The Effect of Electron Transfer in the Electronic Structure of Benzyl Radical

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In the previous paper¹⁾, the correlation between the energy levels of benzyl radical and those of benzene has been shown by the present author, though neglecting all of the interactions between benzene ring and CH_2 in benzyl radical except only the interaction by exchange of π-electrons. However, there is the question as to the different results which may be obtained if the assumption of the calculation is altered. In the present paper, the purpose is to show how the results may be affected by the change of the assumption in the treatment.

In the present paper, the assumption is used that the interaction between benzene ring and CH_2 arises from the transfer of the electron. This assumption is introduced in the calculation by the use of the approximation of integrals suggested by Pariser and Parr²⁾. This treatment is the same as the method of composite systems³⁾.

Calculation

The molecular orbitals of benzene ring are written in the real form as,

$$\left.\begin{aligned}
\varphi_0(\nu) &= \sqrt{6}^{\,-1}\{\chi_1(\nu)+\chi_2(\nu)+\chi_3(\nu) \\
&\quad +\chi_4(\nu)+\chi_5(\nu)+\chi_6(\nu)\} \\
\varphi_1(\nu) &= \sqrt{12}^{\,-1}\{2\chi_1(\nu)+\chi_2(\nu)-\chi_3(\nu) \\
&\quad -2\chi_4(\nu)-\chi_5(\nu)+\chi_6(\nu)\} \\
\varphi_2(\nu) &= 2^{-1}\{\chi_2(\nu)+\chi_3(\nu)-\chi_5(\nu) \\
&\quad -\chi_6(\nu)\} \\
\varphi_3(\nu) &= \sqrt{12}^{\,-1}\{2\chi_1(\nu)-\chi_2(\nu)-\chi_3(\nu) \\
&\quad +2\chi_4(\nu)-\chi_5(\nu)-\chi_6(\nu)\} \\
\varphi_4(\nu) &= 2^{-1}\{\chi_2(\nu)-\chi_3(\nu)+\chi_5(\nu) \\
&\quad -\chi_6(\nu)\} \\
\varphi_5(\nu) &= \sqrt{6}^{\,-1}\{\chi_1(\nu)-\chi_2(\nu)+\chi_3(\nu) \\
&\quad -\chi_4(\nu)+\chi_5(\nu)-\chi_6(\nu)\}
\end{aligned}\right\} \quad (1)$$

In the above $\chi_t(\nu)$ is the $2P\pi$ atomic orbital of νth electron at tth carbon atom, and CH_2 is attached to carbon atom 1 of benzene ring.

The unperturbed wave functions of benzyl

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1) Y. Mori, This Bulletin, **34**, 1031 (1961).

2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

3) A. London, ibid., **13**, 396 (1945); H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 101 (1955); Y. Mori, This Bulletin, **28**, 291 (1955).

TABLE I. THE WAVE FUNCTIONS

Doublet configurations ($M_s=+1/2$)

Non-polar

$^2B_2$

$\Psi_1=|\varphi_0(1)\alpha(1)\varphi_0(2)\beta(2)\varphi_1(3)\alpha(3)\varphi_1(4)\beta(4)\varphi_2(5)\alpha(5)\varphi_2(6)\beta(6)\chi_7(7)\alpha(7)|=|0\bar{0}1\bar{1}2\bar{2}7|$

$\Psi_2=1/2\{|0\bar{0}1\bar{3}2\bar{2}7|-|0\bar{0}\bar{1}32\bar{2}7|+|0\bar{0}1\bar{1}2\bar{4}7|-|0\bar{0}1\bar{1}\bar{2}47|\}$

$\Psi_3=\sqrt{12}^{-1}\{|0\bar{0}1\bar{3}2\bar{2}7|+|0\bar{0}\bar{1}32\bar{2}7|-2|0\bar{0}132\bar{2}\bar{7}|+|0\bar{0}1\bar{1}2\bar{4}7|+|0\bar{0}1\bar{1}\bar{2}47|$
$-2|0\bar{0}1\bar{1}24\bar{7}|\}$

$\Psi_4=1/2\{|0\bar{0}1\bar{3}2\bar{2}7|-|0\bar{0}\bar{1}32\bar{2}7|-|0\bar{0}1\bar{1}2\bar{4}7|+|0\bar{0}1\bar{1}\bar{2}47|\}$

$\Psi_5=\sqrt{12}^{-1}\{|0\bar{0}1\bar{3}2\bar{2}7|+|0\bar{0}\bar{1}32\bar{2}7|-2|0\bar{0}132\bar{2}\bar{7}|-|0\bar{0}1\bar{1}2\bar{4}7|-|0\bar{0}1\bar{1}\bar{2}47|$
$+2|0\bar{0}1\bar{1}24\bar{7}|\}$

$^2A_2$

$\Psi_6=1/2\{|0\bar{0}1\bar{4}2\bar{2}7|-|0\bar{0}\bar{1}42\bar{2}7|-|0\bar{0}1\bar{1}2\bar{3}7|+|0\bar{0}1\bar{1}\bar{2}37|\}$

$\Psi_7=\sqrt{12}^{-1}\{|0\bar{0}1\bar{4}2\bar{2}7|+|0\bar{0}\bar{1}42\bar{2}7|-2|0\bar{0}142\bar{2}\bar{7}|+|0\bar{0}1\bar{1}2\bar{3}7|+|0\bar{0}1\bar{1}\bar{2}37|$
$-2|0\bar{0}1\bar{1}23\bar{7}|\}$

$\Psi_8=1/2\{|0\bar{0}1\bar{4}2\bar{2}7|-|0\bar{0}\bar{1}42\bar{2}7|-|0\bar{0}1\bar{1}2\bar{3}7|-|0\bar{0}1\bar{1}\bar{2}37|\}$

$\Psi_9=\sqrt{12}^{-1}\{|0\bar{0}1\bar{4}2\bar{2}7|+|0\bar{0}\bar{1}42\bar{2}7|-2|0\bar{0}142\bar{2}\bar{7}|-|0\bar{0}1\bar{1}2\bar{3}7|-|0\bar{0}1\bar{1}\bar{2}37|$
$+2|0\bar{0}1\bar{1}23\bar{7}|\}$

Electron transfer

$^2B_2$

$\Psi_{10}=|0\bar{0}12\bar{2}7\bar{7}|$

$\Psi_{11}=|0\bar{0}1\bar{1}2\bar{2}3|$

$\Psi_{12}=|0\bar{0}32\bar{2}7\bar{7}|$

$\Psi_{13}=|0\bar{0}13\bar{3}2\bar{2}|$

$\Psi_{14}=\sqrt{2}^{-1}\{|0\bar{0}12\bar{4}7\bar{7}|-|0\bar{0}1\bar{2}47\bar{7}|\}$

$\Psi_{15}=\sqrt{2}^{-1}\{|0\bar{0}1\bar{1}2\bar{4}3|-|0\bar{0}1\bar{1}\bar{2}43|\}$

$\Psi_{16}=\sqrt{6}^{-1}\{|0\bar{0}12\bar{4}7\bar{7}|-|0\bar{0}1\bar{2}47\bar{7}|-2|0\bar{0}\bar{1}247\bar{7}|\}$

$\Psi_{17}=\sqrt{6}^{-1}\{|0\bar{0}1\bar{1}2\bar{4}3|+|0\bar{0}1\bar{1}\bar{2}43|-2|0\bar{0}1\bar{1}24\bar{3}|\}$

$^2A_2$

$\Psi_{18}=|0\bar{0}1\bar{1}27\bar{7}|$

$\Psi_{19}=|0\bar{0}1\bar{1}42\bar{2}|$

$\Psi_{20}=|0\bar{0}42\bar{2}7\bar{7}|$

$\Psi_{21}=|0\bar{0}1\bar{1}23\bar{3}|$

$\Psi_{22}=\sqrt{2}^{-1}\{|0\bar{0}12\bar{3}7\bar{7}|-|0\bar{0}1\bar{2}37\bar{7}|\}$

$\Psi_{23}=\sqrt{2}^{-1}\{|0\bar{0}1\bar{4}2\bar{2}3|-|0\bar{0}\bar{1}42\bar{2}3|\}$

$\Psi_{24}=\sqrt{6}^{-1}\{|0\bar{0}12\bar{3}7\bar{7}|+|0\bar{0}1\bar{2}37\bar{7}|-2|0\bar{0}\bar{1}237\bar{7}|\}$

$\Psi_{25}=\sqrt{6}^{-1}\{|0\bar{0}1\bar{4}2\bar{2}3|+|0\bar{0}\bar{1}42\bar{2}3|-2|0\bar{0}142\bar{2}\bar{3}|\}$

Quartet configuration ($M_s=+3/2$)

Non-polar

$$^4B_2\quad\begin{cases}\Psi_{26}=\sqrt{2}^{-1}\{|0\bar{0}132\bar{2}7|+|0\bar{0}1\bar{1}247|\}\\ \Psi_{27}=\sqrt{2}^{-1}\{|0\bar{0}132\bar{2}7|-|0\bar{0}1\bar{1}247|\}\end{cases}$$

$$^4A_2\quad\begin{cases}\Psi_{28}=\sqrt{2}^{-1}\{|0\bar{0}142\bar{2}7|+|0\bar{0}1\bar{1}237|\}\\ \Psi_{29}=\sqrt{2}^{-1}\{|0\bar{0}142\bar{2}7|-|0\bar{0}1\bar{1}237|\}\end{cases}$$

Electron transfer

$$^4B_2\quad\begin{cases}\Psi_{30}=|0\bar{0}1247\bar{7}|\\ \Psi_{31}=|0\bar{0}1\bar{1}243|\end{cases}$$

$$^4A_2\quad\begin{cases}\Psi_{32}=|0\bar{0}1237\bar{7}|\\ \Psi_{33}=|0\bar{0}142\bar{2}3|\end{cases}$$

radical used in the present calculation are shown in Table I.

In Table I, $\chi_7(\nu)$ is the 2Pπ orbital of CH_2. The configurations from Ψ_1 to Ψ_9 are those of the previous paper[4] and these are the non-polar configuration. The electron transfer configurations from Ψ_{10} to Ψ_{25} (polar configurations) are neccessary to consider the effect of electron transfer.

By the use of Pariser-Parr approximation, with the neglect of penetration integral and all of the differential overlaps except resonance

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[4] The correlations between the electronic states of benzene and those of benzyl radical are

$\psi(^1A_{1g})-\Psi_1$; $\psi(^1E_{1u})-\Psi_2,\Psi_8$; $\psi(^1B_{1u})-\Psi_4$; $\psi(^1B_{2u})-\Psi_6$; $\psi(^3E_{1u})-\Psi_3$, Ψ_9, Ψ_{29}; $\psi(^3B_{1u})-\Psi_5$, Ψ_{27}; $\psi(^3B_{2u})-\psi_4$, ψ_{28}.

integral, the energies of the electron transfer configurations degenerate in pairs

$$H_{v,v}=H_{v+1,\ v+1}$$

where v is an even number[5].

The matrix elements H_{jk}'s ($j\neq k$) are not zero in the following two cases; 1) between an electron transfer configuration and a non-polar configuration of the same symmetry class both of which differ by the position of just one electron, and 2) between both electron transfer configurations of the same direction and of the same symmetry class. However, the interactions between excited electron transfer configurations are not considered, as these contribute very slightly to the energies and to the wave functions of the lower cxcited states of benzyl radical.

Then by taking the linear combinations

$$\left.\begin{aligned}\Psi_v^+&=\Psi_v+\Psi_{v+1}\\ \Psi_{v+1}^-&=\Psi_v-\Psi_{v+1}\end{aligned}\right\}\qquad(2)$$

each secular determinant is factored as shown in Table II. The values of the integrals are those by Pariser[6].

Then the wave functions of benzyl radical are classified into classes as follows:

The wave functions represented by the linear combinations of

a) Ψ_1, Ψ_3, Ψ_5, Ψ_{11}^-, Ψ_{13}^-, Ψ_{14}^+, Ψ_{17}^-
b) Ψ_2, Ψ_4, Ψ_{10}^+, Ψ_{12}^+, Ψ_{15}^-, Ψ_{16}^+
c) Ψ_6, Ψ_9, Ψ_{18}^+, Ψ_{20}^+, Ψ_{23}^-, Ψ_{23}^+
d) Ψ_7, Ψ_8, Ψ_{19}^-, Ψ_{21}^-, Ψ_{22}^+, Ψ_{25}^-
e) Ψ_{26}, Ψ_{27}, Ψ_{31}^-
f) Ψ_{30}^+
g) Ψ_{28}, Ψ_{33}^-
h) Ψ_{29}, Ψ_{32}^+

Since the non-vanishing dipole matrix elements,

$$eq_{jk}=e\int\Psi_j\sum_{\nu}q(\nu)\Psi_k\mathrm{d}V$$

TABLE II. THE MATRIX ELEMENTS. (The values are given in eV.)

(I) $^2B_2$

(a) $E_1=H_{11}$

	(1)	(3)	(5)	(11⁻)	(13⁻)	(14⁺)	(17⁻)
(1)	E_1						
(3)	0	$E_1+4.1485$					
(5)	0	0	$E_1+3.5895$				
(11⁻)	+1.9359	+1.6766	+1.6766	$E_1+6.1602$			
(13⁻)	0	−1.6766	−1.6766	+0.9470	$E_1+11.2744$		
(14⁺)	0	0	0	+1.3888	0	$E_1+12.7060$	
(17⁻)	0	+1.3689	−1.3689	0	0	0	$E_1+11.1485$

(b) $E_4=H_{44}=E_1+5.9595$

	(2)	(4)	(10⁺)	(12⁺)	(15⁻)	(16⁺)
(2)	$E_4+0.8000$					
(4)	0	E_4				
(10⁺)	+0.9680	+0.9680	$E_4+0.2007$			
(12⁺)	+0.9680	+0.9680	+0.9470	$E_4+5.3152$		
(15⁻)	+1.3689	−1.3689	+1.3888	0	$E_4+6.7465$	
(16⁺)	0	0	0	0	0	$E_4+5.1889$

(II) $^2B_2$

(c) $E_9=H_{99}=E_1+4.1495$

	(6)	(9)	(18⁺)	(20⁺)	(23⁻)	(24⁺)
(6)	$E_9+0.5600$					
(9)	0	E_9				
(18⁺)	+0.9680	−1.6766	$E_9+2.3410$			
(20⁺)	+0.9680	−1.6766	0	$E_9+7.3224$		
(23⁻)	+1.3689	0	−0.6696	0	$E_9+7.9980$	
(24⁺)	0	−1.3689	−1.1598	0	0	$E_9+8.2180$

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5) See Appendix. This relation is plausible in simple MO calculations.

6) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

TABLE II (Continued)

(d) $E_7=H_{77}=E_1+4.7095$

	(7)	(8)	(19^-)	(21^-)	(22^+)	(25^-)
(7)	E_7					
(8)	0	$E_7+2.0500$				
(19^-)	$+1.6766$	-0.9680	$E_7+1.7810$			
(21^+)	-1.6766	$+0.9680$	0	$E_7+6.7624$		
(22^+)	0	-1.3689	-0.6696	0	$E_7+7.4380$	
(25^-)	$+1.3689$	0	-1.1598	0	0	$E_7+7.6580$

(III) $^4B_2$

(e) $E_{27}=H_{27,27}=E_1+3.5895$

	(26)	(27)	(31^-)
(26)	$E_{27}+0.5600$		
(27)	0	E_{27}	
(31^-)	$+1.3689$	-1.3689	$E_{27}+6.1602$

(f) $E_{30^+}=H_{31^+,31^+}=E_1+9.7497$

(IV) $^4A_2$

(g) $E_{28}=H_{28,28}=E_1+4.7095$

	(28)	(33^-)
(28)	E_{28}	
(33^-)	$+1.3689$	$E_{28}+5.705$

(h) $E_{29}=H_{29,29}=E_1+4.1495$

	(29)	(32^-)
(29)	E_{29}	
(32^+)	-1.3689	$E_{29}+5.9305$

TABLE III. THE NON-VANISHING DIPOLE MATRIX ELEMENTS[a]

$q_{12}=[q:13]+[q:24]$
$q_{11^-,10^+}=1/2\{[q:77]-[q:33]\}$
$q_{11^-,12^+}=[q:13]$
$q_{11^-,15^-}=\sqrt{2}[q:24]$
$q_{13^-,12^+}=1/2\{[q:77]-[q:33]\}$
$q_{14^+,15^-}=1/2\{[q:77]-[q:33]\}$
$q_{17^-,16^+}=1/2\{[q:77]-[q:33]\}$
$q_{18}=[q:14]-[q:23]$
$q_{11^-,21^-}=[q:14]$
$q_{14^+,19^-}=-\sqrt{2}^{-1}[q:14]$
$q_{17^-,19^-}=-\sqrt{3/2}[q:14]$

a) $[q:lm]=\int\varphi_l(\nu)q(\nu)\varphi_m(\nu)\mathrm{d}\tau_\nu$

$[q:77]=\int\chi_7(\nu)q(\nu)\chi_7(\nu)\mathrm{d}\tau_\nu$

TABLE IV. THE LOWER ENERGY LEVELS OF BENZYL RADICAL

State	Class	Energy, eV.[a]
$^2B_2$	a	0
$^2B_2$	a	2.75 (2.99)
$^2A_2$	c	3.21 (3.42)
$^2A_2$	d	3.70 (4.33)
$^4B_2$	e	3.92 (4.01)
$^2B_2$	a	4.16 (4.18)
$^4A_2$	h	4.59 (4.57)
$^4B_2$	e	4.74 (4.86)
$^2A_2$	c	5.08 (5.13)
$^4A_2$	g	5.12 (5.42)
$^2B_2$	b	5.29 (6.23)

a) The values in the parentheses are those in the previous paper.

where $q(\nu)$ is the position of the νth electron, are those shown in Table III, the transitions from the ground state to the excited states of classes a and c are almost forbidden but the transitions to the excited states of classes b and d are allowed, though these four transitions are allowed by selection rule.

The energy levels of benzyl radical by the present treatment are show in Table IV.

Discussion

The lowest excitation energy from the ground state to the lowest excited state $^2B_2$ calculated by this treatment is 2.75 eV. and this value will be compared to the transition energy 2.8 eV. of the "V"-band7) of benzyl radical which was observed by Schüler. From the consideration on the transition moments it was shown that the transition to the lowest $^2A_2$ (3.21 eV.) of class c is almost practically forbidden and the transition to $^2A_2$ (3.75 eV.) of class d is allowed. Therefore, the absorption band observed by Porter at about 3100 Å8) will be assigned to the excitation from the ground state to the excited state $^2A_2$ (3.75 eV.; 3300 Å).

In the present treatment, the weak intensities of the lower absorption bands are predicted though the effect of electron transfers was taken into account. There are two directions of the electron transfers. One is the electron transfer from benzene ring to CH_2 and the other is the reverse. Further the effect of these two electron transfers are equal in magnitude and opposite in direction, and cancel each other on the transition moments of the excitation to the states of class a. On the other hand, in the transitions to the states of class b the effect of electron transfer may be considerable, because for these transitions the two electron transfers contribute to enhance the oscillator strengths.

The effect of electron transfer on the transitions to the states of classes c and d is indirect. The directions of these transition moments are orthogonal to the direction of electron transfer. In this case, the transition moments are given by the mixing with the configuration Ψ_8 where the mixing arises from the electron transfer interaction. Therefore, the intensity of the transition to $^2A_2$ (3.21 eV.) may be weak, as no mixing with Ψ_8 occurs and $^2A_2$ (3.75 eV.) will give rise to a strong absorption band by the mixing with Ψ_8.

Consideration may be given to the intensities of the lowest absorption bands of radicals in which the CH_2 group of benzyl radical is substituted by another atom or group. By the substitution, the electronegativity of the attached group or atom is changed from that of CH_2. By this change the difference is given between the weights of contributions from the two opposite electron transfer states. Then the intensities of the lowest bands of these radicals may be more intense than that of benzyl radical because the effects of the two electron transfers of opposite directions do not cancel completely in such radicals.

The results of the present paper are similar to those obtained by the treatment in the previous paper1) and also the inconsistency with the results calculated by the method of MO9,10) is seen. This inconsistency arises from the difference of the configuration interactions included in the calculations as shown in the previous paper. The results of the present paper may be more reliable than that in the previous paper because of the improved procedure of calculation.

Summary

The method of composite system was applied to the calculation of the electronic spectra of benzyl radical. The results are very similar to those in the previous paper1) and there is no important difference between these two results though the procedures of calculation are different.

The effect of electron transfer on the transition moments of lower bands of some radicals was discussed.

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Appendix

The diagonal matrix elements of the electron transfer configurations are written in the form

$$\mathrm{H}_{j\,j}=\mathrm{E}_P(j)+\mathrm{U}(j)$$

In the above, $\mathrm{E}_P(j)$ represents the energies of charge components in the electron transfer j and $\mathrm{U}(j)$ is the Coulomb potential between charged components.

The molecular integral are abbreviated as

$$\mathbf{I}_{mm}=\int\varphi_m(\nu)\mathbf{H}_{core}(\nu)\varphi_m(\nu)\mathrm{d}\tau_\nu$$

$$[ll:mm]=\iint|\varphi_l(\nu)|^2 e^2/r_{\nu\mu}|\varphi_m(\mu)|^2\,\mathrm{d}\tau_\nu\mathrm{d}\tau_\mu$$

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7) H. Schüler, *Z. Naturforsch.*, **A10**, 459 (1955).

8) G. Porter and J. Norman, *Nature*, **174**, 508 (1954).

9) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **A68**, 591 (1955).

10) W. Bingel, *Z. Naturforsch.*, **A10**, 462 (1955).

$$[lm:lm]=\iint\varphi_l(\nu)\varphi_m(\nu)e^2/r_{\nu\mu}\varphi_m(\mu)\varphi_l(\mu)\mathrm{d}\tau_\nu\mathrm{d}\tau_\mu$$

$$(tt:uu)=\iint|\chi_t(\nu)|^2e^2/r_{\nu\mu}|\chi_u(\mu)|^2\mathrm{d}\tau_\nu\mathrm{d}\tau_\mu$$

where $\varphi_l(\nu)$ and $\varphi_m(\nu)$ are the π-electron molecular orbitals of benzene.

Applying the following relations (the last three are Eqs. 28, 46 and 47 in Ref. 6),

$$[11:mm]=[33:mm],\ [22:mm]=[44:mm]$$

$$[12:12]=[34:34],\ [23:23]=[14:14]$$

$$\mathbf{I}_{mm}=\mathbf{W}_{2\mathrm{P}}-\sum_t(C_{mt})^2\sum_{u(\neq t)}(tt:uu)+k_m\beta$$

$$2\sum_{m=0}^{2}[ll:mm]=\sum_t(C_{lt})^2\sum_u(tt:uu)$$

$$2\sum_{m=0}^{2}\{[1m:1m]+[3m:3m]\}$$

$$=2\sum_{m=0}^{2}\{[2m:2m]+[4m:4m]\}=(11:11)$$

one has

$$\mathbf{E}_P(10)=E_P(11),\qquad \mathbf{E}_P(18)=\mathbf{E}_P(19)$$

By the above equations and by the relations

$$[11:33]=[22:44],\quad [01:01]=[02:02]$$

$$[03:03]=[04:04],\quad [13:13]=[24:24]$$

the following is given

$$\mathbf{E}_P(v)=\mathbf{E}_P(v+1)$$

where v is an even number.

The Coulomb potential U(j) is given subject to the symmetry (except U(20) and U(21)),

$$^2\mathbf{B}_2 \text{ and } {}^4\mathbf{B}_2\quad \mathrm{U}(j)=-[11:77]$$

$$^2\mathbf{A}_2 \text{ and } {}^4\mathbf{A}_2\quad \mathrm{U}(j)=-[22:77]$$

The potentials U(20) and U(21) are

$$\mathrm{U}(20)=\mathrm{U}(21)=-2[11:77]+[22:77]$$

Thus the following is given

$$\mathbf{H}_{v,\,v}=\mathbf{H}_{v+1,\,v+1}$$