

EXCHANGE KINETIC ENERGY, CONTRAGRADIENCE,  
AND CHEMICAL BINDING \*

C. WOODROW WILSON JR. \*\* and WILLIAM A. GODDARD III\*\*\*

*Arthur Amos Noyes Laboratory of Chemical Physics †,  
California Institute of Technology, Pasadena, California 91109, USA*

Received 13 January 1970

The energy components of the G1 wavefunction for H<sub>2</sub> are carefully analyzed. It is found that the binding is dominated by the exchange part of the kinetic energy and that this term is dominant because of the contragradience of the orbitals in the bond region.

## 1. INTRODUCTION

It is now possible to carry out reliable *ab initio* calculations of the stability and geometry of many molecules. Hence from determining that the total energy increases or decreases as two atoms approach, we may find whether the resulting molecule will be stable or unstable; however, an examination of the total energy does not necessarily tell us *why* this particular system is bound or unbound. Similarly from an examination of the energy surface for rotation, it is clear that the staggered geometry is preferred in C<sub>2</sub>H<sub>6</sub> but this tells us little about *why* the staggered conformer is stable over the eclipsed one. Instead of looking at the total energy we would prefer to isolate a term which consistently dominates the stability and geometry of the molecule.

After finding the quantity responsible for binding and geometry, we would want to relate it to the orbitals of the atomic or molecular entities of which the system is composed. This is probably necessary if we are to be able to build up the sort of understanding in which we can make useful predictions about systems on which we have *not* carried out calculations. For this reason the basic wavefunctions which we analyze should probably allow an independent particle interpretation in terms of one-particle spatial or-

bitals [1]. But in order to discuss chemical binding, it is necessary to pull the molecules apart and hence it is necessary that the calculated wavefunctions correctly dissociate to the separated atoms (or separated molecules) limit. In addition we should require that the total wavefunction have the correct spin symmetry. This eliminates the use of Hartree-Fock orbitals [1]. We will use wavefunctions based upon the G1 method [1] since they satisfy all of the above conditions. We should note that the G1 wavefunctions cannot account for the instantaneous correlations responsible for van der Waals forces: hence with this method He<sub>2</sub> is considered as unstable. That is, we will be examining what might be called chemical forces and which result in strong chemical bonds rather than the van der Waals forces and weak van der Waals bonds.

In the following we will carefully analyze the G1 wavefunction for H<sub>2</sub>, isolating the quantity of interest and discussing why it is so important. The conclusions obtained here are consistent with those from the study of many larger systems, the results of which will be presented in a full length paper elsewhere [2].

## 2. THE WAVEFUNCTIONS

The G1 wavefunction for H<sub>2</sub> has just the simple form [1]

$$(\phi_a \phi_b + \phi_b \phi_a)(\alpha\beta - \beta\alpha), \quad (1)$$

where the  $\phi_a$  and  $\phi_b$  are the best possible functions (for each internuclear separation  $R$ ). Two

\* Partially supported by grants (GP-6965 and GP-15423) from the National Science Foundation.

\*\* National Science Foundation Trainee.

\*\*\* Alfred P. Sloan Research Fellow.

† Contribution No. 3994.

cases will interest us here: the G1 wavefunction (with the orbitals self-consistently optimized for each  $R$ ) and the case where the orbitals are optimized at  $R = \infty$ , frozen, and then brought to the  $R$  we are considering (i.e., for  $H_2$  this is just the Heitler-London wavefunction). We will refer to these two cases as the SCF and frozen wavefunctions, respectively.

If instead of the spatial part of (1), we use the classical or Hartree wavefunction

$$\phi_a(1)\phi_b(2), \quad (2)$$

the energy becomes

$$E^{Cl} = T^{Cl} + V^{Cl}, \quad (3)$$

where

$$T^{Cl} = \langle a | -\frac{1}{2}\nabla^2 | a \rangle + \langle b | -\frac{1}{2}\nabla^2 | b \rangle, \quad (4)$$

$$V^{Cl} = \langle a | v^n | a \rangle + \langle b | v^n | b \rangle + J_{ab} - 1/R, \quad (5)$$

$v^n$  is the Coulomb potential due to the nuclei, and  $J_{ab}$  is the usual Coulomb interaction energy between electrons in orbitals  $a$  and  $b$ . (Note that for simplicity we often denote  $\phi_a$  by just  $a$ , as in (4) and (5).) The energy of the G1 wavefunction is just

$$\begin{aligned} E &= \langle ab | \mathcal{H} | ab + ba \rangle / \langle ab | ab + ba \rangle \\ &= [\langle a | h | a \rangle + \langle b | h | b \rangle + 2\langle a | h | b \rangle \langle b | a \rangle \\ &\quad + J_{ab} + K_{ab}] / [1 + \langle a | b \rangle^2] = E^{Cl} + E^X, \end{aligned} \quad (6)$$

where  $E^{Cl}$  is defined by (3), (4), and (5),

$$E^X \equiv EG1 - E^{Cl} = T^X + V^{nX} + v^{ex}; \quad (7)$$

$$\begin{aligned} T^X &\equiv T - T^{Cl} = \{2\langle a | -\frac{1}{2}\nabla^2 | b \rangle \langle a | b \rangle \\ &\quad - \langle a | b \rangle^2 [\langle a | -\frac{1}{2}\nabla^2 | a \rangle + \langle b | -\frac{1}{2}\nabla^2 | b \rangle]\} / [1 + \langle a | b \rangle^2], \end{aligned} \quad (8)$$

$$v^{ex} \equiv v^{ee} - J_{ab} = [K_{ab} - \langle a | b \rangle^2 J_{ab}] / [1 + \langle a | b \rangle^2], \quad (9)$$

and  $V^{nX}$  is the same as  $T^X$  except that the  $-\frac{1}{2}\nabla^2$  operator is replaced by  $v^n$ . Here we call  $E^X$  the exchange energy since it results from having exchange terms in the wavefunction. Similarly we refer to  $T^X$  as the *exchange kinetic energy*.

### 3. THE ENERGY ANALYSIS

As we bring two atoms together to form a stable molecule the kinetic energy,  $T$ , decreases at first and then increases until at  $R_e$   $T > T_\infty$ . On the other hand the total potential energy,  $V$ ,

increases at first and then decreases until at  $R_e$   $V > V_\infty$  (for example, see ref. [3], p. 56). Since the bonding should increase monotonically as  $R$  decreases, it would seem that neither  $T$  nor  $V$  alone could yield a direct criterion for determining or predicting stability of the molecule. That is, a single calculation at large  $R$  would generally show a negative  $E - E_\infty$  if the system is to be stable, but it may show positive or negative  $V - V_\infty$  and  $T - T_\infty$  depending on the particular value of  $R$ .

One might consider partitioning  $V$  into the nuclear-nuclear energy ( $V^{nn}$ ), the electron-nuclear energy ( $V^{en}$ ), and the electron-electron energy ( $V^{ee}$ ),

$$V = V^{nn} + V^{en} + V^{ee}. \quad (10)$$

Each of the quantities varies monotonically; however, their variations are essentially the same for both bound and unbound molecules. Thus this partition is not useful for our purposes.

In fig. 1 we show  $E^{Cl}$  and  $E^X$  for  $H_2$  as a function of  $R^*$ . We see that the change in  $E^X$  dominates that in  $E^{Cl}$ , with  $\Delta E^X$  accounting for about

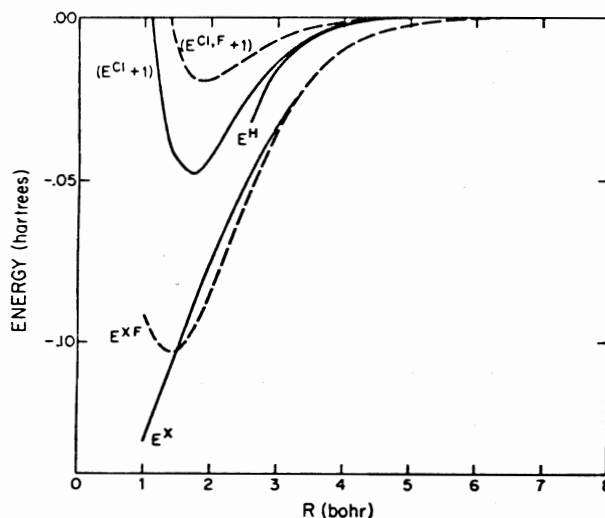


Fig. 1. Partition of the G1 energy for  $H_2$  into classical ( $E^{Cl}$ ) and exchange ( $E^X$ ) contributions. At larger  $R$ , the Hartree energy  $E^H$  is given for comparison to  $E^{Cl}$ . Here  $E^X, F$  and  $E^{Cl, F}$  refer to the values for the frozen wavefunction.

\* The energies reported here are for basis set consisting of optimized 1s Slater orbitals on each center. A study of the changes in  $T^X$  and  $C$  with basis set [2] showed that this basis set is quite adequate for the analyses in this paper.

two-thirds of the binding energy. Thus this partition might effect a separation of the predominant bonding terms from the nonbonding and self-consistency terms.

In an attempt to isolate from  $E^X$  the specific terms that are responsible for bonding, we have partitioned  $E^X$  in terms of  $T^X$ ,  $V^{nX}$ , and  $V^{eX}$  (the kinetic, nuclear attraction and electron repulsion parts of  $E^X$ , respectively) as in (7). These quantities are shown in fig. 2, where we see that only  $T^X$  is negative (favoring bonding) and that  $T^X$  clearly dominates over  $V^{nX}$  and  $V^{eX}$ . We also note here that in contradistinction with the case of total nuclear attraction and electron repulsion energies ( $V^{en}$  and  $V^{ee}$ ),  $V^{nX}$  and  $V^{eX}$  vary relatively slowly with  $R$ , indicating that the latter may be a useful and meaningful partition. Most important however is that throughout the region of chemical interest,  $T^X$  is monotonic and dom-

inates over all other terms. Thus a partition of the total energy as

$$E = T^X + \omega, \quad (11)$$

where  $\omega$  includes everything else, may isolate the bond-determining terms into  $T^X$ . In fig. 2 we see that for  $H_2$  the resulting function  $\omega$  is indeed positive and relatively smooth from  $R = R_e$  to  $R = \infty$ .

The energies in the above discussion were calculated for the optimum orbitals at the specific  $R$  being considered. However at large enough distances the self-consistent orbitals should be essentially the same as the orbitals for  $R = \infty$ . If our partitions are meaningful, we would expect that they be not overly sensitive to whether the frozen or SCF orbitals are used. In fig. 1 we show the  $E^{Cl}$  and  $E^X$  for the frozen orbitals (denoted as  $E^{Cl,F}$  and  $E^{X,F}$ , respectively) and we see that all the way down to  $R = 2.5 a_0$  we have  $E^{X,F} \approx E^X$ , whereas for  $R > 3 a_0$  we have  $E^{Cl,F} \approx \frac{1}{2}E^{Cl}$ . Thus the self-consistency seems mainly to affect only the classical energy. In addition the  $T^X$  for the frozen case is shown in fig. 2, where we find that  $T^{X,F} \approx T^X$ . Thus not only does  $T^X$  seem to include the terms leading to bond formation but it is not even very sensitive to the optimization of the orbitals (although the total energy is sensitive to this optimization).

#### 4. THE MAGNITUDE OF THE EXCHANGE TERMS

In fig. 2, we saw that the magnitude of  $T^X$  was much larger than that of either  $V^{nX}$  or  $V^{eX}$  for the  $H_2$  molecule. Now, it is of interest to understand why the magnitude of  $\Delta T^X$  ( $\Delta T^X$  denotes the change in  $T^X$  from  $R = \infty$  to the current  $R$ ) is much larger than the other terms in the binding energy. In fig. 2 we see that for the  $H_2$  molecule  $T^{X,F}$  behaves very much like  $T^X$  from  $R = \infty$  to  $R = R_e$ . Since  $\Delta T^{X,F}$  is also much easier to study (requiring only the wavefunctions for  $R = \infty$ ), we will concentrate in this section on  $T^{X,F}$ .

As shown in (8) the exchange kinetic energy is

$$T^X = T - T^{Cl} = -SD[\langle a|t|a \rangle + \langle b|t|b \rangle - (2/S)\langle a|t|b \rangle], \quad (12a)$$

where  $S \equiv \langle a|b \rangle$ ,  $t$  denotes  $-\frac{1}{2}\nabla^2$ , and  $D \equiv S'(1+S^2)$ . Integrating by parts in (12a) (and noting that the surface integral is zero), we obtain

$$T^X = -\frac{1}{2}SD[\langle \nabla a \cdot \nabla a \rangle + \langle \nabla b \cdot \nabla b \rangle - (2/S)\langle \nabla a \cdot \nabla b \rangle], \quad (12b)$$

where

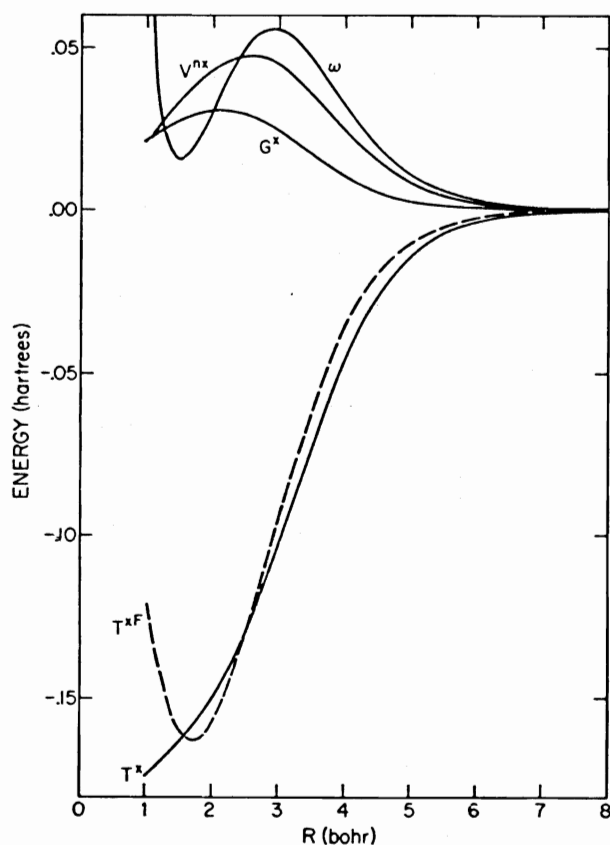


Fig. 2. Partition of the exchange energy ( $E^X$ ) of  $H_2$  into the kinetic ( $T^X$ ), nuclear attraction ( $V^{nX}$ ), and electron-electron repulsion ( $V^{eX}$ ) parts. In addition  $\omega = E + T^X$  and  $T^{X,F}$  are shown.

$$\langle \nabla a \cdot \nabla b \rangle \equiv \int d^3x_1 [\nabla \phi_a(1)] \cdot [\nabla \phi_b(1)].$$

(For convenience we have taken the orbitals as real.)

All other one-electron properties can be divided similarly into classical and exchange parts, and the exchange part can be written as in (12a). (Eq. (12b) is of course specific to the case of kinetic energy.) Next we will compare the changes in  $T^{\text{NX}}$  upon molecule formation in order to determine why the magnitude of  $\Delta T^{\text{X}}$  is so much larger than  $\Delta T^{\text{NX}}$ . Thus we consider

$$T^{\text{NX}} = -SD[ a v^{\text{n}} a + b v^{\text{n}} b - (2 S) a v^{\text{n}} b ], \quad (13)$$

$$= \int d^3x_1 v^{\text{n}}(1) \rho^{\text{X}}(1), \quad (14)$$

where

$$\rho^{\text{X}}(1) \equiv -SD[ \phi_a(1) \phi_a(1) + \phi_b(1) \phi_b(1) - (2 S) \phi_a(1) \phi_b(1) ]. \quad (15)$$

Note that if  $v^{\text{n}}(1)$  is replaced by one, (14) becomes

$$\int d^3x_1 \rho^{\text{X}}(1) = 0. \quad (16)$$

We cannot write  $T^{\text{X}}$  in the form (14) because of the  $\nabla^2$  operator. However, from (12b) we can define the quantity

$$t^{\text{X}}(1) = -\frac{1}{2}SD[ |\nabla \phi_a(1)|^2 + |\nabla \phi_b(1)|^2 - (2 S) \nabla \phi_a(1) \cdot \nabla \phi_b(1) ] \quad (17)$$

so that

$$T^{\text{X}} = \int d^3x_1 t^{\text{X}}(1). \quad (18)$$

Even though the form (18) is similar to (14), there is still an essential difference in the form of the interchange term (the third term) of  $t^{\text{X}}$  as compared to the interchange term of  $\rho^{\text{X}}$ . If  $\phi_a$  and  $\phi_b$  are positive everywhere (as for frozen  $\text{H}_2$ ), then  $-(2 S) \phi_a(1) \phi_b(1)$  is negative everywhere and the interchange term of  $\rho^{\text{X}}$  cancels a large part of the noninterchange terms (the first two terms) - in fact, for  $v^{\text{n}} = 1$  the cancellation is complete (see eq. (16)). However, the interchange term in  $t^{\text{X}}$  involves a dot product and thus is positive wherever  $\nabla \phi_a \cdot \nabla \phi_b$  is negative, that is, in the region in which the orbitals are *contragradient*. In this region the interchange term of  $T^{\text{X}}$  adds to the other terms and enhances binding. In order to isolate the effect on  $t^{\text{X}}$  of this

contragradience, we will define a new function,

$$c(\mathbf{r}) = [ |\nabla \phi_a|^2 + |\nabla \phi_b|^2 - \nabla \phi_a \cdot \nabla \phi_b ], \quad (19)$$

called the contragradience function, so that the contribution of the contragradience to  $t^{\text{X}}$  is given by  $-Dc(\mathbf{r})$ . Then we obtain

$$t^{\text{NC}}(\mathbf{r}) \equiv t^{\text{X}}(\mathbf{r}) + Dc(\mathbf{r}) = -SD[ |\nabla \phi_a|^2 + |\nabla \phi_b|^2 - (2 S) \nabla \phi_a \cdot \nabla \phi_b ], \quad (20)$$

for the noncontragradient part of  $t^{\text{X}}$ . We also define the total contragradience as

$$C = \int d^3r c(\mathbf{r})$$

so that the contribution of the contragradience to  $T^{\text{X}}$  is given by  $DC$  (called the contragradience energy). Then the noncontragradience part of the kinetic energy is

$$T^{\text{NC}} = T^{\text{X}} + DC,$$

so that

$$T^{\text{X}} = T^{\text{NC}} + DC. \quad (21)$$

Since  $c(\mathbf{r})$  is always positive, we have that  $C$  is always positive and always leads to a negative (or zero) contribution to  $T^{\text{X}}$ . However just as for  $t^{\text{NX}}$ , the interchange term of  $t^{\text{NC}}$  opposes the noninterchange terms and thus leads to a reduced value for  $T^{\text{NC}}$ . In fact for frozen  $\text{H}_2$  the resulting  $T^{\text{NC}}$  is zero for all  $R$ . That is, in the case of frozen  $\text{H}_2$  we find that *all of the bonding effect of  $T^{\text{X}}$  is due to the contragradience,  $C$ .*

Thus for the ground state of  $\text{H}_2$ ,  $T^{\text{X}}$  is large and negative because of the contragradient nature of the orbitals on different centers and the concomitant effect on the interchange term in  $T^{\text{X}}$ .

A study of the wavefunctions of a number of other bound and unbound systems [2] has shown that these conclusions about the importance of  $T^{\text{X}}$  and  $C$  for binding are applicable to all systems considered and hence could have broad general significance\*.

## 5. DISCUSSION

From these studies we would view the formation of a chemical bond in the following way: (1) freeze the orbitals of the separated atoms;

\* In cases in which the orbitals to be coupled are in different rows of the tableau, the  $D$  term multiplying  $C$  is negative and hence the contragradience term opposes binding. When such terms are dominant, the system is not chemically stable (see ref. [2]).

(2) bring the atoms together to their positions in the molecule (this leads to  $\Delta T^{\text{XF}}$  and to about the correct binding energy); and  
 (3) allow the orbitals to relax to their SCF forms. Step (3) may be divided up into (3a) allowing hybridization, and (3b) allowing the orbitals to contract more about each nucleus and to spread onto the other centers, readjusting the various nuclear attraction, electron repulsion, and kinetic energy terms until self-consistency is achieved (after which the virial theorem, Hellmann-Feynman theorem, etc., would hold). However the crucial step is (2). In order for a strong bond to form, this must lead to a large negative  $\Delta T^{\text{XF}}$ .

### 5.1. Comment on the electrostatic interpretation of binding

From (15) we see that for the lowest singlet state of  $\text{H}_2$ ,  $\rho^{\text{X}}$  is positive in the region between the nuclei. This corresponds to an increase in density in the region over what would be expected classically. For the lowest triplet state of  $\text{H}_2$ ,  $\rho^{\text{X}}$  has the form of (15) except that  $D = S(1 - S^2)$ . Thus in this case of the repulsive state, the density decreases in the bonding region. Because of this correlation between bonding and antibonding an increase or decrease in amplitude in the bonding region, there has in the past been speculation that the latter is the cause of the former. This has led to the idea (see, for example, ref. [5]) that the bond forms because an electron in between the two nuclei can attract both nuclei, leading to a decrease in the energy. This electrostatic viewpoint of bonding has already been effectively criticized by Ruedenberg [5]. From our point of view a bond forms because of a favorable contragradience and the resulting decrease in kinetic energy. However, the conditions for a favorable contragradience also lead to a positive  $\rho^{\text{X}}$ ; thus this increase of density in the bonding region is an effect due to the bond rather than the cause of the bond.

### 5.2. Comparison with Ruedenberg's theory

In a lucid and erudite discussion of chemical binding Ruedenberg [5] suggested partitioning the pair density kernel into classical and exchange parts. He then proceeded to partition the kinetic, nuclear attraction, and electron repulsion energies into various types of quasi-classical, promotion, interference, and self-pairing terms. These partitions were based on an analysis of the wavefunction in terms of atomic-like basis functions and hence were independent of the type of wavefunction being considered (e.g.,

configuration interaction or Hartree-Fock). For the Weinbaum wavefunction of  $\text{H}_2$  he found that  $\Delta T$  consisted of two parts, the promotion part  $T^{\text{P}} = \langle \chi(1.193) | \chi(1.193) \rangle - \langle \chi(1.0) | \chi(1.0) \rangle = 0.4230$  (where  $\chi(\zeta)$  is a pure 1s Slater orbital with exponent  $\zeta$ ) and an interference part,

$T^{\text{I}} = 2\rho(\text{A}|\text{B})T^{\text{A},\text{B}}$ , defined in terms of the bond order,  $\rho(\text{A}|\text{B})$ , and the kinetic interference term,  $T^{\text{A},\text{B}}$ . The resulting value of  $T^{\text{I}}$  is  $T^{\text{I}} = -0.275$ .

If the G1 orbitals in (32) are taken as pure Slater functions on centers A and B,  $\chi_{\text{A}}$  and  $\chi_{\text{B}}$ , then  $T^{\text{I}}$  would just be our  $T^{\text{X}}$  and  $T^{\text{P}} + 1.0$  would be  $T^{\text{Cl}}$ . However in the SCF case, even for a minimum basis set, each G1 orbital is a linear combination of  $\chi_{\text{A}}$  and  $\chi_{\text{B}}$  and thus  $T^{\text{Cl}}$  and  $T^{\text{X}}$  differ from  $T^{\text{P}}$  and  $T^{\text{I}}$ . In fact we find that  $T^{\text{Cl}} = 1.312$  and  $T^{\text{X}} = -0.164$ . In addition for the frozen G1 wavefunction we use  $\chi(1.0)$  rather than  $\chi(1.193)$  and hence again obtain different results,  $T^{\text{Cl},\text{F}} = 1.0$ , and  $T^{\text{XF}} = -0.156$ . Thus for  $\text{H}_2$  Ruedenberg's  $T^{\text{I}}$  is somewhat related to our  $T^{\text{X}}$ , but not identical. From his analysis of  $\text{H}_2$  Ruedenberg concluded that it is the decrease in  $T^{\text{I}}$  which is responsible for the bonding in  $\text{H}_2$ , in agreement with and anticipation of our similar conclusions. Since Ruedenberg's partition is basis set dependent, it is not obvious how close the correspondence between  $T^{\text{X}}$  and  $T^{\text{I}}$  will be for larger basis sets and for systems with more electrons.

### SUMMARY

From a study of the G1-type wavefunctions of  $\text{H}_2$  we found that the changes in the exchange kinetic energy,  $T^{\text{X}}$ , dominated the changes in the total energy. In addition we found that the orbital contragradience in the region around and between the nuclei led to the dominant component of  $T^{\text{X}}$ . It is hoped that principles based on these ideas might allow one to predict and discuss the stabilities and reaction surfaces for larger systems without carrying our complete calculations.

### REFERENCES

- [1] W. A. Goddard III, Phys. Rev. 157 (1967) 81.
- [2] C. W. Wilson and W. A. Goddard III, to be published.
- [3] J. C. Slater, Electronic structure of molecules (McGraw-Hill, New York, 1963).
- [4] J. H. van Vleck and A. Sherman, Rev. Mod. Phys. 7 (1935) 167.
- [5] K. Ruedenberg, Rev. Mod. Phys. 34 (1962) 326.