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In-Bond Orbitals: A Comprehensive Graphical Expression of Orbital Interaction

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The minimal linear-combination-of-atomic-orbitals (LCAO) has a clear chemical meaning, namely, that a molecular orbital consists of atomic orbitals of the member atoms. In organic chemistry, this concept has been applied to graphical expression of orbital interactions. However, the minimal LCAO method is inadequate to illustrate such interatomic interactions. Based on a general idea in quantum chemistry, we have proposed pictorial "in-bond orbitals" to compensate for the shortcomings of the minimal LCAO scheme without destroying its simple concept. In-bond orbitals well express the qualitative electronic structures of bonding and antibonding internuclear regions. Furthermore, they are continuously correlated with the AOs of the united atom. In this paper, (1) we discuss the conceptual problems of the minimal LCAO expression in interaction between atoms, (2) we show the importance of the contribution of AOs with higher quantum numbers to the chemical interaction nominally given by AOs with the lowest quantum number, (3) we show that the introduction of a minimal number of in-bond orbitals is a simple method to solve the continuity problem of the correlation diagram and to improve the electronic structure, (4) a selection scheme for in-bond orbitals is proposed, and (5) as an example, the concept of the in-bond orbital is applied to the prediction of the direction of pyramidalization of the olefinic carbon atoms of norbornene.

The concept that a molecular orbital (MO) consists of a linear combination of atomic orbitals (LCAO) fully agrees with the deep-rooted chemical idea that a molecule consists of atoms. Here, the basic idea is "interaction between atomic orbitals (AOs)". The concept goes back to the early 1930s when the idea of molecular orbital was proposed.[1,2] An MO of a separated-atoms system seems to be well correlated with an atomic orbital of the united atom by the correlation diagram based on the non-crossing rule concerning orbital symmetry.[3] Thus, the idea of "orbital interaction" has been widely applied in chemistry and is most effective in predicting reaction products.[4,5]

However, if one inspects such simple ideas without a preconception of success, unacceptable contradictions will be encountered. An example is given by considering a simple case where two hydrogen atoms give a bonding MO (ψ_g^1) and an antibonding MO (ψ_u^2). According to the simplified correlation diagram of the separated atoms and the united atom, ψ_g^1 gives 1s AO and ψ_u^2 is correlated with 2p AO of the helium atom as the distance (R), approaching zero. The former correlation is acceptable but the latter is not acceptable at all because the AOs have reverse phases and by $R \rightarrow 0$, they must be cancelled out. Another difficulty is the fact that the minimal LCAO can not express correctly the electronic structure of the bonding or anti-bonding regions because they are fixed spherical functions.

To solve such difficulties, extended basis sets wherein basis functions of various sizes and/or those with higher quantum numbers are incorporated, as members in the LCAO, have been prevalent in computational chemistry. Although this incorporation improves the total energy of the system, a problem of how to arbitrarily select those basis functions arises and the simplicity of the concept is negated. In quantum chemistry, the methods that place basis functions between atoms have been frequently used in order not only to obtain lower energetic wave functions but also to express appropriate electronic structures between atoms. The methods range from the floating gaussian function method to the bond function methods.[6—16] Thus, although the methodology itself is not new, we found that if a few ghost AOs (in-bond orbitals) are introduced between atoms and added to the minimal LCAO expansion, a satisfactory graphical expression of the electronic structure of atoms can be attained. This method also provides support for the "lumps" proposed by Ohwada et al. that develop on AOs by mutual interaction.[17—20] In this article, (1) we discuss the conceptual problems of the conventional minimal LCAO expression, (2) we show the importance of AOs with higher quantum numbers to the interaction between AOs even with the lowest quantum number, (3) we show that the introduction of in-bond orbitals is a simple way not only to solve the above-mentioned continuity problem but also to improve the electron distribution, (4) a selection scheme for in-bond AOs is proposed, and (5) as an example, the concept of the in-bond orbital is applied to the prediction of the nonequivalent HOMO extension of norbornene.

Conceptual Problems in the Minimal LCAO Expression Concerning the Formation of New Orbitals (In-Bond Orbitals) Based on the Correlation Diagram of the Separated Atoms and the United Atom

Suppose that two hydrogen atoms, H_a and H_b, are placed on the z axis with distance R. According to the simple correlation diagram, the symmetric interaction of two 1s AOs gives ψ_g^1 which leads to 1s AO of the united atom (He), while antisymmetric interaction of these atoms (ψ_u^2) leads to the $2p_\sigma$ AO. First, we will discuss a conceptual problem of this picture in the minimal LCAO method.

The minimal LCAO method expresses ψ by,

$$\psi = \sum_{r=1}^{n} c_r \chi_r . \qquad (1)$$

Here, χ are atomic orbitals from both atoms and c are the coefficients. For the H_2 system, one bonding (ψ_g^1) and one antibonding orbital (ψ_u^2) are considered:

$$\begin{aligned}\psi_g^1 &= c_1^1\chi_a + c_2^1\chi_b , \\ \psi_u^2 &= c_1^2\chi_a + c_2^2\chi_b . \end{aligned} \qquad (2)$$

They have orbital energies ε_1 and ε_2 and the relationships, $c_1^1c_2^1 > 0$, $c_1^2c_2^2 < 0$ hold.

$$\varepsilon_1 = \frac{1}{2+2S}(h_{aa} + h_{bb} + 2h_{ab}) , \qquad (3)$$

$$\varepsilon_2 = \frac{1}{2-2S}(h_{aa} + h_{bb} - 2h_{ab}) . \qquad (4)$$

Here, S and h_{ab} are

$$S = \int \chi_a\chi_b \mathrm{d}\tau , \qquad (5)$$

$$h_{ab} = \int \chi_a(1)\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_a}{r_{1a}} - \frac{Z_b}{r_{1b}}\right)\chi_b(1)\mathrm{d}\tau_1 . \qquad (6)$$

The physical meaning of h_{aa} or h_{bb} is easily acceptable as the expectation energy of an electron that moves in one atom with a potential from another nucleus.

Let us inspect whether or not the idea that ψ_g^1 gives the 1s AO whereas ψ_u^2 gives the $2p_\sigma$ AO is appropriate to express the reality. When R is 0, χ_a equals χ_b affording $S = 1$. In this case, ε_1 becomes h_{aa} and is the new 1s orbital energy of the united atom (He). On the other hand, as Eq. 4 shows, ε_2 becomes indeterminate (0/0) and it would be found that ψ_u^2 must disappear. Namely, the density probability of ψ_u^2 is expressed by Eq. 7 and when $S_{ab} = 1$, it is null.

$$\int \psi_2^2 \mathrm{d}\tau = \left(c_1^2\right)^2 + \left(c_2^2\right)^2 - 2\left(c_1^2c_2^2\right)S_{ab} = 0 . \qquad (7)$$

This is a natural outcome since waves with opposite phase must be cancelled out. Thus, the conventional correlation diagram between the hydrogen molecule and the helium atom is appropriate in the formation of the helium 1s orbital, but not in the $2p_z$ orbital even though the symmetry is correct.

Contribution of AOs with Higher Quantum Number to Formation of Low-Lying MOs

Homonuclear System: H_2. The contribution of AOs with higher quantum number to formation of low-lying MOs has been pointed out even in the beginning of the interaction.[1—3] Although its importance cannot be overemphasized in practical application, this is liable to be overlooked in organic chemistry, especially in orbital interaction theories. Let us examine the importance of the contribution of AOs with higher quantum number in the case of the H_2 system.

Table 1 shows coefficients of AOs in ψ_g^1 and ψ_u^2 as functions of R when AOs up to 3d AOs (in terms of STO-3G[21]) are incorporated, where coefficients for $2p_x$, $2p_y$, $3p_x$, $3p_y$, $3d_{+1}$, $3d_{-1}$, $3d_{+2}$, and $3d_{-2}$ are always null by a symmetry requirement and are not shown. At any distance, a large contribution from 2s, $2p_z$, $3p_z$ and even 3d orbital ($3d_0$) is observed. Look at the case at $R = 0.7122$ Å (the optimized distance for H_2). Although the coefficients of both 1s AOs are larger than that of any other AO in ψ_g^1, a considerable contribution to ψ_u^2 is found to be from the AOs with larger quantum numbers.[22]

Now consider the united atom. Since the minimal LCAO method gives an indeterminate solution for ψ_u^2 at $R = 0$, let us examine the case at $R = 0.01$ Å, which corresponds to the near united atom state. In ψ_g^1, the AO coefficients of 1s, 2s, 3s, and $3d_0$ belong to the same phase symmetry. Although the coefficients of $2p_z$'s and $3p_z$'s become enormous, they are cancelled out since they have the same values with opposite phases. Consequently, the remaining contribution for ψ_g^1 is only from 1s, 2s, 3s, and a small amount from $3d_0$.

Such an interaction scheme is very different in ψ_u^2, where the contribution from only $2p_z$'s and $3p_z$'s survives: the large contribution from s-type AOs as well as a small amount of contribution from $3d_0$ are exactly cancelled out at the near united atom state. Consequently, it may be said that both ψ_g^1 and ψ_u^2 have large contributions from upper AOs even at the bonding distance and that the $2p_z$ AO in the united atom should be correlated not with 1s AOs but with $2p_z$ (and $3p_z$) AOs of the separated atoms.

A Comprehensive Method for Better Expression of the Internuclear Region. A large contribution from upper AOs in ψ_g^1 and ψ_u^2 even at the bonding distance is a natural outcome to express better electron distributions. However, as already mentioned, inclusion of AOs with a higher quantum number negates the simplicity of orbital interaction. An efficient way is to place appropriate upper AOs as the basis orbitals (in-bond orbitals) somewhere on the line that connects two nuclei, typically at the center of the bond for homonuclear bonding. As for heteronuclear bonding, the in-bond orbitals may be so shifted so as to express the best electronic structure.

The conventional correlation diagram between separated atoms and united atoms tells clearly what kind of in-bond orbital should be selected. For example, for the bonding

Table 1. Contribution of Atomic Orbitals with Higher Quantum Numbers in Forming Molecular Orbitals in the H_2 System[a)]

R[b)]	Total E[c)]			ε[c)]	1s	2s	$2p_z$	3s	$3p_z$	$3d_0$
5.00	−0.764839	ψ^1	a	−0.28262	0.5745	0.0211	0.0033	0.1522	−0.0216	0.0027
			b		0.5745	0.0211	−0.0033	0.1522	0.0216	0.0027
		ψ^2	a	−0.17251	0.5828	0.0268	0.0006	0.1480	0.0129	−0.0015
			b		−0.5828	−0.0268	0.0006	−0.1480	0.0129	0.0015
2.00	−0.919534	ψ^1	a	−0.38666	0.5458	0.0172	−0.0293	0.0682	−0.0083	0.0084
			b		0.5458	0.0172	0.0293	0.0682	0.0083	0.0084
		ψ^2	a	−0.04253	0.5883	−0.0018	0.0268	0.1985	0.1390	−0.0205
			b		−0.5883	0.0018	0.0268	−0.1985	0.1390	0.0205
r_e[d)]	−1.118334	ψ^1	a	−0.59857	0.6627	−0.2419	−0.0995	0.0824	0.0111	0.0237
			b		0.6627	−0.2419	0.0995	0.0824	−0.0111	0.0237
		ψ^2	a	0.13355	1.9387	4.7092	−0.4490	3.1092	−2.0505	0.1423
			b		−1.9387	−4.7092	−0.4490	−3.1092	−2.0505	−0.1423
0.30	−0.624511	ψ^1	a	−0.76670	0.8527	−0.5485	−0.0349	0.1873	0.1036	−0.0069
			b		0.8527	−0.5485	0.0349	0.1873	−0.1036	−0.0069
		ψ^2	a	0.16502	1.2436	4.3179	0.9149	8.5743	−2.3165	−0.0174
			b		−1.2436	−4.3179	0.9149	−8.5743	−2.3165	0.0174
0.10	2.632650	ψ^1	a	−0.85498	0.9900	−0.6914	0.7027	0.2253	0.9069	−0.0594
			b		0.9900	−0.6914	−0.7027	0.2253	−0.9069	−0.0594
		ψ^2	a	0.17362	4.7334	15.3287	0.7385	23.4398	−2.2062	0.0979
			b		−4.7334	−15.3287	0.7385	−23.4398	−2.2062	−0.0979
0.01	50.212242	ψ^1	a	−0.87035	1.0146	−0.7148	8.6272	0.2311	10.2312	−0.0697
			b		1.0146	−0.7148	−8.6272	0.2311	−10.2312	−0.0697
		ψ^2	a	0.17485	49.6389	157.2027	0.6902	227.4440	−2.1675	1.1167
			b		−49.6389	−157.2027	0.6902	−227.4440	−2.1675	−1.1167

a) The nuclei were placed along z axis. All the scale factors of the atomic orbitals are set to be 1.00. b) Internuclear distance in Å. c) In au. d) $r_e = 0.7122$ Å.

orbital (ψ_g^1) between two 1s AOs, a 1s-type orbital may be placed between the atoms, whereas for the antibonding orbital (ψ_u^2), a $2p\sigma$-type orbital is used instead. As a result, representation of the AOs' shape in molecular orbitals is switched to that as shown in Fig. 1.

Figure 1-**a** shows approximate changes of orbital shapes from separated atoms to a united atom. We regard such a change of shape as the result of a superposition of original AOs and in-bond orbitals: At longer R, the contribution of the in-bond orbitals is smaller; however, as R is reduced, such contribution becomes large and, at the united atom, MOs are replaced solely by the in-bond orbitals.

Examination of the New Concept. Here we inspect the new concept using the H_2^{2+} system. Since the SCF procedure obscures the meaning of unoccupied orbitals, we exclude electrons. At the center of R, 1s-, $2p_x$-, $2p_y$-, and $2p_z$-type orbitals were placed as in-bond orbitals (which are marked by the suffix i): each in-bond orbital was expanded by three primitive Gaussian functions with the same scale factor, ζ, for all of them. The nuclear charges of in-bond orbitals are always set at zero. The scale factor was introduced to optimize the size of the in-bond orbital. The molecular orbitals are expressed by linear combinations of in-bond orbitals and two hydrogen 1s AOs.

$$\psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_{i1s} + c_4\chi_{i2p_x} + c_5\chi_{i2p_y} + c_6\chi_{i2p_z}. \qquad (8)$$

Table 2 shows the coefficients of the basis orbitals when the scale factors of in-bond orbitals are optimized to give the lowest orbital energies. The maximum distribution from the functional origin when an electron occupies the in-bond orbital is also shown. Coefficients of χ_5 and χ_6 are null by a symmetry requirement and are not shown.

In the bonding orbital, ψ_g^1, the coefficient of 1s-type in-bond orbital (c_3) increases, while c_1 and c_2 decrease as R decreases. The coefficient for $2p_x$-type in-bond orbital is null because it belongs to a different symmetry group from that of ψ_g^1. The change of the scale factors of the in-bond orbitals indicates that the orbital swells at a larger R and shrinks at a smaller R. This means that the in-bond orbitals are appropriately incorporated to give the proper electronic wave functions.

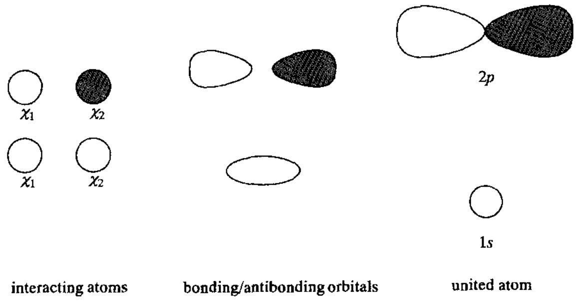
Let us take a qualitative look at the change of coefficients in the antibonding orbital. This time c_3 (1s-type in-bond orbital) is always zero for the same reason mentioned above. The values of c_1 and c_2 become large as the R is shortened and the role of their orbital looks large. However, negative overlap between them nullifies the contributions of the original AOs. (This will be quantitatively discussed in the next section.) As R is shortened, the role of the in-bond orbital becomes larger and, at the united atom, replaces that of the original AOs.

A Quantitative Examination. The electron distribution by such an LCAO wave function as ψ_g^1 or ψ_u^2 is expressed

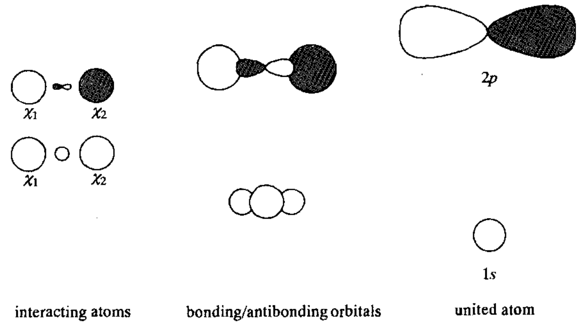
Table 2. Coefficients for Basis Atomic Orbitals in H_2^{2+}

	Bonding orbital (ψ^1)						Antibonding orbital (ψ^2)					
$R^{a)}$	$\zeta^{b)}$	Max$^{c)}$	c_1	c_2	c_3	c_4	$\zeta^{b)}$	Max$^{c)}$	c_1	c_2	c_3	c_4
5.00	0.34	1.5560	0.6617	0.6617	0.1691	0.0000	0.50	2.1170	0.6213	−0.6213	0.0000	0.2086
2.00	0.70	0.7560	0.4917	0.4917	0.3148	0.0000	0.82	1.2910	0.5700	−0.5700	0.0000	0.2775
$r_e^{d)}$	1.67	0.3170	0.4624	0.4624	0.1648	0.0000	1.03	1.0280	0.3617	−0.3617	0.0000	0.7409
0.30	1.73	0.3060	0.1593	0.1593	0.6983	0.0000	1.01	1.0480	0.1887	−0.1887	0.0000	0.9414
0.10	2.00	0.2650	0.0594	0.0594	0.8904	0.0000	0.98	1.0800	0.2919	−0.2919	0.0000	0.9702
0.01	2.16	0.2450	0.0946	0.0946	0.8278	0.0000	0.98	1.0800	2.4823	−2.4823	0.0000	0.9747

a) Internuclear distance in Å. b) Optimized scale factor. c) The distance (in Å.) of the maximum distribution of electron from the origin when an electron occupies the in-bond orbital. That is given by solving the following equation, $\frac{\mathrm{d}}{\mathrm{d}r}[\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\{\chi(r,\theta,\phi)\}^2 r^2 \sin\theta \mathrm{d}\theta \mathrm{d}\phi]=0$. d) $r_e = 0.7122$ Å.



a. Change of orbital shapes from separated atoms to a united atom



b. Concept of in-bond orbitals

Fig. 1. Concept of in-bond orbital (H_2 system as an example). The bulkiness of in-bond orbitals does not mean the spatial one but the degree of contribution.

by

$$\int (\psi^l)^2 \mathrm{d}\tau = \sum_{r,s} c_r^l c_s^l S_{rs}. \tag{9}$$

In the present case l is 1 or 2. If two electrons are included, the bonding orbital (ψ_g^1) consists of χ_1, χ_2, and χ_{i1s}, while the antibonding orbital (ψ_u^2) consists of χ_1, χ_2, and χ_{i2p_x}. Equation 9 is partitioned into three parts. As for ψ_g^1,

$$\begin{aligned} \int (\psi^1)^2 \mathrm{d}\tau &= A+B+C, \\ A &= \left(c_1^1\right)^2 + \left(c_2^1\right)^2 + 2c_1^1c_2^1S_{12}, \\ B &= \left(c_3^1\right)^2, \\ C &= 2c_1^1c_3^1S_{13} + 2c_2^1c_3^1S_{23}. \end{aligned} \tag{10}$$

Concerning ψ_u^2, A, B, and C are similarly defined as,

$$\begin{aligned} A &= \left(c_1^2\right)^2 + \left(c_2^2\right)^2 + 2c_1^2c_2^2S_{12}, \\ B &= \left(c_4^2\right)^2, \\ C &= 2c_1^2c_4^2S_{14} + 2c_2^2c_4^2S_{24}. \end{aligned} \tag{11}$$

Here, A, B, and C are interpreted as the contribution of original AOs, the in-bond orbital, and the mixed term between original and in-bond orbitals.

Table 3 shows A, B, and C as functions of R in ψ_g^1 and ψ_u^2. The contribution of the in-bond orbital in ψ_g^1 (B) increases as R is shortened and has its maximum at around 0.2 Å. At the united atom, 1s AO consists of the in-bond orbital and a small amount of the original 1s AO. The contribution of the in-bond orbital in ψ_u^2 monotonously increases as the system approaches the united atoms at which the in-bond orbital takes place of the $2p_\sigma$ AO. The change in those values assures that the new concept of orbital interaction is very appropriate.

Unlike-Nuclear Interaction: HeH^+. In heteronuclear diatomic systems, there are no centers of symmetry, such as were present in the H_2 system. Now consider the case of such an unlike-nuclear interaction using the HeH^+ system. The fact that the system has no center of symmetry allows mixing of MOs: A simple non-crossing rule predicts that the anti-bonding orbital, ψ^2, must be correlated with the 2s AO in the united atom.[2]

Table 4 shows the contribution of atomic orbitals with higher quantum numbers when forming molecular orbitals in the HeH^+ system under the same computational conditions as those of H_2. Here again, the coefficients for $2p_x$,

Table 3. Contribution of Basis Orbitals to Molecular Orbitals in H_2^{2+}

	Bonding orbital (ψ^1)			Antibonding orbital (ψ^2)		
$R^{a)}$	A	B	C	A	B	C
5.00	0.8758	0.0286	0.0956	0.7719	0.0435	0.1846
2.00	0.5412	0.0991	0.3597	0.5724	0.0770	0.3506
$r_e^{b)}$	0.7175	0.0272	0.2553	0.0842	0.5489	0.3669
0.30	0.0976	0.4876	0.4148	0.0054	0.8863	0.1084
0.10	0.0140	0.7928	0.1932	0.0015	0.9414	0.0571
0.01	0.0358	0.6852	0.2790	0.0011	0.9500	0.0489

a) Internuclear distance in Å. b) $r_e = 0.7122$ Å.

Table 4. Contribution of Atomic Orbitals with Higher Quantum Numbers in Forming Molecular Orbitals in the HeH^+ System[a)]

R[b)]	Total E[c)]			ε[c)]	1s	2s	$2p_z$	3s	$3p_z$	$3d_0$
5.00	−2.814414	ψ^1	a	−1.00756	0.9693	0.0284	−0.0062	0.0402	−0.0012	0.0012
			b		−0.0014	0.0056	0.0034	−0.0067	−0.0060	−0.0009
		ψ^2	a	−0.49483	−0.0005	−0.0021	0.0014	0.0035	−0.0031	0.0005
			b		0.9767	0.0368	0.0006	−0.0138	−0.0012	−0.0001
2.00	−2.819924	ψ^1	a	−1.17329	0.9777	0.0464	−0.0371	0.1442	−0.0752	0.0284
			b		0.0195	−0.0173	0.0252	−0.1170	−0.0912	−0.0089
		ψ^2	a	−0.48158	−0.1334	−0.0492	−0.0227	0.0276	0.0047	0.0060
			b		0.9804	0.0341	−0.0090	−0.0233	−0.0178	−0.0074
r_e[d)]	−2.877823	ψ^1	a	−1.51362	1.0575	0.5292	−0.1558	0.6564	−0.2551	0.0536
			b		0.0417	−0.6967	0.0539	−0.5317	−0.3257	−0.0036
		ψ^2	a	−0.32359	−0.3902	0.0379	−0.1985	0.2018	−0.0723	0.0392
			b		0.7701	−0.1404	−0.1657	−0.0213	−0.1074	−0.0211
0.30	−2.060742	ψ^1	a	−2.17815	−1.4308	−2.3621	−0.0643	−2.4338	0.2537	0.0207
			b		0.2549	2.7672	0.0687	2.1128	0.5767	0.0356
		ψ^2	a	−0.16961	−0.3240	−0.5004	−0.0801	0.4395	−0.1297	0.0242
			b		0.1243	0.3534	0.0767	0.6647	0.0928	0.0255
0.10	4.039794	ψ^1	a	−2.56786	2.2197	6.8507	1.2339	5.0178	0.2280	−0.0778
			b		−1.5336	−6.3929	−1.2796	−4.9436	−0.8738	−0.0754
		ψ^2	a	−0.18344	−0.4277	−1.3878	−0.4377	−0.9475	−0.1592	0.0272
			b		0.2838	1.3144	0.3852	1.9364	0.3617	0.0280
0.01	99.047186	ψ^1	a	−2.66706	−2.5028	−8.5297	−14.3726	−5.8988	−4.9746	0.0881
			b		2.0453	7.6976	14.3793	5.9389	5.0521	0.0781
		ψ^2	a	−0.18701	0.4711	1.7063	4.1903	1.3076	1.6529	−0.0242
			b		−0.3725	−1.6163	−4.1840	−2.2735	−1.6783	−0.0260

a) Nucleus a (He) and b (H) were placed on the z axis. The scale factor for the $1s_{He}$ orbital is set to be 1.69. The others are 1.00.
b) Internuclear distance in Å. c) In au. d) $r_e = 0.9295$ Å.

$2p_y$, $3p_x$, $3p_y$, $3d_{+1}$, $3d_{-1}$, $3d_{+2}$, and $3d_{-2}$ are always null by a symmetry requirement and are not shown. In a separated system, both ψ^1 and ψ^2 have contribution from the symmetry-allowed AOs. Apart from 1s AOs, the absolute values of the coefficients for $2p_z$ AOs of He and H are different in both ψ^1 and ψ^2. An interesting difference from the H_2 system is that ψ^2 has large coefficients for s-type AOs and ψ^1 has large ones for p-type AOs. Besides, since the overlap integrals between AOs are smaller than unity, the cancelling by superposition of waves is small. Thus, we must admit that both ψ^1 and ψ^2 include large contributions from upper AOs at bonding distances.

At positions near the united atom, $R = 0.01$ Å, both ψ^1 and ψ^2 have considerable contributions from AOs with higher quantum numbers. However, in ψ^1, coefficients for $2p_z$ and $3p_z$ are nearly cancelled out and the contribution from the s-type AOs survives: the major contribution is from 1s and 2s AOs. In ψ^2, the major contribution is from the s-type AOs, as the non-crossing rule predicts.

Let us examine the case when the in-bond orbitals are introduced into unlike-nuclear interactions. Since the two nuclei are not equal, it is easily expected that the participation of an in-bond orbital to MO depends on its locations and that the s-type and p-type in-bond orbitals have their own location for the minimum or maximum contribution. Table 5 shows examples of the positions of the in-bond orbital that has no contribution to ψ^1 or ψ^2 in the HeH^+ system with the internuclear distance of 0.9295 Å. When p-type in-bond orbital is placed at 0.5937 Å from the He nucleus, it has no contribution to ψ^1 and at 0.4283 Å, s-type in-bond orbital

Table 5. Splitting of the Location of In-Bond Orbitals That Give Null-Contribution to Molecular Orbitals in HeH^+[a)]

	Total E[b)]	ε[b)]	$1s_{He}$	$1s_H$	$1s_i$	$2s_i$	$2p_{iz}$
Coefficients at $R_{He\text{-}in} = 0.5937$ Å[c)]							
ψ^1	−2.863760	−1.51553	0.9059	0.2444	0.0944	−0.1860	$\underline{0.0}$
ψ^2		−0.32678	−0.3935	0.6056	0.1460	0.1098	0.4184
Coefficients at $R_{He\text{-}in} = 0.4283$ Å[c)]							
ψ^1	−2.862114	−1.51298	0.9006	0.2686	0.0768	−0.1862	−0.0066
ψ^2		−0.32636	−0.3778	0.7151	$\underline{0.0}$	0.0746	0.4127

a) The nuclei were placed along the z axis. The scale factor of $1s_{He}$ orbital is set to be 1.69. The others are at 1.00. b) In au. c) The distance between the nuclei was set to be 0.9295 Å.

Table 6. Coefficients for Basis Atomic and In-Bond Orbitals in Ethylene[a)]

		Bonding orbital (ψ^1)				Antibonding orbital (ψ^2)			
R[b)]	Total E[c)]	c_1	c_2	c_3	c_4	c_1	c_2	c_3	c_4
2.00	−76.856565	0.5197	0.5197	0.3177	0.0000	0.4764	−0.4764	0.0000	0.4233
1.75	−76.988671	0.4900	0.4900	0.3320	0.0000	0.4269	−0.4269	0.0000	0.5087
1.50	−77.100727	0.4641	0.4641	0.3361	0.0000	0.3597	−0.3597	0.0000	0.6191
r_e[d)]	−77.130011	0.4553	0.4553	0.3185	0.0000	0.2968	−0.2968	0.0000	0.7142
1.25	−77.118118	0.4563	0.4563	0.3070	0.0000	0.2772	−0.2772	0.0000	0.7419
1.00	−76.815601	0.4915	0.4915	0.1955	0.0000	0.1805	−0.1805	0.0000	0.8613
0.75	−75.490527	0.5817	0.5817	−0.0425	0.0000	0.0718	−0.0718	0.0000	0.9583
0.50	−70.814893	0.7454	0.7454	−0.4779	0.0000	0.0135	−0.0135	0.0000	1.0052

a) The scale factors of in-bond orbitals (2p, 3d) are set to be 1.00. b) Internuclear distance in Å. c) In au. d) $r_e = 1.3060$ Å.

has no contribution to ψ^2. Thus, if we place the in-bond orbitals at proper positions, we can equally apply the idea of the in-bond orbital to unlike-nuclear interaction just as in the like-nuclear bond formation.

π-Type Interaction between 2p AOs. According to the correlation diagram between separated and united atoms, π-type bonding interaction of two p-type orbitals leads to a 2p AO of the united atom, while that of antibonding interaction leads to a 3d AO. Accordingly, the new concept for such orbital interactions may be shown in Fig. 2.

In order to ascertain such an idea, the in-bond orbitals are placed at the exact center of the π bond of ethylene and their contributions are examined in the range of bond lengths between 2.0 and 0.5 Å The results are shown in Tables 6 and 7, where Eqs. 10 and 11 define the contribution of AO. In the calculation, two carbon nuclei are placed on the x-axis and only $2p_z$ and $3d_{xz}$ orbitals are employed. The nuclear charges for $2p_z$ and $3d_{xz}$ are set at zero.

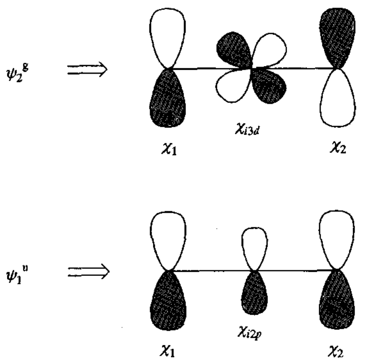


Fig. 2. In-bond orbitals for π bond.

Table 7. Contribution of Basis Orbitals to Molecular Orbitals in Ethylene[a)]

	Bonding orbital (ψ^1)			Antibonding orbital (ψ^2)		
R[b)]	A	B	C	A	B	C
2.00	0.5755	0.1010	0.3236	0.4244	0.1792	0.3965
1.75	0.5326	0.1102	0.3572	0.3247	0.2588	0.4166
1.50	0.5071	0.1130	0.3799	0.2129	0.3833	0.4038
r_e[c)]	0.5191	0.1014	0.3795	0.1318	0.5100	0.3582
1.25	0.5321	0.0942	0.3737	0.1110	0.5504	0.3386
1.00	0.6848	0.0382	0.2770	0.0380	0.7419	0.2202
0.75	1.0779	0.0018	−0.0797	0.0042	0.9183	0.0775
0.50	1.9793	0.2284	−1.2077	0.0001	1.0105	−0.0106

a) The scale factors of in-bond orbitals (2p, 3d) are set to be 1.00.
b) Internuclear distance in Å. c) $r_e = 1.3060$ Å.

In the bonding MO (ψ_u^1), the best contribution of the 2p-type in-bond orbital is found at R of around 1.5 Å It is difficult to interpret the role of the 2p-type in-bond orbital at a shorter R. However, since total energy without in-bond

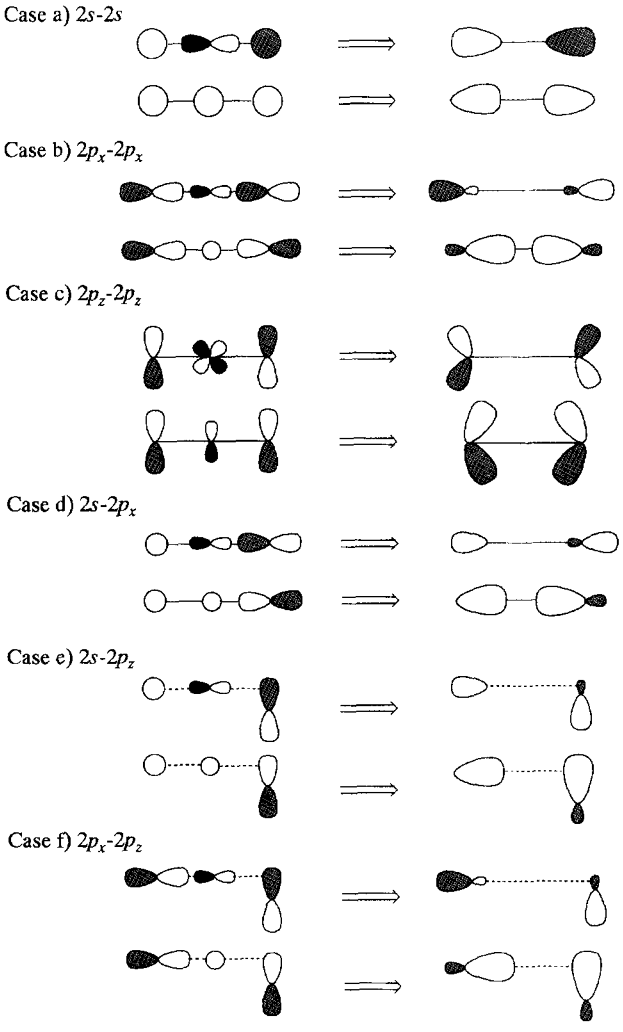


Fig. 3. General expression of in-bond orbitals.

orbitals at r_e is -77.073955 au, considerably higher than that in Table 6, one can clearly find that the bonding MO is better expressed by adopting the 2p-type in-bond orbital. The contribution of the in-bond 3d orbital in the antibonding MO (ψ_g^2) becomes greater as R becomes shorter, indicating that the orbital changes to a 3d AO at the united atom.

AO Interaction Scheme. As discussed above, the concept of the emerging in-bond orbitals in bond formation seems to be generally effective. We present the in-bond orbital scheme shown in Fig. 3.

An Application of the Concept of In-Bond Orbitals

Pyramidalization of the Olefinic Carbons of Norbornene. It may be effective to give an example showing how the concept of the in-bond orbitals is rather more reasonable when compared to the conventional idea. Let us examine the pyramidalization of the olefinic carbon atoms of norbornene (Fig. 4). The carbon atoms at the 2 and 3 positions are pyramidalized so as to tilt the attached hydrogens to the side of the ethano bridge (the *endo* direction). Inagaki et al.[5] explained this phenomenon as a result of nonequivalent HOMO extension (to the *exo* direction) of norbornene, using the orbital mixing rule (or σ–π mixing method). Here we compare this and our in-bond orbital method.

To this end, we will arrange all of the participating orbitals (or lobes) all in-phase (blank lobes or +). Then, the first order interaction which is used by both methods is represented either by [+] or [−] and the second-order interaction (which is used only by the σ–π mixing rule) with (+) or (−). In the orbital mixing rule, the phase relationship between the perturbing orbital of interest and the second-order perturbing orbital is obtained by [ ]×( ). The resulting sign (+ or −) is marked with a square frame. If it is ⊞, these two orbitals mix in-phase while if it is ⊟, they mix out-of-phase.

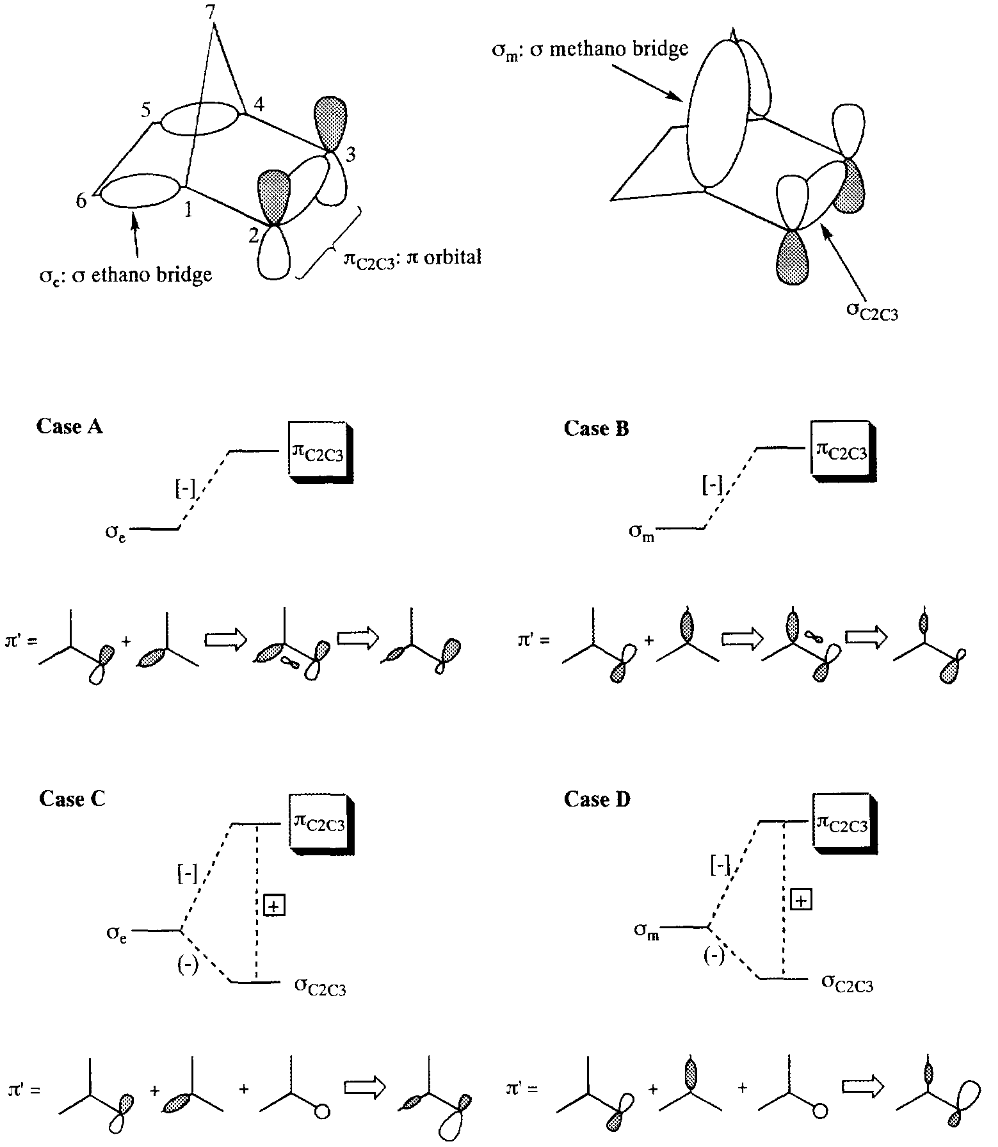


Fig. 4. Prediction of the direction of nonequivalent HOMO extension of norbornene either by the in-bond orbital method (case **A** and **B**) or the orbital mixing rule (case **C** and **D**). The direct perturber is the ethano bridge (σ_e) for **A** and **C** and the methano bridge (σ_m) for **B** and **D**.

In Fig. 4, we present the orbitals of π_{C2C3} (the orbital of interest), the direct perturbers (the methano bridge: σ_m or the ethano bridge: σ_e) and the second-order perturber (σ_{C2C3}). The energy level of π_{C2C3} is higher than those of the other orbitals (σ_m, σ_e, and σ_{C2C3}).

The predictions obtained by the σ–π mixing method and the in-bond orbital method are shown in Fig. 4. In the Fig. 4, cases **A** and **C** correspond to the one in which the σ_e is assumed as the direct perturber and cases **B** and **D** correspond to the one in which the σ_m is the direct perturber.

As seen from Fig. 4, the correct prediction is obtained in case **A** and case **D**. In case **A**, the direct perturber is the σ_e, while it is the σ_m in case **D**. Since all chemical results obtained so far indicate clearly, that σ_e is the direct perturber,[23] it is obvious that the in-bond orbital method is the only reliable method for the prediction of the direction of nonequivalent orbital extension.

The in-bond orbital method gives, without exception, the correct prediction of pyramidalization of trigonal carbon atoms in all kinds of alkenes. Care should be taken, however, as the method cannot be applied to alkenyl ions (cations or anions) if the ionic center is near enough in space to interact with the π-bond. Applications of the in-bond orbital method to these ions will be discussed elsewhere following this series.

Concluding Remarks

It is well known that in order to express the correct electronic structure of a chemical bond, a large number of basis orbitals must be included in the LCAO formalism. This method has been prevalent in computational chemistry. It is true that the electronic structure is considerably improved by doing so. However, the simple chemical idea that a molecular orbital consists of atomic orbitals of the included atoms is apparently negated. Quantum mechanically, the coordinate center of any basis orbital is not necessarily fixed at the corresponding atomic nucleus. For example, Brown proposed a molecular-orbital treatment in which the orbitals are represented as linear combinations of united-atom orbitals, located in every bond in the molecule.[6] Many other examples are seen in the literature.[7—16] However, the chemical meaning of such basis functions is ambiguous.

We have proposed an idea that atomic orbital interaction produces in-bond orbitals between the atoms. The electronic structure of the internuclear region is determined by such in-bond orbitals and the latter are correlated with AOs of the united atom. This idea seems reasonable because a correlation diagram between the separated atoms and the united atom is well established and provides a clear chemical meaning of the in-bond orbital. To show the usefulness of the in-bond orbital method, it was applied to explain the pyramidalization problem of olefinic carbon atoms of norbornene: The necessary selection of the ethano bridge as the perturber in the in-bond orbital method accords with experimental facts.

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References

1 R. S. Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

2 For review, see e.g. : J. C. Slater, "Quantum Theory of Molecules and Crystals," McGraw-Hills, New York (1963), Vol. 1.

3 J. v. Neumann and E. P. Wigner, *Phys. Z.*, **30**, 467 (1929).

4 R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); "The Conservation of Orbital Symmetry," Academic Press, New York (1970).

5 S. Inagaki, H. Fujmoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4054 (1976).

6 R. D. Brown, *J. Chem. Soc.*, **1953**, 2615.

7 A. A. Frost, *J. Chem. Phys.*, **47**, 3707 (1967); *Theor. Chim. Acta*, **18**, 156 (1970).

8 H. Preuss, *Z. Naturforsch. A*, **20**, 21 (1965).

9 F. Fratev, R. Janoschek, and H. Preuss, *Int. J. Quantum Chem.*, **4**, 529 (1970).

10 R. Ahlrichs, *Theor. Chim. Acta*, **17**, 348 (1970).

11 R. Ahlrichs and W. Kutzelnigg, *Chem. Phys. Lett.*, **1**, 651 (1968).

12 S. Rothenberg and H. F. Schaefer, III, *J. Chem. Phys.*, **54**, 2764 (1971).

13 T. Vladimiroff, *J. Phys. Chem.*, **77**, 1983 (1973).

14 D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.*, **82**, 2418 (1985).

15 M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer, III, *J. Chem. Phys.*, **84**, 2279 (1986).

16 X. L. Huang, J. J. Dannenberg, M. Duran, and J. Bertran, *J. Am. Chem. Soc.*, **115**, 4024 (1993).

17 T. Ohwada, *J. Am. Chem. Soc.*, **114**, 8818 (1992).

18 T. Ohwada, I. Okamoto, N. Haga, and K. Shudo, *J. Org. Chem.*, **59**, 3975 (1994).

19 I. Okamoto, T. Ohwada, and K. Shudo, *J. Org. Chem.*, **61**, 3155 (1996).

20 T. Ohwada, M. Uchiyama, M. Tsuji, I. Okamoto, and K. Shudo, *Chem. Pharm. Bull.*, **44**, 296 (1996).

21 a) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970). b) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). c) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976). The calculation has been carried out on an IBM RS/6000-590 computer using GAUSSIAN-90 package (J, M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1990).

22 Quantitative contributions of atomic orbitals in H_2 were calculated by the extended method of Eq. 10. The results at r_e are given as,

	1s	2s	$2p_z$	3s	$3p_z$	$3d_0$
$\psi^1{}_g$	1.553	0.223	0.009	0.026	0.000	0.002
$\psi^2{}_u$	1.745	4.002	0.630	1.079	14.855	0.021

In ψ_u^2, a large population appears in $3p_z$. Cancellation to hold $\int \psi^2 d\tau = 1$ takes place by cross terms with s-type orbitals.

23 F. A. Carey and R. J. Sundberg, "Advanced Organic Chemistry," 3rd ed, Plenum Press (1990), Part A, pp. 319—326, and references cited therein.