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Commentationes

The Role of Kinetic Energy in Chemical Binding

I. The Nonclassical or Exchange Kinetic Energy*

C. WOODROW WILSON, JR.** and WILLIAM A. GODDARD III***
Arthur Amos Noyes Laboratory of Chemical Physics†,
California Institute of Technology, Pasadena, California 91109, USA

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The wavefunctions and various partitions of the energy are examined for a variety of small molecules (H_2, H_3, H_4, HeH, HeH_2, He_2, LiH, and BH) in order to isolate the factors crucial for bond formation. We find that a natural partition of the energy leads to the conclusion that the crucial factor is the exchange, or nonclassical, part of the kinetic energy, T^x. The change in T^x upon pushing the atoms towards one another is the dominant term in the binding energy; it is negative when the resulting molecule is stable and positive when it is unstable. We show that T^x is related to the interference kinetic energy considered by Ruedenberg.

Die Wellenfunktionen und verschiedene Zerlegungen der Energie werden für eine Reihe kleiner Moleküle untersucht (H_2, H_3, H_4, HeH, HeH_2, He_2, LiH und BH), um die Faktoren zu finden, die für die Bindungsbildung ausschlaggebend sind. Die natürliche Zerlegung der Energie läßt die Folgerung zu, daß der bestimmende Faktor der Austauschanteil T^x (oder nichtklassische Anteil) der kinetischen Energie ist. Die Änderung von T^x beim Zusammenführen der Atome ist der dominierende Term für die Bindungsenergie; er ist negativ, wenn das resultierende Molekül stabil ist, und positiv, falls es instabil ist. Es wird gezeigt, daß T^x im Zusammenhang zum Wechselwirkungsanteil der kinetischen Energie nach Ruedenberg steht.

1. Introduction

A number of molecules, such as H_2, BH, and HF are strongly bound, with binding energies on the order of several electron volts and bond distances of less than three bohr[1]. This type of bond is often referred to as a chemical bond and is often viewed as involving sharing of electrons between the bonding atoms [1]. On the other hand many other systems, such as He_2 are only very weakly bound, with energies of less than 0.1 eV and bond distances of more than five bohr. This type of bond is often referred to as a van der Waal's bond is viewed as involving instantaneous correlation between the motions of the electrons of the two atoms [1]. The chemical forces dominate at short distances and the van der Waal's forces dominate at large distances. Compressing molecules such as He_2 to distances

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** National Science Foundation Predoctoral Trainee. Present address: Department of Chemistry, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

*** Alfred P. Sloan Foundation Research Fellow.

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[1] Atomic units are used throughout; in these units $e = \hbar = m_e = 1$, 1 hartree = 27.211 eV = 627.51 kcal mole^{-1} is the unit of energy, and 1 bohr = 0.52917 Å is the unit of length. (Cohen, E.R., Du Mond, J.W.M.: Rev. mod. Physics **37**, 537 (1965).)

characteristic of chemical binding generally leads to large repulsive or antibonding forces; that is, the chemical forces are antibonding but short range and the van der Waal's forces are bonding but long range. Thus the binding energy and equilibrium geometry involve a balance between those two effects. On the other hand for molecules such as BH, both forces are attractive and the stronger chemical forces determine the equilibrium geometry. This distinction between chemical and van der Waal's forces is especially meaningful since we can actually construct wave functions which include the first but not the second effect (see below).

In this paper our objective is to study the chemical forces and determine why they lead to bonding in some systems (e. g., H_2) and antibonding in others (e. g., He_2). We will start from rigorous self-consistent field wave functions and attempt to effect a partition of the energy in such a way that the parts responsible for chemical bonding are separated out from the other terms. The resulting partition leads to the conclusion that the dominant term for bonding is the change in the exchange or nonclassical part (T^x) of the kinetic energy (T). This term is negative for systems such as H_2 and LiH and positive for systems such as He_2 and H_3, and the sign of this term can be predicted from general considerations of the states of the separated molecules.

The conclusion that it is a decrease in the kinetic energy which is responsible for chemical bonding is in agreement with the earlier ideas of Hellmann [2] and Ruedenberg [3]. In addition the general philosophy of our approach is very much the same as Ruedenberg's and some of our concepts are similar to his. However the details of our approach are distinctly different and the final definition of the nonclassical part of T is not at all the same, as will be discussed later.

Although the total energy and its partitions are very important to us here, we wish to extract other information out of the wave function. In particular we want to be able to make a quantitative comparison of, say, the orbitals of the H_2 molecule and the H_2 part of H_2H, in order to determine just why H_2H is not stable and why the energy is lower for linear H_2H than for the bent case. Unfortunately, it is not possible, in general, to discuss the exact wave functions in terms of orbitals in such a way. However there is a class of very accurate wave functions which does allow a somewhat rigorous discussion of the many-electron wave function in terms of orbitals. Since use will be made of such wave functions, we summarize next some of their important features.

2. Independent Particle Wave Functions

In some approximations the wave function, Ψ, of a system of N identical particles may be discussed in terms of a set of N one-particle functions, called orbitals, each of which may be interpreted as the eigenstate of an individual particle moving in the average field due to the other $N-1$ particles. In this section, we will discuss several approximations which lead to such interpretations.

In the Hartree method the N-electron wave function, Ψ^H, is taken as a simple product of orbitals and spin functions,

$$\Psi^{H} = \Phi^{H}\chi\,, \tag{1}$$

where

$$\Phi^{H}(1,2,\ldots,N) = \varphi_1^{H}(1)\,\varphi_2^{H}(2)\cdots\varphi_N^{H}(N) \tag{2}$$

and χ is a suitable product of one-electron spin functions. In this case the total energy is given by

$$E^{\mathrm{H}} = \sum_{i}^{N} \langle \phi_i | h | \phi_i \rangle + \sum_{i>j}^{N} J_{ij}, \tag{3}$$

where $h = -\frac{1}{2}\nabla^2 + v^{\mathrm{N}}$, v^{N} is the nuclear attraction operator, and J_{ij} is the usual Coulomb integral

$$J_{ij} = \left\langle \phi_i \phi_j \left| \frac{1}{r_{12}} \right| \phi_i \phi_j \right\rangle . \tag{4}$$

The orbitals in (2) should be optimized so as to minimize the total energy (3). The resulting equations for the optimum orbitals can be written

$$H_k^{\mathrm{H}} \phi_k = \varepsilon_k \phi_k, \qquad k = 1, \ldots, N \tag{5}$$

where

$$H_k^{\mathrm{H}} = h + U_k^{\mathrm{H}}, \tag{6}$$

$$U_k^{\mathrm{H}} = \sum_{j \neq k}^{N} J_j, \tag{7}$$

and J_j is the Coulomb operator

$$J_j(1) = \left\langle \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_j(2) \right\rangle . \tag{8}$$

(In (8) the integration is over the coordinates of electron 2.)

Unfortunately the wavefunction of (1) is in general not appropriate for Fermions (or Bosons) since it is not an eigenfunction of the transposition operators. Note that the spin function χ in (1) could be taken as an eigenfunction of $\hat{S}^2$ (rather than a simple product) and the Eqs. (3)–(8) would still apply. Thus the primary fault of the Hartree wavefunction is that it violates the Pauli Principle, not that it has the wrong spin symmetry.

For (1) the probability distribution (i. e., electron density) is

$$\varrho^{\mathrm{H}}(1) = \sum_{i}^{N} |\phi_i(1)|^2 \tag{9}$$

and the total energy (3) and potential (7) are just those expected classically from such a charge distribution (omitting self-repulsion terms).

In the Hartree-Fock method the wave function is taken as a Slater determinant

$$\psi^{\mathrm{HF}} = \mathscr{A}(\Phi^{\mathrm{HF}} \chi), \tag{10}$$

where $\mathscr{A}$ is the N-particle antisymmetrizer and Φ^{HF} and χ are products of one-electron spatial and spin functions, respectively. In this case the energy expression is the same as (3) except for additional terms, called exchange integrals, which result from the permutation of orbitals of the same spin in (10). The orbitals in Φ^{HF} are required to be optimized (so as to make the total energy stationary), resulting in the following equations

$$H_k^{\mathrm{HF}} \phi_k = \varepsilon_k \phi_k, \qquad k = 1, \ldots, N \tag{11}$$

where

$$H_k^{\mathrm{HF}} = h + U_k^{\mathrm{HF}} \tag{12}$$

and U_k^{HF} is the same as U_k^{H} except for the presence of exchange terms. However, the electron density still has the form of (9) and all one-electron spatial properties can be expressed in the same form as in the Hartree case,

$$\langle F\rangle = \sum_{i}^{N} \langle \phi_i | f | \phi_i \rangle,$$

where f is a one-electron spatial operator, and F is the corresponding many-electron operator. The wave function (10) satisfies the Pauli principle for any Φ^{HF} but *is not necessarily an eigenfunction of* $\hat{S}^2$. In order to obtain the correct spin symmetry, we generally force the orbitals to be doubly occupied (once with each spin). However this double-occupation restriction then leads to difficulties due to improper dissociation of the wave function[2]. We can obtain the correct dissociation by dropping the double occupation restriction (to obtain the unrestricted Hartree-Fock (UHF) wave function); however the resulting wave function does not have the correct spin symmetry.

This leads us to consider the wave functions [4]

$$\psi^{G1} = G_1^{\gamma}(\Phi^{G1}\chi) \tag{13}$$

analogous to (10) but in which the group operator, G_1^{γ}, takes care of both the Pauli and spin symmetry [5] so that (13) satisfies Pauli's Principle and is an eigenfunction of $\hat{S}^2$ for *all* spatial functions Φ^{G1}. We restrict Φ^{G1} and χ to be products of spatial and spin functions, respectively, but require that the orbitals be optimized (with respect to the total energy). The resulting variational equations have the form

$$H_k^{G1}\phi_k^{G1} = \varepsilon_k \phi_k^{G1}, \quad k = 1, \ldots, N \tag{14}$$

where the one-particle operator H_k^{G1} has the form

$$H_k^{G1} = h + U_k^{G1} \tag{15a}$$

with the effective potential U_k^{G1} similar to U_k^{H} except for the occurrence of many exchange terms (involving both h and $1/r_{ij}$). Here U_k^{G1} can be expressed as

$$U_k^{G1} = U_k^{Cl} + U_k^{x}, \tag{15b}$$

where U_k^{Cl} is given by (7) and is just the average classical electrostatic potential and U_k^{x} contains *all* of the exchange terms (arising from the Pauli principle and spin symmetry requirements). Similarly, the total energy may be expressed as

$$E^{G1} = E^{Cl} + E^{x}, \tag{16}$$

where E^{Cl} is the energy we would obtain if the wave function were a simple product of orbitals, as given in (3). Note that E^{x} involves exchange contributions not only from the electron-electron interactions but also from the one-electron terms, i. e., kinetic energy and nuclear attraction. The orbitals in Φ^{G1} cannot be taken as orthogonal and thus the one-electron properties are given by[3]

$$\langle F\rangle = \sum_{ij}^{N} \langle \phi_i | f | \phi_j \rangle D_{ij},$$

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[2] By improper dissociation we mean those cases in which the energy of the molecular system with $R = \infty$ is higher than the sum of the atomic energies (using the same method of calculation), e.g., this is true for H_2. For further discussion, see Ref. [4].

[3] The normalization constant is included in the D_{ij}'s. For a further discussion of these orbital density matrices see Ref. [4] (where they are denoted as D_j^i).

where D_{ij}, the orbital density matrix, is no longer the unit matrix ($D_{ij} = \delta_{ij}$) as it was in the Hartree and HF cases [4]. Here we can write the value for a one-electron property as

$$\langle F \rangle = F^{Cl} + F^{x}, \tag{17a}$$

where

$$F^{Cl} = \sum_{i=1}^{N} \langle i | f | i \rangle \tag{17b}$$

is the classical part (arising from an orbital product wave function) and[4]

$$F^{x} = \sum_{i>j=1}^{N} D_{ij} [2 \langle i | f | j \rangle - \langle i | j \rangle (\langle i | f | i \rangle + \langle j | f | j \rangle)] \tag{17c}$$

is the quantum mechanical or *exchange part* of the property. Thus the electron density is no longer given by (9) but becomes

$$\varrho_{(1)}^{G1} = \sum_{i,j} D_{ij} \phi_i^*(1) \phi_j(1),$$

which can be written as

$$\varrho_{(1)}^{G1} = \varrho_{(1)}^{Cl} + \varrho_{(1)}^{x}. \tag{18}$$

In this case

$$\int d^3 x_1 \varrho^{Cl}(1) = N$$

$$\int d^3 x_1 \varrho^{x}(1) = 0,$$

so that ϱ^x might be described as an interference density (a somewhat related term, ϱ^I, has been defined by Ruedenberg [3] in terms of an expansion of the density in terms of atomic basis functions).

3. Analysis of Energies of the Wave Functions

Next we consider the G^1 wave functions for several molecules and examine various partitions of the classical and nonclassical energies and the variation of these energies with internuclear distance, R. We consider the starting point as systems A and B infinitely far apart, with the wave functions as optimum for the separated A and B systems (note here that A and B may be atoms or molecules). Then we will consider A and B at a distance $R = R_{\text{large}}$, such that chemical forces may already be operating, but for which the wave function is still well approximated by the product of the wave functions of the separated systems A and B. At R_{large} we will consider wave functions in which the orbitals are forced to be those appropriate for $R = \infty$ (but displaced to the new nuclear positions), and we will also consider the wave functions with the orbitals reoptimized for $R = R_{\text{large}}$. These two types of wave functions will be referred to as the *frozen* and SCF wave-functions, respectively. Note here that at all finite R we take the many-electron wave function to be the $G1$ wave function[5]; that is, even at large R, we correctly

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[4] Here, for convenience, we assume the orbitals are real.

[5] For the molecules with three or more electrons, we should optimize the spin coupling to obtain the spin-coupling optimized GI or SOGI wave function. (Ladner, R. C., Goddard III, W. A.: J. chem. Physics **51**, 1073 (1969).) However for these systems and the larger distances considered here, the differences between $G1$ and SOGI are negligible for our present analysis.

include the exchange of electrons of A with those on B. In some cases we will examine the energies over a large range of R, but our primary concern is to establish how the various types of energy change from $R=\infty$ to $R=R_{\text{large}}$ and especially which energy changes are different for bonding systems such as H_2 as compared to nonbonding systems such as He_2.

First we will consider the H_2 molecule for various internuclear distances from $R=R_e$ to $R=\infty$.

A. The H_2 *Molecule*

One typical partition of the energy is to separate it into the kinetic energy, T, and the total potential energy V,

$$E=T+V.$$

However as shown[6] in Fig. 1 for H_2, neither T nor V is monotonic as R decreases from $R=\infty$ to $R=R_e$. Since the binding energy *is* monotonic in this region, it is clear that the T, V partition does not effect a partition of the bonding effects from those unrelated to bonding. One might also consider partitioning V into electron-electron repulsion (V^{en}), electron-nuclear attraction (V^{en}), and nuclear-nuclear repulsion (V^{nn}) parts. These qunatities are monotonic but vary far more rapidly

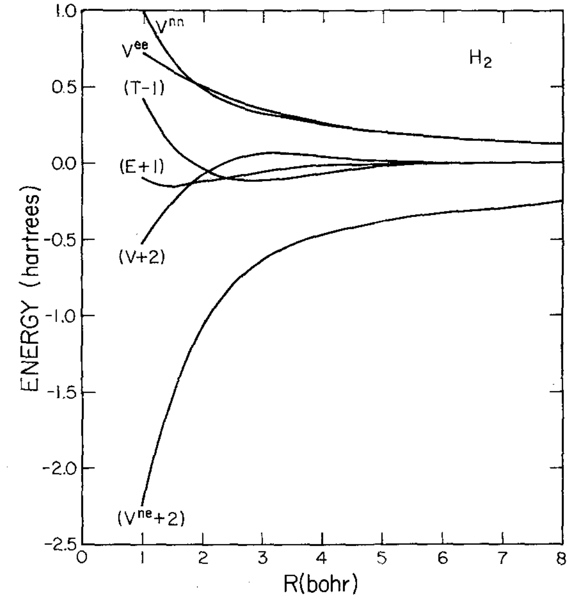

Fig. 1. The total binding energy (E), kinetic energy (T) and potential energy (V) for H_2 molecule (obtained for GI wavefunctions, see Footnote 6). The potential energy has also been partitioned into the electron-electron (V^{ee}), electron-nuclear (V^{en}), and nuclear-nuclear (V^{nn}) parts. All quantities have been referenced with respect to the value for $R=\infty$

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[6] The GI wavefunctions discussed here are all for optimized minimum basis set wavefunctions. In Appendix A we consider the effect of the basis set upon the partitions considered here and find it to be minimal.

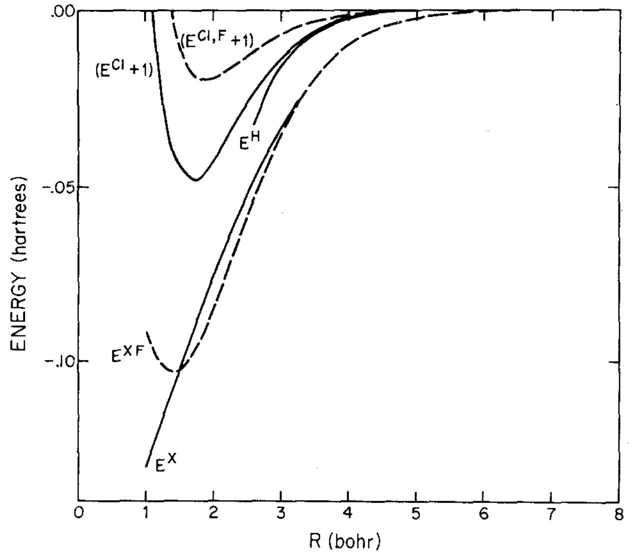

Fig. 2. The classical (E^{Cl}) and exchange (E^x) parts of the total energy of H_2. The broken lines indicate the quantities obtained from the frozen wavefunctions

with R than does E or V (see Fig. 1). That is, there are various parts of these quantities that cancel each other out.

An alternative partition of E into the classical and exchange parts (16), leads to quantities which vary monotonically with R (see Fig. 2) [6]. In this case E^x is larger than E^{Cl}, accounting for about two-thirds of the binding at R_e. However it would appear that some binding effects are contained in both E^{Cl} and E^x.

We considered partitioning E^x into its kinetic energy (T^x), nuclear-electron attraction (V^{nx}), and electron-electron repulsion (V^{ex}) parts

$$E^x = T^x + V^{nx} + V^{ex}$$

and found that E^x is dominated by T^x, with the other contributions both repulsive [6]. In addition, T^x follows the binding energy rather well suggesting a partition of the energy into T^x plus everything else (ω),

$$E = T^x + \omega\,. \tag{19}$$

In Fig. 3 we see that T^x and the total energy behave similarly and that the change in ω is relatively small and smooth.

Below we will examine partitions (16) and (19) for a number of other molecules, both stable and unstable ones, to test the generality of the above results. First, however, there is an additional point to consider concerning the above partitions. All energies were calculated for the optimum orbitals at the specific R being considered[6]. 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, they should not be overly sensitive to whether the frozen or SCF orbitals are used. The E^{Cl} and E^x for the frozen orbitals of H_2 are also shown in Fig. 2 where we see that $E^{xF} \approx E^x$ for $R > 2.5\,a_0$, whereas for $R > 3a_0$ we had $\Delta E^{Cl,F} \approx \frac{1}{2}\Delta E^{Cl}$

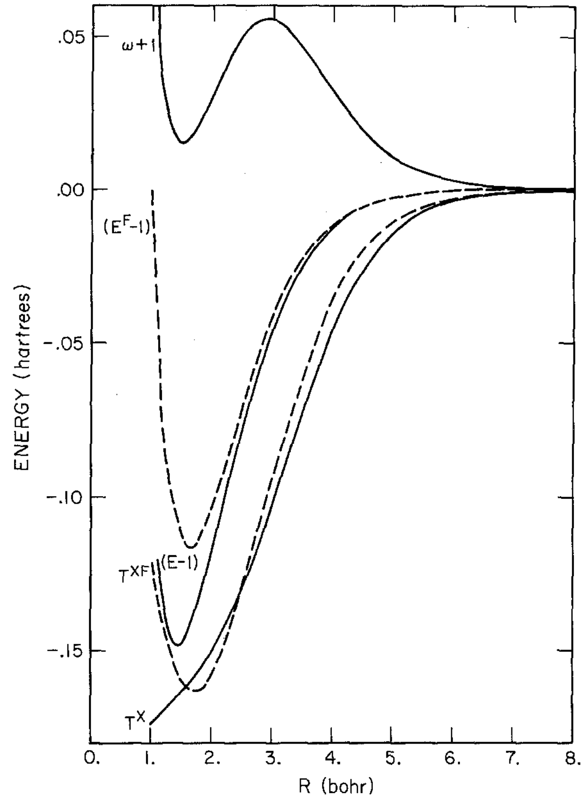

Fig. 3. The energy E and exchange kinetic energy T^x for H_2. The broken lines indicate the quantities obtained from the frozen wavefunctions. For the SCF case $\omega = E - T^x$ is also shown

(where ΔE is the difference between the value at R and the value at $R = \infty$). Thus it is the classical energy which seems primarily affected by self-consistency. In addition, the T^x for the frozen case is shown in Fig. 3, where we find that $T^{xF} \approx T^x$. Thus not only does T^x seem to include the terms responsible for bond formation but it is not very sensitive to the optimization of the orbitals[7].

B. Other Systems

In order to test the generality of the results for H_2, we considered a number of small systems of varying degrees of stability and instability. For each one we have considered two distances, $R = \infty$ and $R = R_{\mathrm{large}}$, where R_{large} is chosen so that the chemical forces would be small but significant. The basis sets and other details of these calculations are given in Appendix A. For each system we have considered both the frozen and SCF orbitals at R_{large} and calculated E^{Cl}, E^x, T^x, and ω. In Table 1, we show how these change from $R = \infty$ to $R = R_{\mathrm{large}}$ (here ΔT^x denotes the change in T^x, etc.).

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[7] The Weinbaum wave function (Weinbaum, S.: J. chem. Physics **1**, 593 (1933)) is equivalent to the minimum basis set $G1$ wave function for H_2, and the Heitler-London wave function (Heitler, W., London, F.: Z. Physik **44**, 455 (1927)) is equivalent to the frozen $G1$ wave function for H_2.

Table 1. Partitions of the $G1$ energy for several systems. The energies are in Hartree atomic units[a]. Here Δ refers to the value at finite R minus the value at $R = \infty$

System	Self-consistent orbitals[b]				Frozen orbitals[c]			
	ΔE^{Cl}[d]	ΔE^{x}[d]	ΔT^{x}[e]	$\Delta \omega$[e]	ΔE^{ClF}[d]	ΔE^{xF}[d]	ΔT^{xF}[e]	$\Delta \omega^{F}$[e]
H_2[f]	−0.00188	−0.00766	−0.03598	0.02644	−0.00118	−0.00729	−0.02851	0.02005
HeH[g]	−0.00004	0.00103	0.00451	−0.00353	−0.00031	0.00142	0.00649	−0.00637
H_2H[h]	0.00023	0.00126	0.00730	−0.00581	−0.00060	0.00229	0.00974	−0.00805
H_2H[i]	0.00002	0.00147	0.00806	−0.00657	−0.00062	0.00244	0.01034	−0.00852
He_2[j]	0.00009	0.00005	0.00063	−0.00050	−0.00005	0.00020	0.00122	−0.00107
HeH_2[k]	0.00072	−0.00031	0.00062	−0.00021	−0.00013	0.00059	0.00312	−0.00266
$(H_2)_2$[l]	0.00071	0.00017	0.00300	−0.00212	−0.00029	0.00130	0.00580	−0.00479
LiH[m]	0.00188	−0.01195	−0.02877	0.01870	−0.00132	−0.00706	−0.02107	0.01269
BH[j]	−0.00633	−0.01073	−0.04220	0.02514	0.01221	−0.02456	−0.03248	0.02013

[a] See Footnote 1.

[b] By self-consistent orbitals we mean that the optimum $G1$ orbitals are used.

[c] By frozen orbitals we mean that the orbitals are optimum for $R = \infty$, but that the wavefunction is a $G1$-like wavefunction for the finite R.

[d] E^{Cl} and E^{x} are the classical and exchange parts of the energy, $E = E^{Cl} + E^{x}$.

[e] T^{x} is the exchange part of the kinetic energy and ω contains the remaining parts of the energy, $\omega = E - T^{x}$.

[f] $R = 4.2\, a_0$.

[g] $R = 4.643\, a_0$.

[h] $R_{12} = 1.4304242\, a_0$, $R_{23} = 4.285\, a_0$, linear.

[i] $R_{12} = 1.4304242\, a_0$, $R_{23} = 4.285\, a_0$, $\theta = 30°$.

[j] $R = 5.0\, a_0$.

[k] $R_{12} = 4.643\, a_0$, $R_{23} = 1.4304242\, a_0$, linear.

[l] $R_{12} = R_{34} = 1.4304242\, a_0$, $R_{23} = 4.285\, a_0$, linear.

[m] $R = 6.0\, a_0$.

For the frozen orbitals we find (see Table 1) that T^{x} decreases with R for the bound systems H_2, LiH, and BH and increases for the unbound systems. The remaining energy term, ω, behaves in the opposite direction; however T^{x} dominates in every case. Upon adjusting the orbitals self-consistently, we find that ΔT^{x} is still negative for bound systems and positive for unbound systems, and all cases ΔT^{x} still dominates $\Delta \omega$. Thus it would seem that the terms responsible for binding or antibinding are isolated into T^{x} for all of these systems.

For each of these systems we have also listed in Table 1 the ΔE^{x} and ΔE^{Cl} for the frozen and self-consistent cases. For the frozen orbitals we find that $E^{Cl,F}$ decreases with R in every case, except BH, whether the system is bound or unbound. Correspondingly E^{xF} decreases for the bound systems, increases for the unbound systems, and dominates ΔE^{Cl}. However when the orbitals are adjusted for self-consistency the above trends change. Here we find that except for H_2 and HeH, E^{Cl} increases as R decreases and that except for H_2, HeH_2, LiH, and BH, ΔE^{x} also increases. Thus it would appear that the terms responsible for binding are not well isolated by the $\{E^{x}, E^{Cl}\}$ partition.

From the calculations discussed above it appears that the factors responsible for the chemical bond are isolated into the exchange kinetic energy.

Next we will consider the H_2^+ ion. Since H_2^+ has only one electron, it would appear that $T^{x} = 0$ at all R; yet H_2^+ is more than half as stable as H_2 [7].

C. *The* H_2^+ *Molecule*

Consider first two H atoms separated by a large distance, R; let one be in the $1s$ state, ϕ_{1s}, and the other in the ns state, ϕ_{ns}. There are two possible states of the system – the excitation could be on the left proton or on the right one. We will denote the wave functions for these states as

$$\Phi^{\mathrm{L}}(1,2)=\phi_{ns}^{\mathrm{L}}(1)\,\phi_{1s}^{\mathrm{R}}(2) \tag{20}$$

and

$$\Phi^{\mathrm{R}}(1,2)=\phi_{1s}^{\mathrm{L}}(1)\,\phi_{ns}^{\mathrm{R}}(2) \tag{21}$$

respectively. Classically we could specify which atom is excited, and the wave function would be (20) or (21), but quantum mechanically the total wavefunction for the adiabatic states of the system must be the symmetric (or antisymmetric) combination of the above states,

$$\Phi^{\mathrm{total}}=\Phi^{\mathrm{L}}+\Phi^{\mathrm{R}}\,. \tag{22}$$

In addition we have to take into account Pauli's Principle, and for a singlet state the spatial part of the total wave function becomes

$$\Psi^{\mathrm{total}}=[e+(12)]\,(\Phi^{\mathrm{L}}+\Phi^{\mathrm{R}})\,, \tag{23}$$

where e is the identity permutation and (12) interchanges particles 1 and 2. Thus in the total wave function we not only obtain exchange terms arising from the $[e+(12)]$ operator (which we also found for the ground state), but in addition we get exchange terms [8] from the degeneracy of the states (20) and (21).

Now consider the limit in which ϕ_{ns} is in the continuum, that is, the H_2^+ molecule. In this case at large R we have

$$\Phi^{\mathrm{L}}=\phi_{1s}^{\mathrm{R}}\,, \tag{24}$$

$$\Phi^{\mathrm{R}}=\phi_{1s}^{\mathrm{L}} \tag{25}$$

and the total wave function is

$$\Psi^{\mathrm{total}}=\phi_{1s}^{\mathrm{R}}+\phi_{1s}^{\mathrm{L}}\,. \tag{26}$$

Here the classical wave function is either (24) or (25) and the quantum mechanical wave function is (26). Thus here we do not find the type of exchange term due to $[e+(12)]$, but we still have the other type of exchange term due to the degeneracy of the states (24) and (25). Thus for H_2^+ we define E^{Cl} as

$$E^{Cl}=\langle\phi_{1s}^{\mathrm{L}}|h|\phi_{1s}^{\mathrm{L}}\rangle=\langle\Phi^{\mathrm{R}}|h|\Phi^{\mathrm{R}}\rangle\,,$$

where h is the total one-electron Hamiltonian. In this case we define the exchange energy as[8]

$$\bar{E}^{x}=E-E^{Cl}\,,$$

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[8] Feinberg, M. J., Ruedenberg, K., Mehler, E. L. (Advances quant. Chem. **5**, 28 (1970)) have started with a quasi-classical density function ϱ^{QC} and defined an interference density function ϱ^{I} as the remainder of the total density. Because of the symmetry of the system, the energies they associate with ϱ^{QC} are equivalent to our classical energies and their interference energies are exactly our exchange energies. Thus their conclusions on the H_2^+ system are in agreement with our own. We thank Dr. Ruedenberg for a copy of this paper prior to publication. Feinberg and Ruedenberg (Feinberg, M. J.: Theoret. chim. Acta (Berl.) **19**, 109 (1970); Feinberg, M. J., Ruedenberg, K.: J. chem. Physics **54**, 1495 (1971); **55**, 5804 (1971)) have also found their analysis to be valid for other one-electron diatomics.

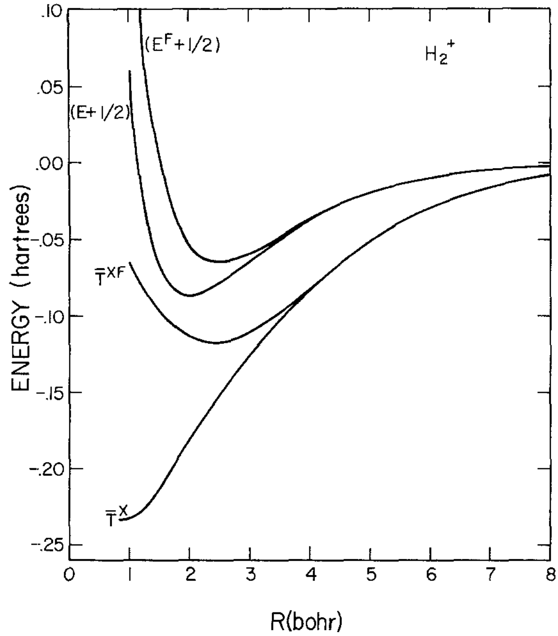

Fig. 4. Comparison of the total energy E and exchange kinetic energy $\bar{T}^x$ for the frozen and exponent optimized wave function of H_2^+. (A minimum basis set was used)

where the bar over $\bar{E}^x$ indicates that the second kind of exchange is involved, and similarly for the exchange kinetic energy, $\bar{T}^x = T - T^{Cl}$. Fig. 4 shows $\bar{T}^x$ and E for H_2^+ in the case where the orbitals are frozen (i. e., H atom orbitals). We see that E^F is negative for all R and is dominated by $\bar{T}^{xF}$. Thus again it seems that the exchange kinetic energy is the crucial term in forming the chemical bond.

We also carried out self-consistent calculations as a function of R (these were minimum basis set calculations, thus only the orbital exponents were really free to vary). The resulting total energy is shown in Fig. 4, where we see that down to about 3 a_0, the results were only slightly lower than for the frozen orbitals.

Given a ϕ^{L} or a ϕ^{R} it is simple to solve for ϕ^{total} as in (22); however there does not appear to be a nonarbitrary, unique way of solving for ϕ^{L} or ϕ^{R} when Φ^{total} is given[9]. In the case of H_2^+, Φ^{total} is a symmetric function and there are an infinite number of ϕ^{L} and ϕ^{R} which add up to yield ϕ^{total}. For this reason we have arbitrarily defined the SCF ϕ^{L} as just the part of ϕ^{total} which uses basis functions centered on the left proton. This is consistent with ϕ^{L} for the frozen case and yields reasonable results as shown in Fig. 4. We see that just as in H_2, $\bar{T}^x$ continues to drop as R decreases through R_e (the equilibrium value). In any case $\bar{T}^{xF}$ and $\bar{T}^x$ are nearly the same for $R > 3a_0$, and we still find that the exchange kinetic energy dominates.

In general for degeneracies such as in H_2^+, a definition of the classical energy as the energy for a single one of the degenerate states leads to a reasonable and

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[9] The total energy is invariant under transformations symmetrically mixing ϕ_{1s}^{R} and ϕ_{1s}^{L} of (26), and hence a subsidiary condition such as maximum localization of the orbitals would have to be applied.

satisfactory partition of the energy into classical and exchange parts. This applies not only to ions such as Li_2^+, but also to excited states of molecules, which often lead to such additional degeneracies. Such cases will be deferred to a later paper.

D. Summary

In summary we see that the partition of the $G1$ energy into T^x and ω appears to isolate into T^x the major effects characterizing chemical forces.

4. Comparison with Other Analyses of Bonding

In a lucid and erudite discussion of chemical binding Ruedenberg [3] 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 wave function in terms of atomic-like basis functions and hence were independent of the type of wave function being considered (e. g., configuration interaction or Hartree-Fock). In this approach the classical density, ϱ^{Cl}, is defined in terms of the *atomic basis functions* (not the molecular orbitals) used in the expansion of the wave function, so that ϱ^{Cl} has the form

$$\varrho^{Cl}(1,1') = \sum_{A} \varrho_A^{Cl}(1,1'),$$

where the summation is over atomic centers (A), ϱ_A^{Cl} involves only basis functions on center A and the trace of ϱ^{Cl} is just the number of electrons. The remainder of $\varrho(1,1')$ is defined as the interference density, ϱ^I. The classical and interference parts of the kinetic energy are then defined in terms of these densities. Ruedenberg found [3, 9] that bound molecules exhibit a large negative interference kinetic energy, T^I.

Since Ruedenberg's ϱ^{Cl} is defined in terms of the atomic basis functions and our ϱ^{Cl} [see (18)] is defined in terms of the $G1$ molecular orbitals, there clearly is no direct correspondence between them. For the Weinbaum wavefunction (equivalent to the minimum basis set $G1$ wave-function) of H_2, Ruedenberg obtains $T^{Cl} = 1.0 + T^P = 1.423$ and $T^I = -0.275$, whereas we obtain $T^{Cl} = 1.312$ and $T^x = -0.164$ for the SCF $G1$ orbitals, and $T^{Cl,F} = 1.0$ and $T^x = -0.156$ for the frozen $G1$ orbitals (the calculated binding energy is 0.148).

We should make it clear here that despite the differences between T^x and T^I, Ruedenberg was the first person to recognize and quantify the importance of the nonclassical kinetic energy to chemical binding, one of the more significant developments in the theory of chemical bonding since Pauling's classic papers [10]. Ruedenberg and co-workers performed analyses on the Hartree-Fock wavefunctions of several systems including H_2O and several diatomics [9], and found the bond to be due largely to a large drop in the interference kinetic energy, T^I. This approach can be applied to any wavefunction involving basis functions, including GI wavefunctions. As we saw above for H_2 the resulting T^I is different from T^x; however we have not applied Ruedenberg's approach to GI wavefunctions for other molecules. Since the Ruedenberg partition is basis set dependent, it is not obvious how close the correspondence between T^x and T^I will be for larger basis sets and for systems with more electrons. For example, for a numerical wavefunction, the Ruedenberg partition is not well defined, but since T^x is defined in terms of GI orbitals and not basis functions, there is no difficulty in obtaining T^x.

Hellmann [2] used a model of the atom and the molecule to study bond formation and found that an initial drop in the kinetic energy was responsible for bonding. This model corresponds to a frozen calculation, and therefore, contrary to some arguments against his conclusions, need not satisfy the virial theorem [3]. (Only wave functions optimized with respect to a scaling need satisfy the virial theorem.) Pauling [10] and London [11] suggested that "resonance" was responsible for bonding. The "resonance" energy is, of course, quite similar to E^x. Pauling also noticed the density contraction effect.

The above studies of Ruedenberg, Hellmann, London, and Pauling examined how the molecule is formed. There is a second type of study [12] that examines only electron density from the final SCF wavefunction for the molecule. Since such treatments can treat only the final density contraction, these studies necessarily miss T^x. Thus if T^x is the significant quantity important for binding, any attempt to analyze bonding in terms of electron density would be futile since the information needed to construct T^x would be absent. (The first-order density matrix, however, can be used to construct T^x and hence could be used in analyzing bonding.)

Recently the charge density interpretation of binding has been extended by by Bader and Preston [13]. They partition the total kinetic energy density $K(\boldsymbol{x})$ as

$$K(\boldsymbol{x}) = L(\boldsymbol{x}) + G(\boldsymbol{x}),$$

where $L(\boldsymbol{x}) = -\frac{1}{4}\nabla^2 \varrho(\boldsymbol{x})$ is the Laplacian of the density and $G(\boldsymbol{x})$ is the remainder (involving gradients of $\varrho(\boldsymbol{x})$). Although the integral of $L(\boldsymbol{x})$ is zero,

$$\int L(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} = 0,$$

they note that a small negative curvature in $\varrho(\boldsymbol{x})$ leads to small positive contributions to $L(\boldsymbol{x})$ and thus (they suggest) a smaller local contribution to the kinetic energy than would otherwise be expected. They conclude that bound molecules are systems for which it is favorable to decrease the curvature in the bonding region. Of course, any change in the charge distribution would lead to $\Delta \int L(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} = 0$ and hence no net change in the contribution of $L(\boldsymbol{x})$ to the kinetic energy.

The integral of $G(\boldsymbol{x})$, is the total kinetic energy and includes both T^{Cl} and T^x. Thus for a stable molecule the integral of $G(\boldsymbol{x})$ dominates the potential terms and aids bonding at large distances but opposes binding and is dominated by the potential terms at short distances. That is, this partition into kinetic and potential terms would seem to lead to bonding effects in either term depending on the distance. As discussed in Section 3 the partition of the kinetic energy into T^{Cl} and T^x leads to the quantity T^x which dominates the bonding in molecules such as H_2 from R_e to ∞.

5. Discussion

Our whole discussion here has been based on GI-type wavefunctions which involve an orbital product modified by an operator which takes care of the necessary symmetries of the molecular system[10]. For such a wavefunction it is quite natural to partition the energy and other quantities into the classical part involving just the orbital product and the remainder involving orbital exchanges. The orbitals involved in such wavefunctions lead to a qualitative description of molecular systems similar to the valence bond description and compatable with common intuitive ideas about such systems. Since other types of wavefunctions such as obtained from configuration interaction (CI) also lead to a proper description of bonding, we might wonder how our interpretation would apply to such wavefunctions. The orbitals in a CI wavefunction do not generally correspond directly chemically interpretable quantities and so one problem will be to transform the wavefunction to obtain more interpretable orbitals. Since the GI and CI wavefunctions both lead to very good descriptions of the total wavefunction, the overlap of these wavefunctions should be very large. Thus we might start with the CI wavefunction and obtain from it a set of GI-like orbitals by maximizing the overlap [14]

$$\frac{|\langle \Phi_{\mathrm{GI}} | \Phi_{\mathrm{CI}} \rangle|^2}{\langle \Phi_{\mathrm{GI}} | \Phi_{\mathrm{GI}} \rangle \langle \Phi_{\mathrm{CI}} | \Phi_{\mathrm{CI}} \rangle}.$$

That is, we find a GI-like wavefunction with largest projection on the CI wavefunction. Using these new GI-like orbitals, we can interpret the CI wavefunction just as if it were a GI wavefunction. Such an approach might also be used to obtain approximate GI-like orbitals from Hartree-Fock wavefunctions [15]. Thus although the GI orbitals form a natural framework for interpreting bonding, one can probably obtain similar orbitals from other types of wavefunctions without actually carrying out GI calculations.

6. Summary

We find from an analysis of various partitions of the total energy that the nonclassical or exchange kinetic energy appears to dominate chemical bonding. This has been tested by examining the results for several stable and unstable molecular systems.

Appendix A: Basis Sets

We will now describe the basis sets used in the calculations reported herein.

Most of the calculations of H_2 used a minimum basis set. The reason is that this basis yields partitions of the energy quite comparable to those of larger basis sets, as is shown in Table 2, and in addition calculations can be simply and efficiently carried out for a number of internuclear distances. It is apparent from Table 2 that our conclusions are not greatly altered by the use of a larger basis set. Note in particular, how insensitive the total contragradience is with respect to the basis set.

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[10] As indicated in the H_2^+ discussion, this type of analysis applies also to cases in which the usual group operator, G_i^γ (used to ensure spin and Pauli symmetry), is supplemented by spatial symmetry operators to ensure the proper spatial symmetry.

Table 2. Basis set dependence of the energy partitions for self-consistent $G1$ wavefunctions of H_2 (all calculations for $R = 1.4\, a_0$)

Number of basis functions	E^a	T^{xa}	V^{nxa}	ω^a	$-DC^b$
2^c	-1.147777	-0.164937	0.031475	-0.982840	-0.142663
4^d	-1.151345	-0.152065	0.022477	-0.999280	-0.146613
6^e	-1.151526	-0.159958	0.029630	-0.991568	-0.148577
8^f	-1.151887	-0.157300	0.026950	-0.994587	-0.148252

[a] E is the total energy, T^x is the exchange kinetic energy, V^{nx} is the exchange nuclear attraction, and ω is $E - T^x$.

[b] $-DC$ is the contragradience energy, see Ref. [6].

[c] $\zeta_{1s} = 1.2005$.

[d] $\zeta_{1s} = 1.1909$, $\zeta_{2p} = 2.0928$.

[e] $\zeta_{1s} = 1.3129$, $\zeta_{2s} = 1.1566$, $\zeta_{2p} = 1.9549$.

[f] $\zeta_{1s} = 1.3092$, $\zeta_{2s} = 1.1273$, $\zeta_{2p} = 1.700$, $\zeta_{3d} = 2.35$.

In polyatomic systems involving H_2, we have used the optimum[11] minimum basis set and distance calculated for H_2, $R_e = 1.4304242$ and $\zeta_{1s} = 1.1937847$ (not all of these figures are significant).

The He atom basis set for the HeH and HeH_2 calculations consists of four Slater functions [16] with ζ_{1s}, $\zeta_{2s} = 3.30$ and $\zeta_{1s'}$, $\zeta_{2s'} = 1.433$, whereas the He_2 calculations[12] used an added optimized $2p\sigma$ orbital (orbital exponent 0.4). The intermolecular distances used here were chosen to be approximately comparable, based on he van der Waals radii of the molecules involved. From the resulting $\Delta E'$ it appears that the He_2 distance is somewhat too large in comparison to the $(H_2)_2$ distance.

The Li atom basis set for LiH consists of seven Slater functions [16] with one $1s(\zeta = 3.0)$, four $3s's(\zeta = 5.4$, 2.999, 1.347, 0.841), and two $4s's(\zeta = 5.33$, 7.32), all optimized for a Li atom.

The basis set for BH consists of an $(11s, 5p/4s)$ primitive set of Gaussian-type orbitals contracted to a $(5s, 3p/2s)$ set [17].

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[11] The optimum R we calculated is somewhat different from the Weinbaum value[7] $R = 1.4166$, but is in good agreement with the value obtained by Adamov and Bulychev (Adamov, M. N., Bulychev, V. P.: Zh. Teor. Eksp. Khim. **2**, 685 (1966); English Translation: J. theoret. Exp. Chem. **2**, 502 (1966)).

[12] We wish to thank Dr. W. E. Palke for his unpublished He_2 results.

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Dr. C. W. Wilson
Arthur Amos Noyes Laboratory
of Chemical Physics
California Institute of Technology
Pasadena, California 91109, USA