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The Role of Kinetic Energy in Chemical Binding

II. Contragradience*

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In a preceding paper, we examined the GI wavefunctions of small molecules and found that the nonclassical or exchange kinetic energy, T^x, dominates the changes in energy involved in chemical binding. Here we examine more closely the changes in T^x with internuclear separation and find that ΔT^x is large for valence orbitals centered on different atoms because of the large region in which the orbitals are contragradient (i.e., have gradients in obtuse directions). In fact for H_2 this contragradience accounts for 93% of the calculated binding energy. In addition, the behavior of T^x and ΔT^x can usually be predicted from consideration of the permutational symmetry (Young tableau) involved in the wavefunction. The concepts developed here provide an alternative interpretation of the nature of the chemical bond.

Die in einer vorhergehenden Arbeit durchgeführten Untersuchungen der GI-Wellenfunktionen kleiner Moleküle führten zu dem Ergebnis, daß der nichtklassische oder Austauschanteil der kinetischen Energie T^x bei Änderungen der Energie chemischer Bindungen überwiegt. In dieser Arbeit werden die Änderungen von T^x mit dem Kernabstand näher untersucht. Wir finden ein großes ΔT^x für an verschiedenen Atomen zentrierte Valenzorbitale wegen der großen Region, in der die Orbitale „kontragradient" (d. h. sie haben Gradienten in Richtungen, die einen stumpfen Winkel miteinander bilden) sind. Für H_2 sind 93% der berechneten Bindungsenergie auf diese „Kontragradienz" zurückzuführen. Ferner kann das Verhalten von T^x und ΔT^x normalerweise aus der Permutationssymmetrie (Young Tafeln) der Wellenfunktionen vorausgesagt werden. Die hier entwickelten Methoden erlauben eine alternative Interpretation der chemischen Bindung.

1. Introduction

In a preceding paper [1] we examined the GI wavefunctions [2, 3] of a number of small systems (both bound and unbound) and found in every case that chemical binding is dominated by the change in one term in the energy expression: the *exchange kinetic energy*, T^x. Here we investigate why T^x is so important and find that T^x is dominated by a term (the contragradience) that is uniquely large for multicentered systems, i.e., molecules. Further examination of this term leads to concepts in terms of which general aspects of binding can be predicted using simple considerations of the spatial permutation symmetry forced on the elec-

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tronic wavefunction by the spin symmetry coupled with the Pauli Principle. This leads to an alternative simple model of the chemical bond.

The GI wavefunction involves a number of orbitals (equal to the number of electrons), each of which is solved for self-consistently in the field due to the other electrons. As the nuclear configuration changes, the fields change, and hence the orbitals change. However, in some cases it is useful to consider to treat a molecular complex AB using the orbitals appropriate for the separated systems A and B. Such wavefunctions will be referred to as the *frozen wavefunctions* of AB or sometimes more simply as the frozen AB case.

2. The Magnitude of the Exchange Terms

In Fig. 1 we see that for the H_2 molecule the magnitude of T^x is much larger than the exchange part of the electron-nuclear attraction energy (V^{nx}) or the exchange part of the electron repulsion energy (V^{ex}). In Table 1 of I, we saw that ΔT^x (the change in T^x from the value at $R = \infty$) dominates the binding energy for all molecules considered, determining its sign in every case. Consequently, it is of interest to understand why the magnitude of ΔT^x is much larger than the other terms in the binding energy. First we will consider the ground state of H_2.

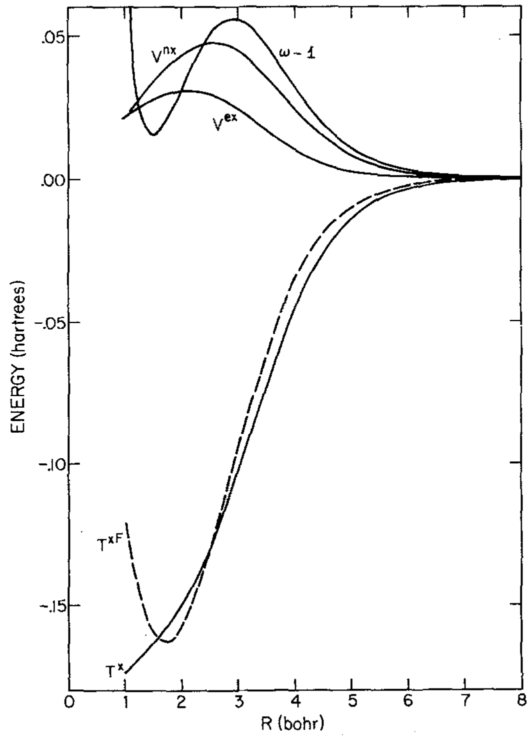

Fig. 1. The exchange kinetic energy (T^x), exchange nuclear attraction energy (V^{nx}) and exchange electron repulsion energy (V^{ex}) for the ground state of H_2. T^{xF} refers to the T^x for the frozen wavefunction, and $\omega = E - T^x$

A. The H_2 *Singlet State*

In Fig. 1 we see that T^{xF} (T^{x} for the frozen wavefunction of H_2) behaves very much like the T^{x} from $R=\infty$ to $R=R_e$. In addition, in Table 1 of I we saw that ΔT^{x} and ΔT^{xF} are comparable (and of the same sign) for a number of bound and unbound systems (all systems considered). Since ΔT^{xF} is also much easier to study (requiring only the wavefunctions for $R=\infty$), we will concentrate in this section on T^{xF}.

The spatial part of the frozen G1 wavefunctions is

$$\Phi^{\mathrm{sp}} = O_{11}ab = \tfrac{1}{2}[ab+ba]\,, \tag{1}$$

where a and b are just H 1s functions on the two protons. Thus, from Eq. (A-8) of Appendix A, the exchange kinetic energy is given by [4]

$$T^{x} = -SD\left\{\langle a|t|a\rangle + \langle b|t|b\rangle - \frac{2}{S}\langle a|t|b\rangle\right\}, \tag{2a}$$

where $S=\langle a|b\rangle$ is the orbital overlap, and $D=S/(1+S^2)$ is the off-diagonal element of the orbital density matrix. Integrating by parts in (2a), we obtain

$$T^{x} = -\tfrac{1}{2}SD\left\{\langle \nabla a\cdot\nabla a\rangle + \langle \nabla b\cdot\nabla b\rangle - \frac{2}{S}\langle \nabla a\cdot\nabla b\rangle\right\}, \tag{2b}$$

where

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

All other one-electron properties can also be divided into classical and exchange parts with the exchange part of the form in (2a); however, Eq. (2b) is specific to the case of kinetic energy.

Now we will compare the changes upon molecule formation of the exchange parts of various properties in order to determine why the magnitude of ΔT^{x} is so large. Replacing the t operator in (2a) by the simple scalar operators 1 and v^n, we obtain

$$N^{x} \equiv -SD\left[\langle a|a\rangle + \langle b|b\rangle - \frac{2}{S}\langle a|b\rangle\right], \tag{3a}$$

$$V^{\mathrm{nx}} = -SD\left[\langle a|v^{\mathrm{n}}|a\rangle + \langle b|v^{\mathrm{n}}|b\rangle - \frac{2}{S}\langle a|v^{\mathrm{n}}|b\rangle\right], \tag{3b}$$

for the exchange parts of the total change and of the nuclear attraction energy, respectively. Eqs. (3a) and (3b) can be rewritten as

$$N^{x} = \int dx_1^3\varrho^{x}(1) \tag{4}$$

and

$$V^{\mathrm{nx}} = \int dx_1^3 v^{\mathrm{n}}(1)\,\varrho^{x}(1)\,, \tag{5}$$

where

$$\varrho^{x}(1) \equiv (-SD)\left[\phi_a(1)\,\phi_a(1) + \phi_b(1)\,\phi_b(1) - \frac{2}{S}\phi_a(1)\,\phi_b(1)\right] \tag{6}$$

is the *exchange electron density* [see (18) of I]. We cannot write T^x in this way because of the ∇^2 operator; however, from (2b) the quantity

$$t^x(1) = -\tfrac{1}{2}SD\left[|\nabla\phi_a(1)|^2 + |\nabla\phi_b(1)|^2 - \frac{2}{S}\nabla\phi_a(1)\cdot\nabla\phi_b(1)\right] \tag{7}$$

can be defined so that

$$T^x = \int d^3x_1 t^x(1)\,. \tag{8}$$

Even though the form (8) is similar to that of (4) and (5), there is still an essential difference due to the difference in the form of the *interchange term* (the third term) of t^x as compared to the interchange term of ϱ^x. If ϕ_a and ϕ_b are positive everywhere (as for frozen H_2), then $-(2/S)\,\phi_a(1)\,\phi_b(1)$ is negative everywhere and the interchange term may cancel a large part of the noninterchange terms (the first two terms – in fact, for N^x the cancellation is sufficient to lead to $N^x = 0$ for all R. However, the interchange term in t^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^x adds to the other terms and enhances binding. In order to isolate the effect of this contragradience on t^x, we will define a new function,

$$t^{\mathrm{nc}} \equiv \tfrac{1}{2}SD\left[|\nabla\phi_a|^2 + |\nabla\phi_b|^2 - \frac{2}{S}|\nabla\phi_a|\,|\nabla\phi_b|\right], \tag{9}$$

called the *noncontragradient* part of t^x. The total noncontragradient part of T^x is then

$$T^{\mathrm{nc}} = \int dr^3 t^{\mathrm{nc}}(r)\,.$$

We also define

$$c(\boldsymbol{r}) \equiv [|\nabla\phi_a|\,|\nabla\phi_b| - \nabla\phi_a\cdot\nabla\phi_b] \tag{10}$$

to be the *contragradience function* and

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

to be the *total contragradience*. Thus the contribution of the contragradience to T^x is given by $-DC$ and we obtain

$$T^x = T^{\mathrm{nc}} - DC\,. \tag{11}$$

Since $c(\boldsymbol{r})$ is always positive, C is always positive; thus, since D is always positive for a singlet state, the contragradience contribution to T^x is always negative (or zero). However, just as for ϱ^x, the interchange term of t^{nc} opposes the noninterchange terms and thus leads to a reduced value for T^{nc}. In fact for the frozen wavefunction of H_2, the resulting T^{nc} is zero for all R. That is, in this case *all of the bonding* effect of T^x is due to the contragradience, C. The essential reason for this difference between N^x, V^{nx}, and T^x can be seen in Fig. 2, where the integrands of the interchange terms are plotted along the internuclear axis. We see that for N^x, V^{nx}, and T^{nc} the plots are comparable. But $-c(\boldsymbol{r})$ is zero outside the bonding region and quite negative in the bonding region, leading to a $t^x(r)$ term which is positive outside and negative inside the bonding region. In fact, the interchange term of T^x is negative only in a sphere of diameter R passing through both nuclei.

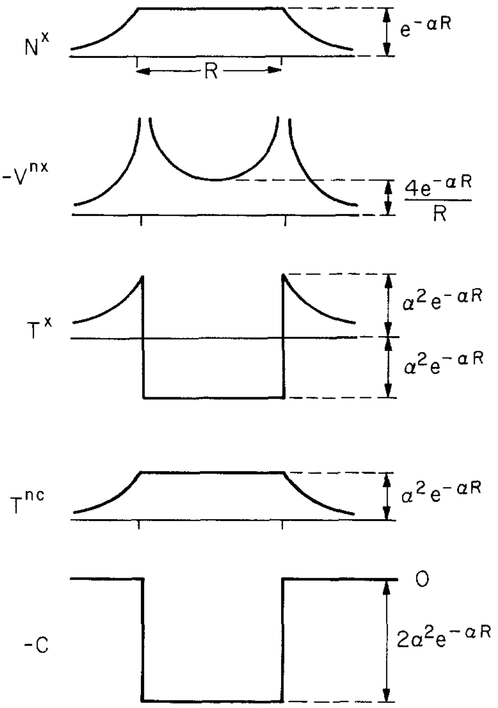

Fig. 2. The interchange part of the integrand of various operators using the frozen G1 wavefunctions of H_2

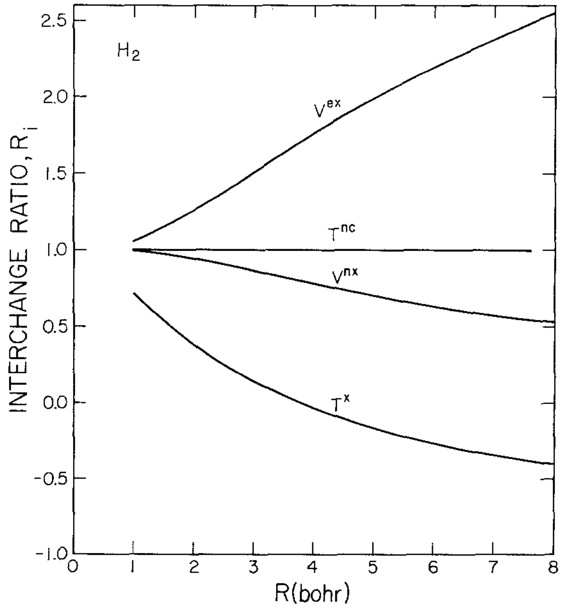

Fig. 3. Ratio of the interchange term to the noninterchange term in the expressions for T^x, V^{nx}, V^{ex}, and T^{nc} as a function of R using the frozen wavefunction of H_2. A ratio of 1.0 corresponds to exact cancellation, a negative ratio corresponds to enhancement of the quantity

As will be discussed below, a consideration of the contragradience function $c(r)$ leads to a reasonable indication of which region of space contributes most to the bond.

In Fig. 3 we show the ratio, R_i, of the interchange term to the non-interchange terms as a function of internuclear distance (frozen H_2) for T^x, V^{nx}, and the exchange electron-electron interaction energy

$$V^{ex} = -SD\left\{[aa|bb] - \frac{1}{S}[ab|ab]\right\}, \tag{12}$$

where $[aa|bb]$ and $[ab|ab]$ are the Coulomb and exchange integrals. For V^{nx} and V^{ex} we have $R_i \leqq 1$, and thus $V^{nx} \geqq 0$ at all distances. Only for T^x is $R_i \leqq 1$, and consequently $T^x \leqq 0$ at all distances. As a result of these effects, T^x is inordinately large in molecules.

In summary, for H_2 T^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^x.

So far we have examined the energy changes for frozen orbitals. For each fixed R we should now allow the orbitals to readjust self-consistently. Since C dominates the ΔE we would expect the self-consistency readjustments of the orbitals to also modify C. In fact for H_2 the change in C in proceeding from the frozen wavefunction to the SCF wavefunction is small for larger R, and even at $R_e = 1.4a_0$ the change in proceeding from the minimum basis SCF result to the large basis (optimized basis with s, p, and d functions) SCF result is only 1% (see Table 2 of I).

B. Comparison with Other Descriptions

The lowering of the kinetic energy associated with chemical bonding has been observed by a number of workers starting with Hellmann [5] who viewed molecule formation as an expansion of the effective confines of the valence electrons, thereby decreasing their kinetic energy. A more quantitative description was provided by Feinberg and Ruedenberg [6] who partitioned the kinetic energy of H_2^+ into contributions parallel and perpendicular to the bond axis. In confirmation of Hellmann's original suggestion, they found a large decrease in the parallel contribution, $T_{||}$, while the perpendicular components $T_{\perp}$ maintained essentially unchanged (from the value for the separated atoms). They traced this effect to the small magnitude of $\partial\phi/\partial z$ in the region between the nuclei (ϕ is the wavefunction and z is parallel to the internuclear axis); in fact, the decrease occurs predominately in the portion, $T_{||}^{b}$, of $T_{||}$ arising from the bond region.

Our previous analysis [1] of the frozen wavefunction of H_2^+ differs from our above treatment of frozen H_2 only in the form of the density matrix D; hence the effects described by Fig. 2 carry over to the H_2^+ case. Clearly then for H_2^+, C contains the same kinetic energy annihilating effect as does $T_{||}^{b}$. The shape of $C(r)$ shown in Fig. 2 has about the same shape for all σ bonds. Consequently, we expect the conclusions of Feinberg and Ruedenberg about $T_{||}^{b}$ to be correct also for σ bonds of many-electron systems even though the corresponding $\{\partial\varphi_i/\partial z\}$ need not decrease drastically between the nuclei. It should also apply to polyatomic systems where the bond region may not be readily definable.

C. *Other Two-Electron States*

So far in this section only the singlet state of H_2 has been considered. For a two-electron triplet state the G1 spatial wavefunction is

$$\Phi^{\mathrm{sp}} = O_{11}ab = \tfrac{1}{2}[e-(12)]ab = \tfrac{1}{2}(ab-ba)\,, \tag{13a}$$

[cf. Eq. (1)] and thus the off-diagonal element of the orbital density matrix becomes [2]

$$D = -\frac{S}{(1-S^2)} \tag{13b}$$

rather than as in (2a). All the quantities (1)–(12) will have the same form, but now D is negative. Hence the contragradience is still dominant but now *opposes* bond formation.

For a given pair of frozen orbitals the contragradient part of the energy is

$$-\frac{SC}{1+S^2} \tag{14a}$$

for the singlet state and

$$+\frac{SC}{1-S^2} \tag{14b}$$

for the triplet state. For a typical bond distance $(1.4a_0)$ and pair of bonding valence orbitals, $S \sim 0.7$ so that the magnitude of (14b) is about three times that of (14a). Thus antisymmetric coupling of orbitals as in (13a) is three times as antibonding as symmetric coupling (1) would be bonding.

Since C opposes bonding for the triplet state, we may expect that the changes in ϕ_a and ϕ_b upon going from frozen to SCF will now be such as to minimize the magnitude of C. In fact this is the case and for many-electron systems, similar arguments can be used in understanding the changes that occur as orbitals readjust self-consistently.

D. *Atoms and Ions*

We have considered pairs of orbitals centered at different points and found that if each orbital decreases monotonically, then the orbitals are contragradient in the bonding region and lead to a positive value of

$$\left[\langle a|t|a\rangle + \langle b|t|b\rangle - \frac{2}{S}\langle a|t|b\rangle\right].$$

However, if both orbitals are centered on the same center this need not occur. Consider a two-electron singlet state as in He or H^-. Here each orbital is spherically symmetric and monotonically decreasing. Thus

$$\nabla\phi_a \cdot \nabla\phi_b = |\nabla\phi_a|\,|\nabla\phi_b|$$

everwhere and C is identically zero; that is, there is no contragradience. Since it is C that makes T^x so important for molecules, it may be that completely different parts of the energy are important for the stability of atoms and ions.

E. Larger Systems

For systems with more electrons, the projection operator O_{11} involved in the wavefunction is more complicated and involves many permutations. However, as shown in Appendix A, T^x can still be discussed in terms of pair contributions, each of which has the form of (2b). Just in the above comparison of the singlet and triplet states of two electrons, the sign of T^x is generally determined by the corresponding permutation numbers, $U_{11\tau}$, in the projection operator and thus by the tableau, as will be discussed in the next section.

3. The Effect of the Pauli Principle on Bond Formation

The Pauli Principle (PP) states that the total wavefunction of a collection of identical particles must be either *symmetric* (in which case, the particles are called Bosons) or *antisymmetric* (where they are called Fermions) under transposition of the particle coordinates (spatial and spin). Which way the wavefunction behaves is determined by the spin of the particles-integral spin leads only to symmetric wavefunctions; half-integral spin leads only to antisymmetric wavefunctions [7]. We will be interested here in electronic systems and hence with Fermion wavefunctions.

To a good approximation in small molecules, the Hamiltonian may be taken to be independent of spin, so that the energy will depend only on the spatial part of the wavefunction. However, for a given spin symmetry, the PP fixes the permutational symmetry of the spatial part of the wavefunction and thereby determines the form of the energy [3]. For example, for two electrons a singlet spin function is antisymmetric, and thus for Fermions the spatial part of the wavefunction must be symmetric (Fig. 4a) in order that the total spatial-spin wave-

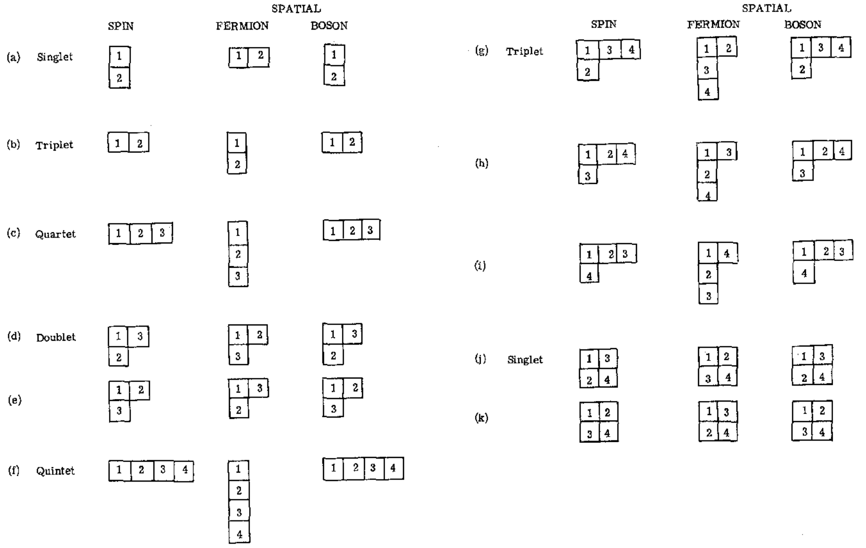

Fig. 4. The spin and spatial tableaux for two, three, and four particle wavefunctions for both Fermion and Boson systems

function be antisymmetric. On the other hand, if electrons were spin-$\frac{1}{2}$ Bosons [7], the spatial wavefunction would have to be antisymmetric (Fig. 4a). Similarly, a two-electron triplet spin function is symmetric; therefore, the Fermion spatial function must be antisymmetric and the Boson spatial function must be symmetric (Fig. 4b).

For more than two particles, discussions of this type are most simply carried out in terms of the Young Tableaux (see Fig. 4), which graphically indicate the permutational symmetry [2, 3]. Here, successive numbers in the same column of a tableau indicate antisymmetrization, and successive numbers in the same row indicate symmetrization (see Ref. [3] for further discussion of the tableaux). For Bosons the spatial and spin tableaux must be the same in order for the total wavefunction to be symmetric, whereas for Fermions these tableaux must be conjugates (that is, related by the interchange of the rows and columns) in order for the total wavefunction to be antisymmetric. The spin tableaux have at most two rows since the spin transformation space is two-dimensional. As a result, the spatial tableaux for Boson wavefunctions can have no more than two rows and those for Fermion wavefunctions can have no more than two columns.

It is well known [8] that for a spin-free Hamiltonian with no nonlocal interactions, the spatial part of the ground state wavefunction is symmetric unless it is forbidden to be so by the PP. Thus we should expect the ground state of a two-Fermion system (spin-$\frac{1}{2}$) to be a singlet state and that of two spin-$\frac{1}{2}$ Bosons to be a triplet state (see Fig. 4ab). The restriction that the spin tableaux have at most two rows for spin-$\frac{1}{2}$ particles implies that for Fermions the spatial tableaux have no more than two columns. Thus for more than two Fermions, the spatial state *cannot* be totally symmetric. For Bosons no such restriction arises, and we would expect the ground state to be a quartet for three particles, a quintet for four particles, *etc.* (see Fig. 4).

A. The Partition of T^x

As shown in Appendix A the exchange part of the kinetic energy can be written as

$$T^x = \sum_{j>k} T^x_{jk} \tag{15}$$

for GI type wavefunctions, where the pair term T^x_{jk} has the form

$$T^x_{jk} = -\sigma_{jk}\tau_{jk}\,, \tag{16}$$

the factor τ_{jk} has the form

$$\tau_{jk} = \left[\langle j|t|j\rangle + \langle k|t|k\rangle - \frac{2}{S_{jk}}\langle j|t|k\rangle\right] \tag{17}$$

[identical with the bracketed factor of (2a)], and σ_{jk} has the form

$$\sigma_{jk} = -D_{jk}S_{jk} \tag{18}$$

Table 1. The diagonal matrix elements $U_{ii(jk)}$ for the various transpositions (jk)

Partition	$[1^2]$	$[2]$	$[1^3]$	$[2,1]$		$[1^4]$	$[2,1^2]$			$[2^2]$	
Spin	0	1	$\frac{3}{2}$	$\frac{1}{2}$		2	1			0	
Tableau	1 2	1 2	1 2 3	1 2 3	1 3 2	1 2 3 4	1 2 3 4	1 3 2 4	1 4 2 3	1 2 3 4	1 3 2 4
Transposition											
(12)	+1	−1	−1	+1	−1	−1	+1	−1	−1	+1	−1
(13)	—	—	−1	$-\frac{1}{2}$	$+\frac{1}{2}$	−1	$-\frac{1}{2}$	$+\frac{1}{2}$	−1	$-\frac{1}{2}$	$+\frac{1}{2}$
(23)	—	—	−1	$-\frac{1}{2}$	$+\frac{1}{2}$	−1	$-\frac{1}{2}$	$+\frac{1}{2}$	−1	$-\frac{1}{2}$	$+\frac{1}{2}$
(14)	—	—	—	—	—	−1	$-\frac{1}{2}$	$-\frac{5}{6}$	$+\frac{1}{3}$	$-\frac{1}{2}$	$+\frac{1}{2}$
(24)	—	—	—	—	—	−1	$-\frac{1}{2}$	$-\frac{5}{6}$	$+\frac{1}{3}$	$-\frac{1}{2}$	$+\frac{1}{2}$
(34)	—	—	—	—	—	−1	−1	$-\frac{1}{3}$	$+\frac{1}{3}$	+1	−1

[cf., Eq. (2a)]. Usually σ_{jk} of (18) is dominated by the term [9]

$$\sigma_{jk} \sim -U_{ii(jk)} S_{jk}^2 , \tag{19}$$

where $U_{ii(jk)}$ is the number specifying the coefficient of the (jk) exchange term in the many-electron wavefunction; the coefficients for various two, three, and four electron systems are given in Table 1 and are easily obtained from a consideration of the tableaux [3].

We will be interested in the intermolecular potentials and hence in the change in the energy, ΔE, as atoms are brought together. Assuming that ΔE is dominated by ΔT^x, we will want to examine the contributions to ΔT^x. Since

$$T_{jk}^x \sim -U_{ii(jk)} S_{jk}^2 \tau_{jk} \tag{20}$$

we expect (especially for the frozen wavefunctions) that the largest changes with internuclear distance will occur for terms for which orbitals ϕ_j and ϕ_k are on different atoms. Of these interatomic T_{jk}^x terms, we expect binding contributions from pairs for which $U_{ii(jk)} > 0$ and antibonding contributions from pairs for wich $U_{ii(jk)} < 0$.

B. The HeH *and* H_2H *Systems*

Consider, for example, the HeH system at large separations. At infinite separation the He and H atoms are independent, with the spatial symmetry of the He atom described by the tableau

$$\boxed{1}\boxed{2} \tag{21}$$

(since He is in the singlet state). The third electron of HeH ($R = \infty$) can be coupled to the He function in two ways,

$$\begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline \end{array} \tag{22}$$

and

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array} \tag{23}$$

The interatomic exchange terms $U_{11(13)}$ and $U_{11(23)}$ are positive $(+1)$ for (22) and negative $(-\frac{1}{2})$ for (23) (see Table 1); hence we expect

$$\Delta T_{13}^{x} < 0, \quad \Delta T_{23}^{x} < 0$$

for (22) and

$$\Delta T_{13}^{x} > 0, \quad \Delta T_{23}^{x} > 0$$

for (23). Thus the wavefunction for (22) should be bound and the wavefunction for (23) should be unbound.

As shown in Table 2, the ΔT^x and ΔE have the signs expected. In addition we note that ΔT^x for (23) is $-\frac{1}{2}$ times the ΔT^x for (22) as expected from the magnitudes of the interatomic $U_{ii(jk)}$. Consistent with this we see that (22) is more stable than (23) is unstable.

Indeed, we would have expected the wavefunction of symmetry (22) to have the lowest energy since it is totally symmetric. However for Fermions (22) is forbidden by the PP. Thus the ground state Fermion wavefunction must be described

Table 2. Comparison of the Energies for HeH, H_2H, H_2H_2, HeH_2, and HeHe with Boson and Fermion spin-one-half electrons. In all cases the orbitals were frozen as the solutions for infinite separation. Here Δ refers to the energy at finite R minus the energy for $R = \infty$

	Fermions		Bosons	
System	ΔE[a]	ΔT^x[a]	ΔE[a]	ΔT^x[a]
HeH[b]	+0.001114	0.006488	−0.003018	−0.012844
H_2H linear[c]	+0.001693	0.009738	−0.004879	−0.01903
H_2H nonlinear[d]	+0.001823	0.010344	−0.005235	−0.020191
H_2H_2 linear[e]	+0.001009	0.005796	−0.002436	−0.011472
HeH_2 linear[f]	+0.000460	0.003119	−0.001212	−0.006214
HeHe[g]	+0.000148	0.001221	−0.000382	−0.002439

[a] E is the total energy and T^x is the exchange part of the kinetic energy. Atomic units are used throughout, $e = \hbar = m_e = 1$; in these units 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., DuMond, J. W. M.: Rev. mod. Physics **37**, 537 (1965).

[b] $R = 4.643$.

[c] H_2 bond length = 1.4304242, the distance from the free H to the closest H of H_2 is 4.285.

[d] Same as c with the angle between the H_2 axis and the vector from middle to third $H = 30°$.

[e] H_2 bond length = 1.4304242, IMD = 4.285 (IMD is the distance between midpoints of the H_2 molecules) [10].

[f] H_2 bond length = 1.4304242, IMD = 4.643.

[g] He_2 bond length = 5.0.

by (23) while the ground state spin $-\frac{1}{2}$ Boson wavefunction is described by (22). In the following, we will refer to (22) as the Boson wavefunction and (23) as the Fermion wavefunction.

For the system H_2 and D at infinite separation the H_2 part of the wavefunction is described by the tableau (21) and the possible tableaux for H_2D are (22) and (23). Thus at large separations the above discussion of HeH applies also to H_2D. As expected the results in Table 2 show that for the frozen wavefunctions of H_2D the Boson wavefunction leads to a bound state while the Fermion wavefunction leads to repulsion between the H_2 and D.

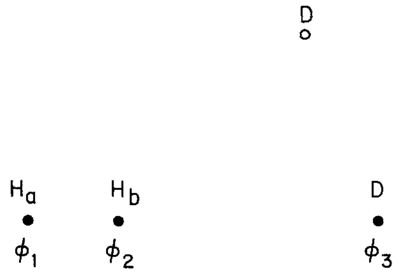

Fig. 5. Geometries for H_2D. The location of each orbital is indicated

For H_2 and D we also can vary the angle between the D and H_2. Consider the geometries indicated in Fig. 5, where D is moved from the linear configuration while maintaining a fixed H_b-D distance. In this case for the frozen wavefunction ΔT_{23}^{x} is nearly unchanged since ϕ_2 and ϕ_3 are the same distance apart (some changes occur due to the presence of a term in D_{23} involving the overlap of ϕ_1 and ϕ_3). However large changes should occur in ΔT_{13}^{x} since ϕ_1 and ϕ_3 move closer together, leading to an increased overlap, S_{13} (since τ_{jk} is dominated by the diagonal terms of (17), we expect only small changes in τ_{13}). From (20) we expect for such nonlinear distortions, that ΔT_{13}^{x} will become more negative in the Boson case and more positive in the Fermion case. Thus for Fermions the most favorable geometry should be linear, and for Bosons the bent geometry should be favored. As shown in Table 2 this is the case. (On the basis of such arguments with frozen wavefunctions one would expect the optimum geometry for Boson H_3 to be an equilateral triangle.) Thus even fine structural details are reflected by T^{x}!

C. The He_2, H_2He, *and* H_2H_2 *Systems*

Now consider He_2 at large separations. At infinite separation we have two independent He atoms described by the tableaux

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline \end{array} \quad \text{and} \quad \begin{array}{|c|c|}\hline 3 & 4 \\ \hline \end{array} \tag{24}$$

respectively. Two ways of coupling these tableaux are

$$\begin{array}{|c|c|c|c|}\hline 1 & 2 & 3 & 4 \\ \hline \end{array} \tag{25}$$

and

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline \end{array}\,. \tag{26}$$

Here (25) should have the lowest energy and should lead to binding, but is allowed only for Bosons. For Fermions the lowest allowed state is (26).

The intermolecular terms now involve the pairs

$$13,\ 14,\ 23, \text{ and } 24$$

each of which leads to $U_{11\pi} = +1$ for (25) and $U_{11\pi} = -\frac{1}{2}$ for (26) (see Table 1). Thus we expect

$$\Delta T^{x} < 0 \quad \text{and} \quad \Delta E < 0$$

for (25) and

$$\Delta T^{x} > 0 \quad \text{and} \quad \Delta E > 0$$

for (26). These expectations are verified by Table 2.

For H_2 and He or H_2 and H_2 the tableaux at infinite internuclear separation are also as in (24) so that the relevant four-electron tableaux are again (25) and (26). Thus for Bosons we obtain binding and for Fermions we obtain repulsion. Fixing the shorter H-He distance and moving the He off axis we see that (just as for H_2D) the Boson wavefunction favors nonlinear geometries for H_2He while the Fermion wavefunction favors linear geometries. Similarly for H_2 and D_2 if the closest H-D distance is fixed and the positions of the other H and D are varied, we see that the Boson wavefunction favors nonlinear geometries while the Fermion wavefunction favors the linear geometry [10].

D. The LiH *Molecule*

The Li^+ ion is a singlet state and is described by the tableau (21). Since the core orbitals ϕ_1 and ϕ_2 of Li^+ should be essentially the same in Li atom, we expect (correctly [11]) the tableau for Li atom to be

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}\,, \tag{27}$$

where ϕ_3 refers to the valence orbital. For Li and H at infinite separation the allowed tableaux for Fermions are then

$$\underset{(28)}{\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline \end{array}} \quad \text{and} \quad \underset{(29)}{\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & \multicolumn{1}{c}{} \\ \cline{1-1} 4 & \multicolumn{1}{c}{} \\ \cline{1-1} \end{array}}\,,$$

where ϕ_4 refers to the H_{1s} orbital. Here (28) describes a singlet state while (29) describes a triplet state. The intermolecular terms involve the pairs

$$14,\ 24,\ \text{and}\ 34;$$

however ϕ_1 and ϕ_2 being Li core orbitals are much more concentrated near the Li nucleus than is the valence orbital ϕ_3. Thus we expect

$$S_{34} \gg S_{14}, S_{24}$$

and for sufficiently large distances

$$|\Delta T^{x}_{34}| \gg |\Delta T^{x}_{14}|,\ |\Delta T^{x}_{24}|.$$

For (28)

$$U_{11(34)} = +1$$

while for (29)

$$U_{11(34)} = -1.$$

Thus from (20) we expect the singlet state of LiH to be bound while the triplet state should be unbound, in agreement with calculations [12] and experiment.

For very short distances we would also have to consider ΔT^{x}_{14} and ΔT^{x}_{24} (note that $\tau_{14}, \tau_{24} \gg \tau_{34}$) both of which are positive for (28) and (29). Thus when the H orbital starts penetrating the Li core we expect new large repulsive terms and consequently a steeply repulsive energy curve. At larger distances the non-involvement of ΔT^{x}_{14} and ΔT^{x}_{24} is consistent with the usual assumption that the core orbitals are not involved in the binding.

E. Interaction between Triplet State Molecules

So far we have examined interactions between systems A and B where A and B are both singlet states or both doublet states or one of each. Now we consider separated systems both of which are triplet states. We will consider A and B to each have two electrons so that the tableaux at infinity will correspond to

$$\begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline \end{array} \quad \text{and} \quad \begin{array}{|c|}\hline 3 \\ \hline 4 \\ \hline \end{array}$$

[e.g., He(^3S) plus He(^3S)] although a more interesting example would be two ground state methylenes, $CH_2(^3B_1)$, combining to form ethylene. At infinite separation the possible tableaux are

$$\underset{(30)}{\begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline 4 \\ \hline \end{array}} \qquad \underset{(31)}{\begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & 4 \\ \hline \end{array}}$$

and the combination

$$\sqrt{\frac{2}{3}}\;\begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1} 4 \\ \cline{1-1}\end{array} \;-\; \frac{1}{\sqrt{3}}\;\begin{array}{|c|c|}\hline 1 & 4 \\ \hline 2 \\ \cline{1-1} 3 \\ \cline{1-1}\end{array} \tag{32}$$

such that $U_{ii(34)} = -1$. The intermolecular terms involve the pairs

$$13,\ 14,\ 23,\ \text{and}\ 24$$

for which

$$\begin{aligned} U_{11\pi} &= -1 && \text{for (30)} \\ U_{11\pi} &= +\tfrac{1}{2} && \text{for (31)} \\ U_{11\pi} &= 0 && \text{for (32)}\,. \end{aligned} \tag{33}$$

and

Thus the quintet state should be quite repulsive, the singlet state should be quite attractive, and the triplet state binding should be determined by higher order terms [13] and self-consistency effects (to become attractive). These conclusions are in agreement with the results of Klein [14] on He(^3S) plus He(^3S). For the interactions of two triplet methylenes we would expect from these considerations that the singlet potential curve should be attractive with no hump at large R.

F. Summary

Considering the above results for Fermion and Boson systems, we see that interacting species A and B are expected to lead to attractive terms when the combined tableau contains electrons in the same row originating on different species, as in (25), (28), and (31). Repulsive terms result when electrons in *different* rows originate on different species, as in (26), (29), and (30). Analyzing these interactions in terms of ΔT_{jk}^{x} for the frozen wavefunctions allows one to predict stabilities and geometries of molecules without detailed computations.

4. Contragradience and the Bond Region

Since the structure and properties of large molecules can generally be rationalized in terms of bonds each localized near a pair of atoms, one would expect that the part of the wavefunction important for a particular bond would be just the part in between (or near) the pair of nuclei. However despite the intuitively clear idea of where the bond region is, it has not been easy to obtain a useful quantitative definition of the bond region. For example, one definition used for diatomic molecules is the region enclosed by the parabolas $-\eta_0 \leqq (r_a - r_b)/R \leqq \eta_0$, where η_0 is an adjustable parameter [6, 14, 15]. By this definition, the bond region includes points infinitely far from either nucleus, contrary to the usual chemical concept. Such a definition leads to obvious problems for polyatomics (for example, empirically established rules such as bond additivity clearly require a finite bond region).

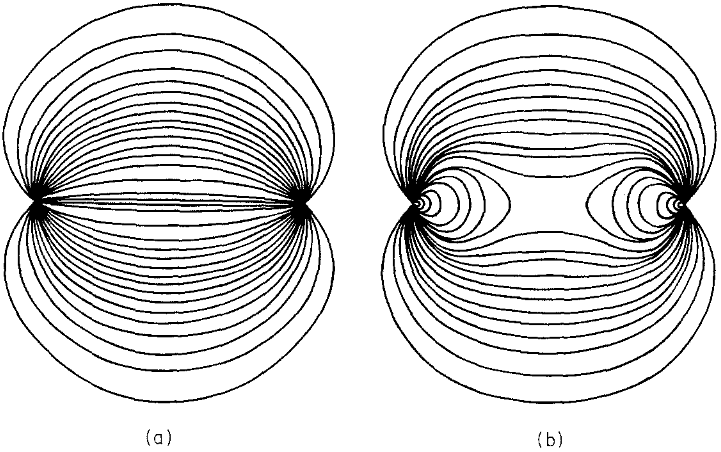

Fig. 6a and b. The contragradience function for the G1 wavefunction of H_2 at $R = 1.4$. (The contours are equally spaced starting at 0.0045 a.u. for the outer contour with increments of 0.0045 a.u.). a Frozen wavefunction. b SCF wavefunction (eight basis functions)

On the other hand, an examination of T^x and the contragradience yields a useful criterion for the bond region. In Section 2, we found that the main contribution to ΔT^x arises from the contragradient nature of the orbitals in the region between the nuclei. We also saw that it is the large drop in the contragradience part of T^x which is reponsible for bond formation. Indeed we might almost say that it is this contragradient nature of the orbitals which is responsible for bonding. Thus it would seem appropriate to consider the regions of largest contragradience to be the regions most important to bonding. This would lead to a natural definition of the bond region as that part of space containing, say, 80% of the contragradience. In Fig. 6 we show the plots of the contragradience for the frozen and SCF (eight basis function) wavefunctions of H_2 for $R = 1.4$. (The regions shown here include about 80% of the total contragradience.) We see that despite the large changes in the wavefunctions due to self-consistency, the contragradience is relatively unchanged except in the heart of the bond region. More importantly the resulting picture of the bond is rather close to the intuitive idea of what a bond is.

Similarly for a pair of orbitals exhibiting antibonding, the plot corresponding to Fig. 6 would display the region important in the antibonding interactions. (The SCF contragradience would be greatly reduced and would differ greatly from Fig. 6b.)

5. Discussion

First we will summarize some of the conclusions from the previous sections.

It is the change in the exchange kinetic energy, ΔT^x, which determines whether a molecular system will be stable, and it is the contragradient part of ΔT^x, which is primarily responsible for this. The contragradience function, $c(\boldsymbol{r})$, for a pair of orbitals is just the product of the magnitudes of the gradients of the two orbitals minus the dot product of the gradients. Thus for a bonding pair such as H_2, $c(\boldsymbol{r})$ favors binding in the region in which the orbitals are contragradient, namely the region between the nuclei and close to the axis. Thus by defining the bond as the region where $c(\boldsymbol{r})$ is large, we arrive at something rather close to the intuitive idea of where the bond is.

As Ruedenberg [17] (also see Ref. [1]) has discussed elsewhere, the bond does not result from electrostatic considerations (such as putting the electron where it can attract both nuclei) [18]. Rather we find that the strength of a bond is determined by the existence of a region in which the orbitals on the two atoms have large slopes in oblique directions, i.e., where the contragradience is large. In general, we find that the sign of ΔT^{x} is determined by consideration of the tableau appropriate for the spin symmetry of the system being considered. In particular the ΔT^{x} can be partitioned into terms arising from various pairs, and for the case of frozen orbitals, the sign of each intermolecular component can be predicted from the tableau. When the combined tableau is G1 [e.g. (26)] this sign is positive for a pair in the same row of the tableau and negative for a pair from different rows. Thus closed-shell systems repel each other because the intermolecular pair terms, T^{x}_{jk}, involve orbitals in different rows.

From these considerations we would view the aspects important for bond formation in terms of the following steps: (1) freeze the orbitals of the separated atoms; (2) bring the atoms together to their positions in the molecule (this leads to T^{xF} and to about the correct binding energy); and (3) allow the orbitals to relax to their SCF forms. In step (3) the orbitals rehybridize somewhat and contract more about each nucleus but also spreading onto the other centers, readjusting the various nuclear attraction, electron repulsion, the 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 ΔT^{xF}, through a decrease in the contragradience contribution to the energy.

Appendix A: The Partition of T^{x}

The spatial part of the GI wavefunctions has the form

$$O_{ii}\Phi \tag{A-1}$$

where Φ is a product of orbitals and O_{ii} is the permutational operator [2, 3]

$$O_{ii} = \frac{1}{\theta^{\gamma}} \sum_{\pi \in \mathscr{S}_N} U_{ii\pi}\pi \,. \tag{A-2}$$

Here the $U_{ii\pi}$ is the ii matrix element of the representation matrix for the permutation π (see Table 1 for the values of some $U_{ii\pi}$).

The kinetic energy, T, of the wavefunction (A-1) is given by

$$T = \left\langle \Phi \middle| \sum_{j=1}^{N} t_j \middle| O_{ii}\Phi \right\rangle / \langle \Phi | O_{ii}\Phi \rangle \,, \tag{A-3}$$

where t_j is the one-electron kinetic energy operator, $-\frac{1}{2}\nabla^2$, for electron j. Eq. (A-3) is expanded as

$$T = \sum_{j,k=1}^{N} D_{jk} \langle \phi_j | t | \phi_k \rangle \tag{A-4}$$

in terms of the *orbital density matrix*, [19] D_{jk}, which depends upon the representation matrices $U_{ii\pi}$ and upon the overlaps of the various orbitals. For most cases of interest to us here [see, for example (A-13) to (A-16)] D_{jk} is dominated by the term

$$D_{jk} \sim U_{ii(j,k)} S_{jk} \tag{A-5}$$

where S_{jk} is the overlap of orbitals ϕ_j and ϕ_k.

Next we consider the partition of the exchange kinetic energy (T^{x}) into pair terms, T^{x}_{jk}. The classical part of T is defined as

$$T^{\mathrm{Cl}} = \sum_{j=1}^{N} \langle j | t | j \rangle \,. \tag{A-6}$$

Thus since the total kinetic energy is given by (A-4), we obtain [20]

$$T^{\mathrm{x}} \equiv T - T^{\mathrm{Cl}} = \sum_{j>k}^{N} 2 D_{jk} \langle j | t | k \rangle - \sum_{i}^{N} (1 - D_{jj}) \langle j | t | j \rangle$$

But by the definition of D_{jk} (see Ref. [2]),

$$\sum_j D_{jk} S_{jk} = 1$$

for any k. Thus we obtain

$$T^{\mathrm{x}} = \sum_{j>k}^{N} T^{\mathrm{x}}_{jk} \,, \tag{A-7}$$

where

$$T^{\mathrm{x}}_{jk} \equiv D_{jk} \{ 2 \langle i | t | k \rangle - S_{jk} [\langle j | t | j \rangle + \langle k | t | k \rangle] \} \,. \tag{A-8}$$

When $S_{jk} \neq 0$, it is more convenient to define

$$\tau_{jk} = \left[\langle j | t | j \rangle + \langle k | t | k \rangle - \frac{2}{S_{jk}} \langle j | t | k \rangle \right] \tag{A-9}$$

and

$$\sigma_{jk} = D_{jk} S_{jk} \tag{A-10}$$

so that

$$T^{\mathrm{x}}_{jk} = -\sigma_{jk} \tau_{jk} \,. \tag{A-11}$$

In this case if orbitals j and k are on different centers, τ_{jk} is relatively insensitive to the internuclear separation and only σ_{jk} varies rapidly with distance. From (A-5) the leading term of σ_{jk} is

$$\sigma_{jk} \sim U_{ii(j,k)} S^2_{jk} \,. \tag{A-12}$$

So that the sign of T^{x}_{jk} is determined by the sign of $U_{ii(j,k)}$.

For convenience in the discussions in this paper we list below the σ_{jk} for several tableaux. For a two-electron singlet state. (see Fig. 4a)

$$\sigma_{12} = S^2_{12} / (1 + S^2_{12}) \,. \tag{A-13}$$

For a two-electron triplet state (see Fig. 4b)

$$\sigma_{12} = -S_{12}^2/(1-S_{12}^2)\,. \tag{A-14}$$

For a three-electron doublet state (see Fig. 4d)

$$\left.\begin{aligned}
\sigma_{12} &= S_{12}^2(1-\tfrac{1}{2}S_{13}S_{23})/N_3\\
\sigma_{13} &= -\tfrac{1}{2}S_{13}^2(1+S_{12}S_{23})/N_3\\
\sigma_{23} &= -\tfrac{1}{2}S_{23}^2(1+S_{12}S_{13})/N_3\\
\text{where}\qquad N_3 &= 1+S_{12}^2-\tfrac{1}{2}S_{13}^2-\tfrac{1}{2}S_{23}^2-S_{12}S_{13}S_{23}\,.
\end{aligned}\right\} \tag{A-15}$$

For a four-electron singlet state (see Fig. 4*j* and 4*k*)

$$\begin{aligned}
\sigma_{ij} = S_{ij}(S_{ij} &- \tfrac{1}{2}S_{ik}S_{kj} - \tfrac{1}{2}S_{il}S_{lj} - \tfrac{1}{2}S_{il}S_{lk}S_{kj}\\
&- \tfrac{1}{2}S_{ik}S_{kl}S_{lj} + S_{ij}S_{kl}^2)/N_4
\end{aligned} \tag{A-16a}$$

and

$$\begin{aligned}
\sigma_{ik} = -\tfrac{1}{2}S_{ik}(S_{ik} &+ S_{ij}S_{jk} + S_{il}S_{lk} + S_{ij}S_{jl}S_{lk}\\
&- 2S_{ik}S_{jl}^2 - 2S_{il}S_{lj}S_{jk})/N_4
\end{aligned} \tag{A-16b}$$

where i and j are in one row and k and l are in the other. Here

$$N_4 = \sum_{m=1}^{4} \sigma'_{nm}$$

for any n, where $\sigma'_{nm} = \sigma_{nm}N_4$ [that is, σ'_{nm} is the numerator in (A-16)]. Thus

$$N_4 = N_3 + \sigma'_{14} + \sigma'_{24} + \sigma'_{34}\,,$$

which is useful in considering LiH at large R. For a system where both S_{12} and S_{34} are large and the S_{ik} are small, then

$$N_4 \sim (1+S_{12}^2)(1+S_{34}^2)\,.$$

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19. We denote the orbital density matrices as D_{jk} rather than D_k^j as in Ref. [2]. In addition, the normalization terms are now included in D_{jk}.
20. Taking the orbitals to be real.

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