab initio* methods to investigate the theoretical basis for resonance theory. In this work we calculated the total energies of benzene, fulvene, 3,4-dimethylene-cyclobutene, trimethylenecyclopropane, hexatriene, and butadiene. The energies are discussed in light of the contributions of the various classes of resonance structures included in the wavefunction. It is suggested that this method may have some promise but that several difficulties must be addressed before it can become a generally used procedure.



## Chapter I

### Determination of Contributions to Intermolecular Forces

In this chapter we investigate the interaction energy due to intermolecular forces by means of the multiconfigurational valence bond (MCVB) method. We first outline some of the theory and background needed to fully appreciate the calculational procedure. We then apply the method to the  $\text{He}_2$  system and also report preliminary calculations on  $\text{Be}_2$ ,  $\text{Be}_3$ , and  $\text{Be}_4$ .

#### Theory:

The calculation of interaction energies due to intermolecular forces is concerned with finding very small energy differences as compared to the total energy of the system. This fact suggests that small errors in the overall energies of the system could dramatically effect the results obtained for the interactions. One of the major problems in calculating interaction energies is a phenomenon known as basis set superposition error (BSSE). BSSE is a result of using

incomplete basis sets, and hence, is possible in all practical calculations. There are two major strategies for reducing the effects of BSSE: 1) the use of nearly complete basis sets, 2) the use of the counterpoise correction. For large systems strategem 1 is not practical at this time. Strategem 2 has been used quite extensively in the area of intermolecular forces and is discussed further in chapter III.

Several methods are presently used to calculate intermolecular forces.<sup>1-18,38</sup> These may be classified in three ways, 1) perturbation theory, 2) orthogonal orbital techniques, and 3) non-orthogonal configuration interaction techniques. We will not cover perturbation theory in this chapter since its application in cases where exchange is important is still very difficult.

The orthogonal methods currently in use include the supermolecule SCF procedure, with dispersion added semi-empirically, and molecular orbital configuration interaction (MOCI) techniques. The supermolecule SCF procedure is described in chapter III. The dispersion contribution is then calculated separately by semi-empirical methods.<sup>38</sup> Most of the MOCI calculations concerning intermolecular forces "localize" the orbitals,<sup>11-14</sup> still keeping them orthogonal, before performing the CI in an attempt to increase the inter-

pretability of the wavefunction and gain a deeper understanding of the nature of intermolecular forces.

Perhaps the most successful of these is the interacting correlated fragments (ICF) method due to Liu and coworkers.<sup>39</sup> In the ICF procedure the MOs are "localized" by taking linear combinations of the "g" and "u" symmetry orbitals of a homonuclear system. The configuration selection scheme is then based on these orbitals.

In our calculations we have used the MCVB<sup>40</sup> method to calculate the interaction energies of van der Waals systems. This method is based on non-orthogonal orbitals which are truly localized at each center. The fact that the orbitals are truly localized and do not change with geometry allows for a "systematic cancellation of errors" in the overall energy expression.<sup>37</sup> Localized orbitals also allow us to directly equate the configurations in the wavefunction to various physical effects.

The "systematic cancellation of errors" can be shown from a variation-perturbation analysis based on the VB method.<sup>37</sup> The result is that the interaction energy of the system does not depend on the accuracy of the asymptotic value.

The fact that the configurations can be directly

equated to physical effects is extremely important in choosing configurations to include in the trial wavefunction and in interpreting the importance of each. We will briefly describe the form of the wavefunction below.

Let us consider two atoms, A and B, which form a van der Waals molecule AB. We can represent the orbital set on A as  $\{u_a^1, u_a^2, \dots, u_a^n, v_a^1, v_a^2, \dots, v_a^m\}$ , and a similar expression for B, where  $u_a^i$  is an occupied orbital and  $v_a^i$  is unoccupied. We can write the principal ground state configuration for weakly interacting systems as

$$\phi_0 = A[u_a^1, u_a^2, \dots, u_a^n, u_b^1, u_b^2, \dots, u_b^m],$$

where  $A$  is the antisymmetrizer. For simplicity we assume that each atom has a closed shell ground state. In terms of tableau functions we write  $\phi_0$  as

$$\phi_0 = \begin{array}{cc} u_a^1 & u_a^1 \\ u_a^2 & u_a^2 \\ \dots & \dots \\ u_a^n & u_a^n \\ u_b^1 & u_b^1 \\ u_b^2 & u_b^2 \\ \dots & \dots \\ u_b^m & u_b^m \end{array}$$

This function contains both the electrostatic and exchange repulsion effects. To include induction/polarization (IP) we would excite one of the electrons on either A or B to one of the unoccupied orbitals on that same atom. For example, we write the tableaux for an excitation of an electron in orbital N on A into the first unoccupied orbital on A as,

$$\phi_{IP} = \begin{array}{cc} u_a^1 & u_a^1 \\ u_a^2 & u_a^2 \\ \dots & \dots \\ u_a^{n-1} & u_a^{n-1} \\ u_b^1 & u_b^1 \\ u_b^2 & u_b^2 \\ \dots & \dots \\ u_b^m & u_b^m \\ u_b^n & v_b^1 \end{array}$$

For charge transfer we could similarly write functions where an electron has been transferred from A to B to give an ionic configuration  $A^+B^-$  for example. The dispersion and intra-atomic correlation are formed from excitations of two electrons. Each atom would have one excited electron in the case of dispersion and both would be from the same atom for intra-atomic correlation. We evaluate the importance of each type of configurations by including them into our trial wavefunction and calculating the energy. The difference between the energies obtained with and without these configurations corresponds to the importance of the physical effect. That is, the greater the effect on the energy the greater the importance.

## 1) He-He Interaction

### Introduction:

The calculation of potential energy curves in the study of intermolecular forces between weakly bound systems such as  $\text{He}_2$  is necessary for the prediction of the properties of non-ideal gases, liquids, and solids, including molecular complexes. From these calculated energy curves we need accurate interaction energies and the ability to gain insight into the physical nature of intermolecular interactions, especially the contribution from charge transfer. In this section we present multi-configurational valence bond (MCVB) calculations on the  $\text{He}_2$  potential energy curve, the simplest closed shell, ground state, non-bonding system. We have determined the various contributions to the total interaction energy of the major physical effects.

The MCVB method is well suited for accurately calculating small interaction energies and determining the contributions of the various type of interactions involved. The MCVB method is a non-orthogonal configuration interaction (CI) method. This allows the orbitals in the calculation to be localized and provides

a clear representation of the physical picture of these interactions. Using the MCVB method we can use large basis sets and large wavefunctions but keep the simple interpretation due to the localized orbitals mentioned earlier.

The first calculations of the He-He potential were done by Slater and Kirkwood<sup>1</sup>. Later, Hirschfelder, Curtiss, and Bird<sup>2</sup> made corrections to the earlier calculations, and subsequent work until 1970 is reviewed by Margenau and Kestner<sup>3</sup>. Recent studies have used either the perturbation approach<sup>4-10</sup> or the completely variational configuration interaction (CI) approach<sup>11-18</sup>. Most of the variational calculations are based on orthogonal orbitals. These previous calculations give interaction energies in good agreement with the experimental value of 34uH (10.74K)<sup>19</sup>.

Previous valence bond (VB) calculations of the He<sub>2</sub> potential energy curve have been given by van der Avoird and coworkers<sup>20,21</sup> and Simonetta and coworkers<sup>22</sup>. These studies discuss the problems associated with basis set superposition error (BSSE) and attempt to solve this problem by eliminating the functions in their CI which give rise to BSSE. This approach has the flaw that, although the removal of the suspect functions eliminates BSSE, it also eliminates charge transfer (CT). We refer