Calculation of the Carbon-13 NMR Chemical Shifts of Some Organic Compounds Using the Improved Virtual Orbital Method

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Using the wavefunction obtained from the improved virtual orbital (IVO) method proposed by Huzinaga, the ^{13}C NMR chemical shifts in some organic compounds (acetylene, ethylene, ethane, pentane, benzene, pyridine and acetone) have been calculated and compared with those obtained from the ordinary SCF-MO method. If the molecule considered is small, highly symmetric and non-polar, it can be expected that there is little difference in the calculated values between these two methods. If the molecule considered is rather large or polar, modification of the calculated values are apt to be induced by the IVO method. As far as qualitative tendencies of the chemical shifts of carbon in a molecule are concerned, both methods give similar results.

The carbon-13 NMR chemical shifts have been calculated by many methods[1,2] for organic compounds using various molecular orbital theories. The sum-over-state method[3,4] is one of such theories. In this method, not only the wavelfunctions for occupied orbitals but also those for virtual (or unoccupied) orbitals are needed in the calculation of the paramagnetic contribution. It is known[5] that in the system of 2N electrons the wavefunctions obtained by the ordinary Hartree-Fock operator are appropriate to the occupied orbitals but not to the virtual orbitals. These wavefunctions for the virtual orbitals are appropriate to the system of 2N+1 electrons rather than 2N electrons because an electron virtually involved in any virtual orbital suffers from the potentials of all the 2N electrons involved in the occupied orbitals. Thus, it is preferable to correct the wavefunctions for virtual orbitals so that they are appropriate for the system of 2N electrons as well as those for occupied orbitals. In an attempt to improve the situation, Huzinaga *et al.*[6,7] reported the improved virtual orbital (IVO) method in which a projection operator is introduced to modify the Hartree-Fock orperator for the virtual orbitals.

The carbon-13 chemical shifts and their tensors in some organic compounds have been calculated by the sum-over-state method without any improvement of the wavefunctions for virtual orbitals.[8,9] It appears that the calculated values systematically deviate from experimental values with relation to the size of the molecules;[9] in saturated hydrocarbons, as the number of carbons increase the paramagnetic contribution to the shielding constant tends to decrease. This trend makes it difficult to compare the relative shifts among the carbons in different molecules. Such a systematic deviation might come from an approximation adopted there, for example, the neglect of the overlap integral or the inexact wavefunction for virtual orbitals described above. This paper will focus on the latter case, *i.e.* the inexact wavefunction for virtual orbitals. The carbon-13 shielding constants will be calculated by the sum-over-state method using the wavefunctions obtained by the IVO method and these will be compared with the calculated results obtained by the ordinary SCF method.

Theoretical

In the sum-over-state method, one of the diagonal components of the paramagnetic shielding tensor of nucleus A, $\sigma^{p}_{\alpha\alpha}$ (α=x, y, or z), is expressed as follows:[3]

$$\sigma^{p}_{xx} = -\frac{2e^2\hbar^2}{m^2c^2}\langle r^{-3}\rangle_{2p}\sum_{i}^{occ}\sum_{k(\neq i)}^{unocc}(\Delta E_{i-k})^{-1}(C_{iy_A}C_{kz_A}-C_{iz_A}C_{ky_A}) \times\sum_{B}(C_{iy_B}C_{kz_B}-C_{iz_B}C_{ky_B}). \quad (1)$$

In these formulas, C_{ix_A} is the coefficient of the $2p_x$ atomic orbital on atom A of the i-th molecular orbital in the LCAO MO theory, ΔE_{i-k} the singlet-singlet excitation energy from the occupied orbital ϕ_i to the unoccupied orbital ϕ_k and $\langle r^{-3}\rangle_{2p}$ the mean inverse cubic radius of a 2p electron. The molecular orbitals are obtained from the IVO method[5-7] based on the MINDO/2 method.[10]

According to Huzinaga *et al.*[5-7] a new Fock operator $\mathbf{F}'_i$ in one-electron excitation from an occupied orbital ϕ_i is given by

$$\mathbf{F}'_i = \mathbf{F} + \mathbf{V}'_i \quad (2)$$

where

$$\mathbf{V}'_i = (\mathbf{1}-\mathbf{P})\Omega_i(\mathbf{1}-\mathbf{P}).$$

Here $\mathbf{F}$ is the ordinary Fock operator, $\mathbf{P}$ the projection operator, Ω_i the correction operator for the energy level of the virtual orbitals and these operators are given as follows:

$$\mathbf{F} = \mathbf{H}^{core} + \sum^{occ}(2\mathbf{J}_j-\mathbf{K}_j), \quad (3)$$

$$\mathbf{P} = \sum^{occ}|\phi_j\rangle\langle\phi_j|, \quad (4)$$

$$\Omega_i = -\mathbf{J}_i + 2\mathbf{K}_i, \quad (5)$$

where $\mathbf{J}_i$ and $\mathbf{K}_i$ are the Coulomb and Exchange operators, respectively. In the case of the new Fock operator $\mathbf{F}'_i$, for the occupied orbitals ϕ_j's

$$\mathbf{F}'_i|\phi_j\rangle = \mathbf{F}|\phi_j\rangle = \varepsilon_j|\phi_j\rangle \quad (6)$$

and for the virtual orbitals ϕ_k's

$$\mathbf{F}'_i|\phi_k\rangle = (\mathbf{F}+\Omega_i-\mathbf{P}\Omega_i)|\phi_k\rangle, \quad (7)$$

$$\varepsilon_k = \langle\phi_k|\mathbf{F}+\Omega_i|\phi_k\rangle. \quad (8)$$

That is, the operator $\mathbf{F}'_i$ gives an alteration of the eigenvalues and eigenfunctions for the virtual orbitals. A molecular orbital ϕ_j is given by a linear combination

of atomic orbitals χ_p's as follows:

$$\phi_j = \sum_p C_{jp}\chi_p. \quad (9)$$

Then a matrix representation of the operator $\mathbf{V}_i$ in Eq. 2 based on these atomic orbitals is given as

$$\mathbf{V}_i = (\mathbf{1}-\mathbf{D})\Omega_i'(\mathbf{1}-\mathbf{D}), \quad (10)$$

where $\mathbf{D}$ is the density matrix, Ω_i' the correction operator on the basis of atomic orbitals, which are given by

$$\mathbf{D} \equiv D_{pq} \sum_j^{occ} C_{ip}C_{jq} = \sum_j^{occ} D_{i,pq}, \quad (11)$$

$$\Omega_i' \equiv \Omega_{i,pq}' = \langle\chi_p|\Omega_i'|\chi_q\rangle = \sum_{v,w}\{-(pq|vw)+2(pw|vq)\}D_{i,vw}. \quad (12)$$

In these equations, (pq | vw) and (pw | vq) correspond to the Coulomb and Exchange integrals, respectively. Adopting the semi-empirical molecular orbital method, *i.e.* the MINDO/2 method,[10] the integrals may be estimated by the Slater-Condon parameters.[11] For the numerical values of bond lengths and bond angles the standard values determined by Pople and Gordon[12] were used. The numerical calculation was carried out by an HITAC-8800 computer at the Computer Center of the University of Tokyo.

Results and Discussion

The ^{13}C paramagnetic shielding constants of some organic compounds (acetylene, ethylene, ethane, pentane, benzene, pyridine, and acetone) were calculated using the wavelfunctions obtained from the ordinary Hartree-Fock method and the IVO method.[5-7] The calculated values by both methods are shown in Table 1. The characteristic feature in each compound is as follows:

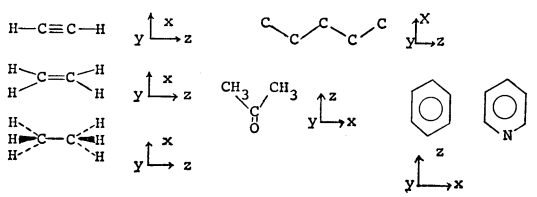
A. Acetylene. The symmetry of the acetylene molecule belongs to the $D_{\infty h}$ point group and its electronic structure is composed of molecular orbitals with symmetry as shown in Table 2, in which the molecular orbitals were calculated by the MINDO/2 method.[10] According to the IVO method, the wavefunctions for the virtual orbitals are modified by the introduction of the correction operator $\mathbf{V}_i$ given in Eq. 2 while those for the occupied orbitals are not modified. This modification in virtual orbitals is responsible for the mixing among the virtual orbitals by the operator $\mathbf{V}_i$. From the viewpoint of the symmetry of the unoccupied orbitals, it is to be expected that the operator $\mathbf{V}_i$ causes the mixing between ϕ_6 and ϕ_{10} and between ϕ_7 and ϕ_8. ϕ_9 is not mixed because of orthogonality with the other unoccupied orbitals. From a considration of symmetry of the occupied and unoccupied orbitals it is possible to predict which transition can contribute to the paramagnetic shielding. As is seen from Eq.1, non-vanishing values of σ_{xx}^p, σ_{yy}^p and σ_{zz}^p are obtained if the transitions obey the selection rule that a direct product representation between the occupied and unoccupied orbitals contains representations of E_{1g}, E_{1g} and E_{2g}, respectively. Thus, two types of transitions can contribute to the σ_{xx}^p and σ_{yy}^p; one is the transition from the occupied orbital with a_{1g} symmetry to the unoccupied orbital with e_{1g} symmetry (σ-π^* transition), and the other is that from the e_{1u} occupied orbital to the a_{2u} unoccupied orbital (π-σ^* transition). Any transition does not contribute to σ_{zz}^p because any direct product representation between the occupied and unoccupied orbitals does not contain the representation of E_{2j}.

Focus will now be made on the molecular orbitals

Table 1. Calculated ^{13}C shielding constants in some organic compounds with and without IVO method

	Calculated without IVO					Calculated with IVO					Observed[a]	
	σ_{xx}^p	σ_{yy}^p	σ_{zz}^p	σ^p [b]	$\Delta\sigma$[c]	σ_{xx}^p	σ_{yy}^p	σ_{zz}^p	σ^p [b]	$\Delta\sigma$[c]	δ[d]	$\Delta\delta$[e]
Acetylene	−356.5	−356.5	0.0	−237.7		−356.5	−356.5	0.0	−237.7			
Ethylene	−528.7	−207.0	−348.4	−361.4		−528.7	−207.0	−348.4	−361.4		122.8	
Ethane	−238.2	−238.2	−221.2	−232.5		−239.0	−239.5	−221.5	−233.2		5.9	
Pentane												
C-1	−199.4	−203.7	−190.2	−197.7	20.0	−194.6	−202.0	−185.8	−194.2	36.1	13.7	20.8
C-2	−211.2	−225.9	−195.1	−210.7	7.0	−215.7	−238.1	−198.7	−217.5	12.8	22.6	11.9
C-3	−217.2	−239.4	−196.5	−217.7	0	−228.2	−255.9	−206.9	−230.3	0	34.5	0
Benzene	−306.2	−194.7	−436.6	−312.5		−310.7	−194.8	−441.2	−315.5		128.7	
Pyridine												
C-2	−449.7	−205.4	−342.2	−332.5	0	−490.0	−205.8	−349.9	−348.5	0	150.6	0
C-3	−391.5	−190.6	−330.8	−304.3	28.2	−392.8	−190.1	−338.3	−307.1	41.4	124.5	26.1
C-4	−304.0	−199.4	−445.0	−316.1	16.4	−297.9	−204.8	−460.0	−320.9	27.6	136.4	14.2
Acetone												
CH_3	−200.0	−224.7	−218.1	−214.3	140.1	−205.5	−224.2	−234.8	−221.5	162.1	30.2	174.9
CO	−445.0	−235.3	−382.8	−354.4	0	−477.3	−237.7	−435.9	−383.6	0	205.1	0

a) Collected from Ref. [1]. b) $\sigma^p = (\sigma_{xx}^p + \sigma_{yy}^p + \sigma_{zz}^p)/3$. c) The most deshielded carbon in each molecule is the reference. d) ppm from TMS. e) The most downfield carbon in each molecule is the reference.



relating to the allowed transitions. New virtual orbitals ϕ_7' and ϕ_8' calculated by the IVO method are expressed as a linear combiantion of unoccupied orbitals ϕ_7 and ϕ_8 which are calculated by the ordinary Hartree-Fock method. When one electron is excited from the occupied orbital ϕ_1 to the unoccupied orbital ϕ_7 or ϕ_8, the wavefunctions of ϕ_7 and ϕ_8 are modified as follows:

$$\phi_7' = 0.7934\phi_7 - 0.6087\phi_8, \quad (13\text{-}1)$$

$$\phi_8' = 0.6087\phi_7 + 0.7934\phi_8, \quad (13\text{-}2)$$

and when one electron is excited from the occupied orbital ϕ_3 to the unoccupied orbital ϕ_7 or ϕ_8,

$$\phi_7'' = 0.7789\phi_7 - 0.6272\phi_8, \quad (14\text{-}1)$$

$$\phi_8'' = 0.6272\phi_7 + 0.7789\phi_8. \quad (14\text{-}2)$$

As the orbitals ϕ_7 and ϕ_8 degenerate with each other as shown in Table 2, the mixing between them by the operator $\mathbf{V}_i$ becomes large. However, if the excitation energy from the occupied orbital ϕ_1 or ϕ_3 to the unoccupied orbital ϕ_7 or ϕ_8 is not modified, induced modifications in the wavefunctions for orbitals ϕ_7 and ϕ_8 will not cause any change in the value of the paramagnetic shielding constant because of the degeneracy between these orbitals. The excitation energy, ΔE_{i-k}, can be simply calculated as a separation in energy levels between the virtual and occupied orbitals in the IVO method. If the excitation energy in the ordinary Hartree-Fock method is calculated from Eq. 15 taking into account Coulomb and Exchange integrals, little difference in the excitation energies with and without the IVO method is seen:

$$\Delta E_{i-k} = \varepsilon_k - \varepsilon_i - J_{ki} + 2K_{ki}. \quad (15)$$

For the other type of transition, when one electron is excited from the occupied orbital ϕ_4 or ϕ_5 to the unoccupied orbitals ϕ_6 and ϕ_{10}, modified wavefunctions for these virtual orbitals are expressed as follows:

$$\phi_6' = 0.9999\phi_6 - 0.0070\phi_{10}, \quad (16\text{-}1)$$

$$\phi_{10}' = 0.0070\phi_6 + 0.9999\phi_{10}. \quad (16\text{-}2)$$

The mixing between the orbitals ϕ_6 and ϕ_{10} by the operator $\mathbf{V}_i$ is very small. Thus, it is expected that there will be little difference in the contribution through these transitions whether the IVO method is used or not. For acetylene, it is seen that the improvement of the wavefunction for the virtual orbital by the IVO method induces little change in the magnetic shielding constant.

B. Ethylene. The ethylene molecule has the symmetry of the D_{2h} point group and has molecular orbitals with symmetry as shown in Table 3. Therefore, the wavefunctions for only two virtual orbitals ϕ_8 and ϕ_{12} are modified by the operator $\mathbf{V}_i$ because the other unoccupied orbitals are orthogonal to one another. The allowed transitions in the expression of σ_{xx}^p, σ_{yy}^p, and σ_{zz}^p are given by the selection rule that direct product representation between the occupied and unoccupied orbitals contains the representation of B_{3g}, B_{2g}, and B_{1g}, respectively; they are $\phi_1 \rightarrow \phi_7$, $\phi_4 \rightarrow \phi_7$, $\phi_6 \rightarrow \phi_8$, and $\phi_6 \rightarrow \phi_{12}$ for σ_{xx}^p, $\phi_5 \rightarrow \phi_7$ and $\phi_6 \rightarrow \phi_{10}$ for σ_{yy}^p, and $\phi_1 \rightarrow \phi_{11}$, $\phi_4 \rightarrow \phi_{11}$, $\phi_2 \rightarrow \phi_{10}$, $\phi_3 \rightarrow \phi_8$, $\phi_3 \rightarrow \phi_{12}$, and $\phi_5 \rightarrow \phi_9$ for σ_{zz}^p. The results on a part of the virtual orbitals ϕ_8 and ϕ_{12} are as follows: when one electron is excited from the occupied orbital ϕ_3 to the unoccupied orbital ϕ_8 or ϕ_{12}, modified wavefunctions ϕ_8' and ϕ_{12}' are expressed as

$$\phi_8' = 0.9854\phi_8 - 0.1705\phi_{12}, \quad (17\text{-}1)$$

$$\phi_{12}' = 0.1705\phi_8 + 0.9854\phi_{12}, \quad (17\text{-}2)$$

and when one electron is excited from the occupied orbital ϕ_6 to the unoccupied orbital ϕ_8 or ϕ_{12}, modified wavefunctions ϕ_8'' and ϕ_{12}'' are

$$\phi_8'' = 0.9997\phi_8 + 0.0255\phi_{12}, \quad (18\text{-}1)$$

$$\phi_{12}'' = -0.0255\phi_8 + 0.9997\phi_{12}. \quad (18\text{-}2)$$

The transition from ϕ_3 to ϕ_8 or ϕ_{12} corresponds to $\sigma \rightarrow \sigma^*$ and that from ϕ_6 to ϕ_8 or ϕ_{12} to $\pi \rightarrow \sigma^*$. It should be noted that the mixing by the operator $\mathbf{V}_i$ for the former type of transition is larger than that for the latter type. However, as the contributions to the paramagnetic shielding constant from the former transitions are vanishingly small, it is expected that the calculated value for σ_{zz}^p is hardly changed by modification of the virtual orbitals, ϕ_8 and ϕ_{12}. On the contrary, for the latter transitions, although a portion of these contributions to σ_{xx}^p is larger, the mixing between the orbitals ϕ_8 and ϕ_{12} due to the operator $\mathbf{V}_i$ is very small. For ethylene the result is similar to that of acetylene, namely the magnetic shielding constant is hardly changed by the IVO method.

C. Acetone. The acetone molecule has the symmetry of the C_{2v} point group and has molecular orbitals with the symmetry shown in Table 4. This compound is different from the above two compounds in that it contains an electronegative oxygen atom. The selection rules for the allowed transitions in the expressions of σ_{xx}^p, σ_{yy}^p, and σ_{zz}^p are, respectively, given by the terms of the direct product representations, B_2, B_1, and A_2, between the occupied and unoccupied orbitals. It is

TABLE 2. SYMMETRY OF MOLECULAR ORBITALS IN ACETYLENE

Occupied orbitals		Virtual orbitals	
ϕ_5	e_{1u} (π)	ϕ_{10}	a_{2u}
ϕ_4	e_{1u} (π)	ϕ_9	a_{1g}
ϕ_3	a_{1g}	ϕ_8	e_{1g} (π^*)
ϕ_2	a_{2u}	ϕ_7	e_{1g} (π^*)
ϕ_1	a_{1g}	ϕ_6	a_{2u}

Acetylene molecule has $D_{\infty h}$ symmetry. The molecular orbitals were calculated by MINDO/2 method.

TABLE 3. SYMMETRY OF MOLECULAR ORBITALS IN ETHYLENE

Occupied orbitals		Virtual orbitals	
ϕ_6	b_{1u} (π)	ϕ_{12}	b_{2u}
ϕ_5	b_{1g}	ϕ_{11}	b_{1g}
ϕ_4	b_{1g}	ϕ_{10}	b_{3u}
ϕ_3	b_{3u}	ϕ_9	a_{1g}
ϕ_2	b_{2u}	ϕ_8	b_{2u}
ϕ_1	a_{1g}	ϕ_7	b_{3g} (π^*)

Ethylene molecule has D_{2h} symmetry. The molecular orbitals were calculated by MINDO/2 method.

Table 4. Symmetry of molecular orbitals in acetone

Occupied orbitals		Virtual orbitals	
ϕ_{12}	b_1 (n)		
ϕ_{11}	a_1 (n)		
ϕ_{10}	b_2 (π)	ϕ_{22}	a_1
ϕ_9	b_1	ϕ_{21}	b_1
ϕ_8	a_2 (π')	ϕ_{20}	a_2 (π'*)
ϕ_7	a_1	ϕ_{19}	b_1
ϕ_6	b_1	ϕ_{18}	a_1
ϕ_5	b_2 (π')	ϕ_{17}	b_2 (π'*)
ϕ_4	a_1	ϕ_{16}	a_1
ϕ_3	b_1	ϕ_{15}	b_1
ϕ_2	a_1	ϕ_{14}	b_2 (π*)
ϕ_1	a_1	ϕ_{13}	a_1

Acetone molecule has C_{2v} symmetry. The molecular orbitals were calculated by MINDO/2 method. (π') denotes the pseudo-π orbitals due to the methyl group.

well-known that the n-π* transition gives a larger contribution to the paramagnetic shielding because of its low excitation energy. So, attention will be focused on the n-π* transitions. Some of the n-π* transitions give the contribution to σ^p_{xx} and σ^p_{zz}, *i.e.* $\phi_{11}\rightarrow\phi_{14}$, $\phi_{11}\rightarrow\phi_{17}$, and $\phi_{12}\rightarrow\phi_{20}$ to σ^p_{xx} and transitions $\phi_{11}\rightarrow\phi_{20}$, $\phi_{12}\rightarrow\phi_{14}$, and $\phi_{12}\rightarrow\phi_{17}$ to σ^p_{zz}. The unoccupied orbitals ϕ_{14} and ϕ_{17} are mixed with each other by the operator $\mathbf{V}_i$ while the unoccupied orbital ϕ_{20} is not mixed. When one electron is excited from the occupied orbital ϕ_{11} to the unoccupied orbital ϕ_{14} or ϕ_{17}, the modified orbitals ϕ'_{14} and ϕ'_{17} are expressed as

$$\phi'_{14} = 0.9809\phi_{14} + 0.1947\phi_{17}, \quad (19\text{-}1)$$

$$\phi'_{17} = -0.1947\phi_{14} + 0.9809\phi_{17}, \quad (19\text{-}2)$$

and when one electron is excited from the occupied orbital ϕ_{12} to the unoccupied orbital ϕ_{14} or ϕ_{17},

$$\phi''_{14} = 0.9843\phi_{14} + 0.1777\phi_{17}, \quad (20\text{-}1)$$

$$\phi''_{17} = -0.1777\phi_{14} + 0.9843\phi_{17}. \quad (20\text{-}2)$$

The virtual orbitals ϕ_{14} and ϕ_{17} are mainly located in the region of the carbonyl and methyl groups in acetone, respectively. Modification of these virtual orbitals decreases their delocalization in this case; the coefficients of the wavefunctions ϕ'_{14} and ϕ''_{14} at the carbonyl carbon are larger than that of ϕ_{14}. Therefore for the paramagnetic shielding of the carbonyl carbon, the values of σ^p_{xx} and σ^p_{zz} calculated by the IVO method are larger than those calculated by the ordinary method. As n-π* transitions do not largely contribute to the shielding constant of the methyl carbon, the corresponding increase in this contribution by the modification of the virtual orbitals is not so large compared to the case of the carbonyl carbon. For σ^p_{yy}, differences between the values calculated with the two methods is hardly the recognized in both of the methyl and carbonyl carbons, since the n-π* transition does not contribute to σ^p_{yy} at all. Ultimately, as far as a difference in the chemical shifts between the methyl and carbonyl carbons is concerned, the value obtained from the IVO method is larger than that from the ordinary method and it is noted that the former becomes closer to the observed one.

D. Other Compounds(ethane, pentane, benzene and pyridine). One of the aims of this paper was to examine whether the systematic deviation from the observed data described above could be avoided by the IVO method. In consequence the paramagnetic shielding constants calculated by the two methods in ethane and pentane will be compared. As shown in Table 1, for the ordinary method, the calculated value for any carbon of pentane is considerably underestimated if ethane is considered as a reference. For ethane, a difference between the calculated values with and without the IVO method is hardly observed. For pentane the contribution to the paramagnetic shielding in the most de-shielded carbon(C-3) increases by the modification of the virtual orbitals while that of the most shielded carbon (C-1) decreases. However, it may be seen that even for the C-3 carbon the underestimation of σ^p is still large. Thus, it does not seem that the IVO method serves to avoid the systematic deviation described above.

A brief examination of the calculated values for aromatic compounds will now be discussed. For benzene, it is seen that a small difference in the value of σ^p_{xx} or σ^p_{zz} is induced by the modification of the virtual orbitals while a small change is induced in the value of σ^p_{yy}. For pyridine, the value of σ^p_{xx} for C-2 carbon bonded to the nitrogen atom is considerably increased by the modification of the virtual orbitals, while the values of σ^p_{yy} and σ^p_{zz} do not increase as much because the n-π* transitions can contribute to only σ^p_{xx}. As far as differences in the chemical shifts among the carbons in pyridine are concerned, the IVO method gives rather poor agreement between the calculated observed results.

Conclusion

Using the wavefunction obtained from the improved virtual orbital (IVO) method proposed by Huzinaga, the ^{13}C NMR chemical shifts in some organic compounds have been calculated and compared with those obtained from the ordinary SCF-MO method. The following points were noted: If the molecule considered is small, highly symmetric and non-polar, it can be expected that there is little difference in the calculated values between these two methods because the mixings among the virtual orbitals are unlikely to be induced except for degenerate orbitals. If the molecule considered is rather large or polar, modification of the calculated values are apt to be induced by the IVO method. As far as qualitative tendencies of the chemical shifts of carbon in a molecule are concerned, both methods give similar results.

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