

An Approximate Expression of Expectation Values for Energy by INDO-CI Method

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(Received 12 Dec. 1995, revised 1 Feb. 1996)

Abstract: We propose an approximate expression of expectation values for energy of ground and excited singlet states of valence-shell electron system within the framework of an INDO (intermediate neglect of differential overlap) CI(configuration interaction) method, paying attention to electron densities and bond orders generalized by one-electron projection operator. The validity of the approximate expression is confirmed for oligoglycines with a planar or helical configuration.

§1. Introduction

One of the most important problems in molecular quantum mechanics is predicting the geometries of molecules. For example, the geometries of molecules in strong electric fields or of electronically excited molecules can be examined theoretically, whereas experimentally these molecules are often very elusive. From the theoretical point of view, the energy of a molecule on the basis of Born–Oppenheimer approximation is a parametric function of nuclear coordinates, and a geometry of the molecule is determined by minimizing its energy with respect to the nuclear coordinates. Along this line, various algorithms for searching local minima of the energy surfaces of the molecules have been developed in the framework of Hartree–Fock calculation.¹⁾

Geometries of molecules have the intimate relation to the electronic structure of the valence-shell electrons of the molecules. On the basis of this idea, a simple relation between bond lengths and bond orders was proposed by minimizing Hartree–Fock energy in intermediate neglect of differential overlap (INDO) approximation.²⁾ The relation reveals that the physical origin of changes in the bond lengths come from bond orders which characterize the electronic structure of molecules. However, an extension of the relation beyond the Hartree–Fock approximation has not been made yet, despite an important problem in order to describe the geometries of molecules in strong electric fields or of electronically excited molecules in terms of the quantities which characterize the electronic structure.

Thus, we have to elucidate a relation between bond lengths and electronic structure beyond the Hartree–Fock approximation. To approach this problem, we first express the energy including configuration interaction (CI), defining electron densities and bond orders

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which include the effect of CI, and then differentiate the energy with respect to bond lengths. In this paper, we propose an approximate expression of expectation values for energy of valence-shell electron system within the framework of INDO-CI approximation, paying attention to the generalized expressions of electron densities and bond orders which include the effect of CI. And the validity of the approximate expression is confirmed for oligoglycines with a planar or helical configuration.

The exposition of the present paper is as follows. In §2 an extended INDO-CI method is reviewed. In §3, the electron densities and bond orders for the singlet states are defined in terms of an one-electron projection operator,³⁾ and a new description of the expectation values for energy of the singlet states is given using these electron densities and bond orders. From the description, an approximate expression of the expectation values for energy is proposed. In §4 the parametrization of the extended INDO-CI method is outlined, and in §5 the validity of the approximate expression proposed in §3 is examined for oligoglycines with a planar or a helical configuration. Finally, the results of the present study are discussed in §6.

§2. Review of an Extended INDO-CI Method

We consider a system consisted of even (2N) valence-shell electrons, and we express its total Hamiltonian as

$$H = H_I + H_{II}, \quad (2.1a)$$

$$H_I = \sum_j H_C(r_j), \quad H_C(r_j) = -(\hbar^2/2m)\nabla^2(r_j) + \sum_j V_A(r_j), \quad (2.1b)$$

$$H_{II} = \sum_{j < k} \sum e^2 / |\mathbf{r}_j - \mathbf{r}_k|. \quad (2.1c)$$

Here $V_A(r_j)$ represents the effective interaction of electron j with atomic core A.

We first introduce Slater-type AOs $\{\chi_{\mu(A)}\}$ of valence-shell electrons on atomic core A with the definitions

$$[-(\hbar^2/2m)\nabla^2(\mathbf{r}) + V_A(\mathbf{r})]\chi_{\mu(A)}(\mathbf{r}) = \alpha_{\mu(A)}\chi_{\mu(A)}(\mathbf{r}), \quad (2.2a)$$

$$\int \chi_{\mu(A)}(\mathbf{r})\chi_{\nu(A)}(\mathbf{r}) d^3\mathbf{r} = (\chi_{\mu(A)} | \chi_{\nu(A)}) = \delta_{\mu\nu}. \quad (2.2b)$$

The orthonormal AOs $\{\lambda_{\mu(A)}\}$ are then constructed in the form

$$\lambda_{\mu(A)}(\mathbf{r}) = \chi_{\mu(A)}(\mathbf{r}) - \sum_{B \neq A} \sum_{\nu(B)} \chi_{\nu(B)}(\mathbf{r}) S_{\nu(B)\mu(A)} / 2 + \cdots, \quad (2.2c)$$

using overlap integral $S_{\nu(B)\mu(A)}$ between $\chi_{\nu(B)}$ and $\chi_{\mu(A)}$.⁴⁾

The 2N valence-shell electrons are assigned to the LCAO MOs

$$\phi_j(\mathbf{r}) = \sum_A \sum_{\mu(A)} \lambda_{\mu(A)}(\mathbf{r}) C_{\mu(A)j}, \quad (2.3a)$$

and the LCAO coefficients $\{C_{\mu(A)j}\}$ and the orbital energy ε_j of ϕ_j are determined from the fol-

lowing ASMO-SCF equation which can be derived by minimizing the total energy E_g of ground-state configuration $\psi(g)$ with respect to $\{C_{\mu(A)j}\}$:

$$\sum_B \sum_{v(B)} F_{\mu(A)v(B)} C_{v(B)j} = C_{\mu(A)j} \epsilon_j. \quad (2.3b)$$

Fock matrix elements $\{F_{\mu(A)v(B)}\}$ in (2.3b) are simplified as follows. First, we notice that

$$S_{\mu(A)v(A+2)} \sim S_{\mu(A)v(A+1)}^2 \quad (2.4)$$

for the nearest $(A+1)$ and the next-nearest neighbor $(A+2)$ of atom A. Neglecting the terms higher than first order of $S_{\mu(A)v(A+1)}$ in $\lambda_{\mu(A)}\lambda_{v(A)}$ and $\lambda_{\mu(A)}\lambda_{v(A+1)}$, and using the Mulliken approximation⁵⁾

$$\chi_{\mu(A)}\chi_{v(B)} \doteq S_{\mu(A)v(B)}(\chi_{\mu(A)}^2 + \chi_{v(B)}^2)/2, \quad (2.5a)$$

we have the following approximate expression

$$\lambda_{\mu(A)}\lambda_{v(B)} \doteq \delta_{\mu v} \delta_{AB} \chi_{\mu(A)}^2. \quad (2.5b)$$

Here $\delta_{\mu v}$ represents Kronecker delta.

Secondly, based on the approximation (2.5b), the matrix elements of core Hamiltonian H_C are taken as

$$H_{C, \mu(A)v(A)} \equiv (\lambda_{\mu(A)} | H_C | \lambda_{v(A)}) \doteq \delta_{\mu v} [\alpha_{\mu(A)} - \sum_{B \neq A} (\chi_{\mu(A)} | V_B | \chi_{\mu(A)})], \quad (2.6a)$$

and the penetration integrals are approximated to be

$$(\chi_{\mu(A)} | V_B | \chi_{\mu(A)}) \doteq -Z_B (\chi_{\mu(A)} \chi_{\mu(A)} | \chi_{s(B)} \chi_{s(B)}), \quad (2.6b)$$

$$(\chi_{\mu(A)} \chi_{\mu(A)} | \chi_{s(B)} \chi_{s(B)}) \equiv \iint \chi_{\mu(A)}(\mathbf{r}) \chi_{\mu(A)}(\mathbf{r}) (e^2 / |\mathbf{r} - \mathbf{r}'|) \chi_{s(B)}(\mathbf{r}') \chi_{s(B)}(\mathbf{r}') d^3r d^3r', \quad (2.6c)$$

by replacing V_B with the spherical charge distribution of density $\chi_{s(B)}^2$. Here $\chi_{s(B)}$ is Slater-type 2s orbital on atomic core B and Z_B denotes the effective nuclear charge of the core. The resonance integral $\beta_{\mu(A)v(B)} \equiv H_{C, \mu(A)v(B)}$ ($A \neq B$), which cannot simply be treated by the approximation (2.5b), is taken to be

$$\beta_{\mu(A)v(B)} \doteq -k_\beta (I_{\mu(A)}^* + I_{v(B)}^*) S_{\mu(A)v(B)} / 2, \quad A \neq B \quad (2.7)$$

according to the Wolfsberg-Helmholtz approximation.⁶⁾ Here k_β is a constant to be semiempirically determined; $I_{\mu(A)}^*$ is the modified valence-state ionization potential of an electron in $\chi_{\mu(A)}$ which will be mentioned in §4.

Thirdly, one-center two-electron Coulomb integrals are approximated as the following expression, according to (2.4b) and the INDO method by Pople *et al.*:⁷⁾

$$\begin{aligned} (\lambda_{\mu(A)} \lambda_{v(A)} | \lambda_{\rho(A)} \lambda_{\sigma(A)}) &\doteq (\chi_{\mu(A)} \chi_{v(A)} | \chi_{\rho(A)} \chi_{\sigma(A)}) \\ &= [\delta_{v\mu} \delta_{\rho\mu} \delta_{\sigma\mu} (\chi_{\mu(A)} \chi_{\mu(A)} | \chi_{\mu(A)} \chi_{\mu(A)}), \delta_{v\mu} \delta_{\sigma\rho} (\chi_{\mu(A)} \chi_{\mu(A)} | \chi_{\rho(A)} \chi_{\rho(A)}), \\ &\quad \delta_{\rho\mu} \delta_{\sigma v} (\chi_{\mu(A)} \chi_{v(A)} | \chi_{\mu(A)} \chi_{v(A)}), \delta_{\rho v} \delta_{\sigma\mu} (\chi_{\mu(A)} \chi_{v(A)} | \chi_{v(A)} \chi_{\mu(A)})]. \end{aligned} \quad (2.8)$$

Strictly speaking, only the first and second integrals in (2.8) are to be considered in the approximation (2.5b). However, the remaining two integrals have nearly the same value as

$(\chi_{\mu(A)}\chi_{\mu(A)}|\chi_{\rho(A)}\chi_{\rho(A)})$, and hence they are also taken into account in the INDO approximation.

According to (2.5b), four-center two-electron Coulomb integrals are approximated as follows:

$$\begin{aligned} (\lambda_{\mu(A)}\lambda_{\nu(B)}|\lambda_{\rho(C)}\lambda_{\sigma(D)}) &\doteq \delta_{\mu\nu}\delta_{AB}\delta_{\rho\sigma}\delta_{CD}\gamma_{\mu(A)\rho(C)}, \\ \gamma_{\mu(A)\rho(C)} &\equiv (\chi_{\mu(A)}\chi_{\mu(A)}|\chi_{\rho(C)}\chi_{\rho(C)}). \end{aligned} \quad (2.9)$$

Finally, paying attention to the respective covariant properties of Fock matrix elements under an orthogonal transformation between Slater-type ($2p_x$, $2p_y$, $2p_z$) orbitals on each atomic core,⁸⁾ we further introduce the following approximations in consistence with (2.6b), with the definitions

$$P_{\mu(A)\nu(B)} = 2 \sum_{j=1}^N C_{\mu(A)j} C_{\nu(B)j}, \quad P_{\nu(B)} \equiv P_{\nu(B)\nu(B)}, \quad P_B \equiv \sum_{\nu(B)} P_{\nu(B)}; \quad (2.10a)$$

$$\sum_{\nu(B)} P_{\nu(B)} \gamma_{\nu(B)\mu(A)} \doteq P_B \gamma_{s(B)\mu(A)}, \quad (2.10b)$$

$$P_{\mu(A)\nu(B)} \gamma_{\mu(A)\nu(B)} \doteq P_{\mu(A)\nu(B)} \gamma_{s(A)s(B)}. \quad (2.10c)$$

In short, the Fock matrix elements in (2.3b) are simplified as follows:

$$F_{\mu(A)\mu(A)} \doteq \alpha_{\mu(A)} + P_{\mu(A)} \gamma_{\mu(A)} / 2 + \sum_{B \neq A} (P_B - Z_B) \gamma_{s(B)\mu(A)} + \sum_{\mu \neq \nu} P_{\nu(A)} (\gamma_{\nu(A)\mu(A)} - \tilde{\gamma}_{\nu(A)\mu(A)} / 2); \quad (2.11a)$$

$$F_{\mu(A)\nu(A)} \doteq -P_{\mu(A)\nu(A)} (\gamma_{\mu(A)\nu(A)} - 3\tilde{\gamma}_{\mu(A)\nu(A)}) / 2, \quad \mu \neq \nu; \quad (2.11b)$$

$$F_{\mu(A)\nu(B)} \doteq \beta_{\mu(A)\nu(B)} - P_{\mu(A)\nu(B)} \gamma_{s(A)s(B)}, \quad A \neq B; \quad (2.11c)$$

$$\gamma_{\mu(A)} \equiv \gamma_{\mu(A)\mu(A)}, \quad \tilde{\gamma}_{\nu(A)\mu(A)} \equiv (\chi_{\nu(A)}\chi_{\mu(A)}|\chi_{\mu(A)}\chi_{\nu(A)}). \quad (2.11d)$$

Here it need hardly to be said that the expressions of (2.11) are different from those of Pople *et al.*⁷⁾ in the following two respects: (i) a term corresponding to the third one in (2.11a) is taken by Pople *et al.* as $\sum_B (P_B - Z_B) \gamma_{AB}$, neglecting the character of atomic orbital $\chi_{\mu(A)}$ (i.e. assuming $\gamma_{\mu(A)s(B)}$ in (2.11a) to be a constant independent of the kind of $\chi_{\mu(A)}$); (ii) $I_{\mu(A)}^*$ and $I_{\nu(B)}^*$ in $\beta_{\mu(A)\nu(B)}$ of (2.7) are taken by them to be constants $-\beta_A^0$ and $-\beta_B^0$, respectively.

The singlet states Φ_r of valence-shell electrons are determined by including all the excited configurations of types $\psi(j, m)$, $\psi(jj, mm)$, $\psi(jj, mn)$ and $\psi(jk, mm)$ in CI calculations:

$$\begin{aligned} \Phi_r = & C_r(g)\psi(g) + \sum_j \sum_m C_r(j, m)\psi(j, m) + \sum_j \sum_m C_r(jj, mm)\psi(jj, mm) \\ & + \sum_j \sum_{m < n} C_r(jj, mn)\psi(jj, mn) + \sum_{j < k} \sum_m C_r(jk, mm)\psi(jk, mm). \end{aligned} \quad (2.12)$$

Here $\psi(g)$ is the ground-state configuration; $\psi(j, m)$ is the singly-excited singlet configuration in which an electron is excited from occupied MO ϕ_j to vacant one ϕ_m ; $\psi(jk, mn)$ is the doubly-excited singlet configuration in which two electrons are excited from occupied (ϕ_j, ϕ_k) to vacant (ϕ_m, ϕ_n). The CI coefficients and the eigenvalue E_r for energy of Φ_r are calculated by diagonalizing the interconfigurational matrix of total Hamiltonian H of (2.1a).

In the present section, an extended INDO-CI method was reviewed for the following

section, and four kinds of approximations for simplifying Fock matrix elements were introduced: (i) the approximation (2.5b) was applied to the overlap population $\lambda_{\mu(A)\nu(B)}$ except resonance integral $\beta_{\mu(A)\nu(B)}$; (ii) $\beta_{\mu(A)\nu(B)}$ was approximated by (2.7) according to the Wolfsberg-Helmholtz approximation; (iii) the penetration integrals were approximated by (2.6b); (iv) the approximations (2.10b) and (2.10c) were introduced for the respective properties of Fock matrix elements under an orthogonal transformation between Slater-type (2p_x, 2p_y, 2p_z) orbitals on each atomic core.

§3. A New Description and an Approximate Expression of E_r

The eigenvalue E_r for energy of singlet state Φ_r consists of the expectation values of H_I and H_{II} in (2.1) for Φ_r :

$$E_r = E_I^{(r)} + E_{II}^{(r)}; \quad (3.1a)$$

$$E_I^{(r)} \equiv \langle \Phi_r | H_I | \Phi_r \rangle, \quad (3.1b)$$

$$E_{II}^{(r)} \equiv \langle \Phi_r | H_{II} | \Phi_r \rangle. \quad (3.1c)$$

First, we now insert the linear expansion (2.12) into (3.1b), and also use (2.3a) to get

$$E_I^{(r)} = \sum_A \sum_B \sum_{\mu(A)} \sum_{\nu(B)} P_{\mu(A)\nu(B)}^{(r)} H_{C, \mu(A)\nu(B)}, \quad (3.2a)$$

$$\begin{aligned} P_{\mu(A)\nu(B)}^{(r)} = & 2 \sum_{i=1}^N C_{\mu(A)i} C_{\nu(B)i} + 2C_r(g) \sum_j \sum_m C_r(j, m) (C_{\mu(A)j} C_{\nu(B)m} + C_{\mu(A)m} C_{\nu(B)j}) \\ & - \sum_m \left[\sum_j C_r(j, m) C_{\mu(A)j} \right] \left[\sum_j C_r(j, m) C_{\nu(B)j} \right] \\ & + \sum_j \left[\sum_m C_r(j, m) C_{\mu(A)m} \right] \left[\sum_m C_r(j, m) C_{\nu(B)m} \right] \\ & + \sqrt{2} \sum_j \sum_m C_r(j, m) C_r(jj, mm) (C_{\mu(A)j} C_{\nu(B)m} + C_{\mu(A)m} C_{\nu(B)j}) \\ & - 2 \sum_j \sum_m C_r^2(jj, mm) (C_{\mu(A)j} C_{\nu(B)j} - C_{\mu(A)m} C_{\nu(B)m}) \\ & + \sum_j \sum_{m \neq n} C_r(j, m) C_r(jj, mn) (C_{\mu(A)j} C_{\nu(B)n} + C_{\mu(A)n} C_{\nu(B)j}) \\ & - \sum_{j \neq k} \sum_m C_r(j, m) C_r(jk, mm) (C_{\mu(A)k} C_{\nu(B)m} + C_{\mu(A)m} C_{\nu(B)k}) \\ & + \sqrt{2} \sum_j \sum_{m \neq n} C_r(jj, mm) C_r(jj, mn) (C_{\mu(A)m} C_{\nu(B)n} + C_{\mu(A)n} C_{\nu(B)m}) \\ & + \sqrt{2} \sum_{j \neq k} \sum_m C_r(jj, mm) C_r(jk, mm) (C_{\mu(A)j} C_{\nu(B)k} + C_{\mu(A)k} C_{\nu(B)j}) \\ & - \sum_j \sum_{m \neq n} C_r^2(jj, mn) C_{\mu(A)j} C_{\nu(B)j} \\ & + \sum_j \sum_m \left[\sum_{n \neq m} C_r(jj, mn) C_{\mu(A)n} \right] \left[\sum_{n \neq m} C_r(jj, mn) C_{\nu(B)n} \right] \\ & + \sum_{j \neq k} \sum_m C_r^2(jk, mm) C_{\mu(A)m} C_{\nu(B)m} \end{aligned}$$

$$-\sum_j \sum_m [\sum_{k \neq j} C_r(jk, mm) C_{\mu(A)k}] [\sum_{k \neq j} C_r(jk, mm) C_{v(B)k}]. \quad (3.2b)$$

If we define one-projection operator³⁾ by

$$\begin{aligned} \langle \phi_j(\mathbf{r}) | \theta_{\mu(A)v(B)}(\mathbf{r}) | \phi_m(\mathbf{r}) \rangle &= \langle \phi_m(\mathbf{r}) | \theta_{\mu(A)v(B)}(\mathbf{r}) | \phi_j(\mathbf{r}) \rangle \\ &\equiv (C_{\mu(A)j} C_{v(B)m} + C_{v(B)j} C_{\mu(A)m}) / 2, \end{aligned} \quad (3.3)$$

then $P_{\mu(A)}^{(r)} \doteq P_{\mu(A)\mu(A)}^{(r)}$ and $P_{\mu(A)v(B)}^{(r)} (\mu(A) \neq v(B))$ can be expressed as

$$P_{\mu(A)}^{(r)} = \left\langle \Phi_r \left| \sum_{j=1}^{2N} \theta_{\mu(A)\mu(A)}(r_j) \right| \Phi_r \right\rangle, \quad (3.4a)$$

$$P_{\mu(A)v(B)}^{(r)} = \left\langle \Phi_r \left| \sum_{j=1}^{2N} \theta_{\mu(A)v(B)}(r_j) \right| \Phi_r \right\rangle. \quad (3.4b)$$

The physical meaning of $P_{\mu(A)}^{(r)}$ and $P_{\mu(A)v(B)}^{(r)} (\mu(A) \neq v(B))$ specify the charge density of Φ_r . When we consider $\psi(g)$, the electron density or the bond order $P_{\mu(A)v(B)} (\mu(A) \neq v(B))$ defined by (2.10a) can be expressed as the same form by replacing Φ_r with $\psi(g)$ in (3.4).

Secondly, $E_{II}^{(r)}$ can be written in the form

$$\begin{aligned} E_{II}^{(r)} &= \sum_A \sum_B \sum_C \sum_D \sum_{\mu(A)} \sum_{v(B)} \sum_{\rho(C)} \sum_{\sigma(D)} [P^{(r)}(\mu(A), v(B), \rho(C), \sigma(D)) (\lambda_{\mu(A)} \lambda_{v(B)} | \lambda_{\rho(C)} \lambda_{\sigma(D)}) / 2 \\ &\quad + P_2^{(r)}(\mu(A), v(B), \rho(C), \sigma(D)) (\lambda_{\mu(A)} \lambda_{\sigma(D)} | \lambda_{\rho(C)} \lambda_{v(B)}) / 4 \\ &\quad + P_3^{(r)}(\mu(A), v(B), \rho(C), \sigma(D)) (\lambda_{\mu(A)} \lambda_{v(B)} | \lambda_{\rho(C)} \lambda_{\sigma(D)})], \end{aligned} \quad (3.5a)$$

$$\begin{aligned} P^{(r)}(\mu(A), v(B), \rho(C), \sigma(D)) &= P_2^{(r)}(\mu(A), v(B), \rho(C), \sigma(D)) = \left(2 \sum_{i=1}^N C_{\rho(C)i} C_{\sigma(D)i} \right) \left\{ \left(2 \sum_{i=1}^N C_{\mu(A)i} C_{v(B)i} \right) \right. \\ &\quad + 4 \sqrt{2} C_r(g) \sum_j \sum_m C_r(j, m) C_{\mu(A)j} C_{v(B)m} - 2 \sum_m [\sum_j C_r(j, m) C_{\mu(A)j}] [\sum_j C_r(j, m) C_{v(B)j}] \\ &\quad + 2 \sum_j [\sum_m C_r(j, m) C_{\mu(A)m}] [\sum_m C_r(j, m) C_{v(B)m}] \\ &\quad + 4 \sqrt{2} \sum_j \sum_m C_r(j, m) C_r(jj, mm) C_{\mu(A)j} C_{v(B)m} \\ &\quad - 4 \sum_j \sum_m C_r^2(jj, mm) (C_{\mu(A)j} C_{v(B)j} - C_{\mu(A)m} C_{v(B)m}) \\ &\quad + 4 \sum_j \sum_{m \neq n} C_r(j, m) C_r(jj, mn) C_{\mu(A)j} C_{v(B)n} - 4 \sum_{j \neq k} \sum_m C_r(j, m) C_r(jk, mm) C_{\mu(A)k} C_{v(B)m} \\ &\quad + 4 \sqrt{2} \sum_j \sum_{m \neq n} C_r(jj, mm) C_r(jj, mn) C_{\mu(A)m} C_{v(B)n} \\ &\quad + 4 \sqrt{2} \sum_{j \neq k} \sum_m C_r(jj, mm) C_r(jk, mm) C_{\mu(A)k} C_{v(B)j} \\ &\quad - 2 \sum_j \sum_{m \neq n} C_r^2(jj, mn) C_{\mu(A)j} C_{v(B)j} + 2 \sum_j \sum_m [\sum_{n \neq m} C_r(jj, mn) C_{\mu(A)n}] [\sum_{n \neq m} C_r(jj, mn) C_{v(B)n}] \\ &\quad + 2 \sum_{j \neq k} \sum_m C_r^2(jk, mm) C_{\mu(A)m} C_{v(B)m} - 2 \sum_j \sum_m [\sum_{k \neq j} C_r(jk, mm) C_{\mu(A)k}] \\ &\quad \times [\sum_{k \neq j} C_r(jk, mm) C_{v(B)k}] \}, \end{aligned} \quad (3.5b)$$

$$P_3^{(r)}(\mu(A), v(B), \rho(C), \sigma(D))$$

$$\begin{aligned}
 &= 2C_r(g) \sum_j \sum_m C_r(jj, mm) C_{\mu(A)j} C_{v(B)m} C_{\rho(C)j} C_{\sigma(D)m} \\
 &\quad + 2\sqrt{2} C_r(g) \sum_j \sum_{m < n} C_r(jj, mn) C_{\mu(A)j} C_{v(B)m} C_{\rho(C)j} C_{\sigma(D)n} \\
 &\quad - 2\sqrt{2} C_r(g) \sum_{j < k} \sum_m C_r(jk, mm) C_{\mu(A)j} C_{v(B)m} C_{\rho(C)k} C_{\sigma(D)m} \\
 &\quad + 2[\sum_j \sum_m C_r(j, m) C_{\mu(A)m} C_{v(B)j}] [\sum_j \sum_m C_r(j, m) C_{\rho(C)j} C_{\sigma(D)m}] \\
 &\quad - [\sum_j \sum_m C_r(j, m) C_{\mu(A)m} C_{\sigma(D)j}] [\sum_j \sum_m C_r(j, m) C_{v(B)m} C_{\rho(D)j}] \\
 &\quad - 2\sqrt{2} \sum_j \sum_m \sum_p C_r(j, m) C_r(pp, mm) C_{\mu(A)p} C_{v(B)j} C_{\rho(C)p} C_{\sigma(D)m} \\
 &\quad + 2\sqrt{2} \sum_j \sum_m \sum_s C_r(j, m) C_r(jj, ss) C_{\mu(A)j} C_{v(B)s} C_{\rho(C)m} C_{\sigma(D)s} \\
 &\quad + 2 \sum_j \sum_m \sum_{s \neq t} C_r(j, m) C_r(jj, st) C_{\mu(A)j} C_{v(B)s} C_{\rho(C)m} C_{\sigma(D)t} \\
 &\quad - 2 \sum_j \sum_{m \neq n} \sum_p C_r(j, m) C_r(pp, mn) C_{\mu(A)p} C_{v(B)j} C_{\rho(C)p} C_{\sigma(D)n} \\
 &\quad + 2 \sum_j \sum_m \sum_{p \neq q} C_r(j, m) C_r(pq, mm) C_{\mu(A)p} C_{v(B)j} C_{\rho(C)q} C_{\sigma(D)m} \\
 &\quad - 2 \sum_{j \neq k} \sum_m \sum_s C_r(j, m) C_r(jk, ss) C_{\mu(A)m} C_{v(B)s} C_{\rho(C)k} C_{\sigma(D)s} \\
 &\quad - 2 \sum_j \sum_m C_r^2(jj, mm) (2C_{\mu(A)j} C_{v(B)j} C_{\rho(B)m} C_{\sigma(D)m} - C_{\mu(A)j} C_{v(B)m} C_{\rho(C)m} C_{\sigma(D)j}) \\
 &\quad + \sum_j [\sum_m C_r(jj, mm) C_{\mu(A)m} C_{\rho(C)m}] [\sum_m C_r(jj, mm) C_{v(B)m} C_{\sigma(D)m}] \\
 &\quad + \sum_m [\sum_j C_r(jj, mm) C_{\mu(A)j} C_{\rho(C)j}] [\sum_j C_r(jj, mm) C_{v(B)j} C_{\sigma(D)j}] \\
 &\quad - 2\sqrt{2} \sum_j \sum_{m \neq n} C_r(jj, mm) C_r(jj, mn) (2C_{\mu(A)m} C_{v(B)n} C_{\rho(C)j} C_{\sigma(D)j} - C_{\mu(A)m} C_{v(B)j} C_{\rho(C)j} C_{\sigma(D)n}) \\
 &\quad + 2\sqrt{2} \sum_j [\sum_m C_r(jj, mm) C_{\mu(A)m} C_{\rho(C)m}] [\sum_{m < n} C_r(jj, mn) C_{v(B)m} C_{\sigma(C)n}] \\
 &\quad + 2\sqrt{2} \sum_{j \neq k} \sum_m C_r(jj, mm) C_r(jk, mm) (2C_{\mu(A)k} C_{v(B)j} C_{\rho(C)m} C_{\sigma(D)m} - C_{\mu(A)k} C_{v(B)m} C_{\rho(C)m} C_{\sigma(D)j}) \\
 &\quad - 2\sqrt{2} \sum_m [\sum_j C_r(jj, mm) C_{v(B)j} C_{\sigma(D)j}] [\sum_{j < k} C_r(jk, mm) C_{\mu(A)j} C_{\rho(C)k}] \\
 &\quad + \sum_j [\sum_{m < n} C_r(jj, mn) C_{\mu(A)m} C_{\rho(C)n}] [\sum_{m \neq n} C_r(jj, mn) C_{v(B)m} C_{\sigma(D)n}] \\
 &\quad + \sum_{m < n} [\sum_j C_r(jj, mn) C_{\mu(A)j} C_{\rho(C)j}] [\sum_j C_r(jj, mn) C_{v(B)j} C_{\sigma(D)j}] \\
 &\quad - \sum_j \sum_{m < n} \sum_{s \neq m} C_r(jj, mn) C_r(jj, ms) (2C_{\mu(A)n} C_{v(B)s} C_{\rho(C)j} C_{\sigma(D)j} - C_{\mu(A)n} C_{v(B)j} C_{\rho(C)j} C_{\sigma(D)s}) \\
 &\quad - \sum_j \sum_{m < n} \sum_{s \neq n} C_r(jj, mn) C_r(jj, sn) (2C_{\mu(A)m} C_{v(B)s} C_{\rho(C)j} C_{\sigma(D)j} - C_{\mu(A)m} C_{v(B)j} C_{\rho(C)j} C_{\sigma(D)s}) \\
 &\quad + 2 \sum_{j \neq k} \sum_m \sum_{m \neq n} C_r(jj, mn) C_r(jk, mm) (2C_{\mu(A)k} C_{v(B)j} C_{\rho(C)n} C_{\sigma(D)m} - C_{\mu(A)n} C_{v(B)j} C_{\rho(C)k} C_{\sigma(D)m}) \\
 &\quad + \sum_m [\sum_{j < k} C_r(jk, mm) C_{v(B)j} C_{\sigma(D)k}] [\sum_{j \neq k} C_r(jk, mm) C_{\mu(A)j} C_{\rho(C)k}]
 \end{aligned}$$

$$\begin{aligned}
 & + \sum_{j < k} \sum_m [\sum C_r(jk, mm) C_{\mu(A)m} C_{\rho(C)m}] [\sum C_r(jk, mm) C_{v(B)m} C_{\sigma(D)m}] \\
 & - \sum_{j < k} \sum_m \sum_{p \neq j} C_r(jk, mm) C_r(jp, mm) (2C_{\mu(A)p} C_{v(B)k} C_{\rho(C)m} C_{\sigma(D)m} - C_{\mu(A)p} C_{v(B)m} C_{\rho(C)m} C_{\sigma(D)k}) \\
 & - \sum_{j < k} \sum_m \sum_{p \neq k} C_r(jk, mm) C_r(pk, mm) (2C_{\mu(A)p} C_{v(B)j} C_{\rho(C)m} C_{\sigma(D)m} - C_{\mu(A)p} C_{v(B)m} C_{\rho(C)m} C_{\sigma(D)j}).
 \end{aligned} \tag{3.5c}$$

Here, in (3.5a) the first (second) term in the right-hand side originates from the Coulomb (exchange) interaction operator in the Hartree–Fock equation from which (2.3b) can be derived, and the third term denotes the many-electron effect that comes out due to the CI calculation.

Thirdly, the extended INDO approximation to (2.11) is applied to $E_1^{(r)}$ and $E_{II}^{(r)}$. The Matrix elements $H_{C, \mu(A)v(A)}$ and $H_{C, \mu(A)v(B)}$ ($A \neq B$) in (3.2a) are approximated as (2.6) and (2.7) respectively, and the integrals $(\lambda_{\mu(A)} \lambda_{v(B)} | \lambda_{\rho(C)} \lambda_{\sigma(D)})$ are approximated as (2.8) or (2.9):

We thus find that

$$E_1^{(r)} \doteq \sum_A \sum_{\mu(A)} P_{\mu(A)}^{(r)} [\alpha_{\mu(A)} - \sum_{B \neq A} Z_B \gamma_{\mu(A)s(B)}] + \sum_{A < B} \sum_{\mu(A)} \sum_{v(B)} P_{\mu(A)v(B)}^{(r)} \beta_{\mu(A)v(B)}, \tag{3.6a}$$

$$\begin{aligned}
 E_{II}^{(r)} \doteq & \sum_A \sum_{\mu(A)} [P_1^{(r)}(\mu(A), \mu(A))/2 - P_2^{(r)}(\mu(A), \mu(A))/4 + P_3^{(r)}(\mu(A), \mu(A))] \gamma_{\mu(A)\mu(A)} \\
 & + \sum_A \sum_{\mu(A) \neq v(A)} [P_1^{(r)}(\mu(A), v(A))/2 - P_2^{(r)}(\mu(A), v(A))/4 + P_3^{(r)}(\mu(A), v(A))] \gamma_{\mu(A)v(A)} \\
 & + \sum_A \sum_{\mu(A) \neq v(A)} \{ \tilde{P}_1^{(r)}(\mu(A), v(A)) - [P_2^{(r)}(\mu(A), v(A)) + \tilde{P}_2^{(r)}(\mu(A), v(A))]/4 \\
 & + \tilde{P}_{31}^{(r)}(\mu(A), v(A)) + \tilde{P}_{32}^{(r)}(\mu(A), v(A)) \} \tilde{\gamma}_{\mu(A)v(A)} \\
 & + \sum_{A \neq B} \sum_{\mu(A)} \sum_{v(B)} [P_1^{(r)}(\mu(A), v(B))/2 - P_2^{(r)}(\mu(A), v(B))/4 + P_3^{(r)}(\mu(A), v(B))] \gamma_{\mu(A)v(B)}.
 \end{aligned} \tag{3.6b}$$

Here the following definitions are used:

$$P_1^{(r)}(\mu(A), \rho(C)) \equiv P_1^{(r)}(\mu(A), \mu(A), \rho(C), \rho(C)), \tag{3.7a}$$

$$P_2^{(r)}(\mu(A), \rho(C)) \equiv P_2^{(r)}(\mu(A), \rho(C), \rho(C), \mu(A)), \tag{3.7b}$$

$$P_3^{(r)}(\mu(A), \rho(C)) \equiv P_3^{(r)}(\mu(A), \mu(A), \rho(C), \rho(C)), \tag{3.7c}$$

$$\tilde{P}_1^{(r)}(\mu(A), v(A)) \equiv P_1^{(r)}(\mu(A), v(A), v(A), \mu(A)), \tag{3.7d}$$

$$\tilde{P}_2^{(r)}(\mu(A), v(A)) \equiv P_2^{(r)}(\mu(A), \mu(A), v(A), v(A)), \tag{3.7e}$$

$$\tilde{P}_{31}^{(r)}(\mu(A), v(A)) \equiv P_3^{(r)}(\mu(A), v(A), v(A), \mu(A)), \tag{3.7f}$$

$$\tilde{P}_{32}^{(r)}(\mu(A), v(A)) \equiv P_3^{(r)}(\mu(A), v(A), \mu(A), v(A)). \tag{3.7g}$$

Now, we rewrite $P_1^{(r)}$, $\tilde{P}_1^{(r)}$, $P_2^{(r)}$ and $\tilde{P}_2^{(r)}$ in (3.7b) in the form

$$P_1^{(r)}(\mu(A), \mu(A)) = P_2^{(r)}(\mu(A), \mu(A)) = [P_{\mu(A)}^{(r)}]^2 - [\Delta P_{\mu(A)}^{(r)}]^2, \tag{3.8a}$$

$$P_1^{(r)}(\mu(A), v(A)) = \tilde{P}_1^{(r)}(\mu(A), v(A)) = P_{\mu(A)}^{(r)} P_{v(A)}^{(r)} - \Delta P_{\mu(A)}^{(r)} \Delta P_{v(A)}^{(r)}, \tag{3.8b}$$

$$\tilde{P}_1^{(r)}(\mu(A), v(A)) = P_2^{(r)}(\mu(A), v(A)) = [P_{\mu(A)v(A)}^{(r)}]^2 - [\Delta P_{\mu(A)v(A)}^{(r)}]^2, \tag{3.8c}$$

$$P_1^{(r)}(\mu(A), v(B)) = P_{\mu(A)}^{(r)} P_{v(B)}^{(r)} - \Delta P_{\mu(A)}^{(r)} \Delta P_{v(B)}^{(r)}, \tag{3.8d}$$

$$P_2^{(r)}(\mu(A), \nu(B)) = [P_{\mu(A)\nu(B)}^{(r)}]^2 - [\Delta P_{\mu(A)\nu(B)}^{(r)}]^2, \quad (3.8e)$$

where $\Delta P_{\mu(A)}^{(r)}$, $\Delta P_{\mu(A)\nu(A)}^{(r)}$, and $\Delta P_{\mu(A)\nu(B)}^{(r)}$ are defined as follows:

$$\Delta P_{\mu(A)}^{(r)} \equiv P_{\mu(A)}^{(r)} - P_{\mu(A)}, \quad (3.9a)$$

$$\Delta P_{\mu(A)\nu(A)}^{(r)} \equiv P_{\mu(A)\nu(A)}^{(r)} - P_{\mu(A)\nu(A)}, \quad (3.9b)$$

$$\Delta P_{\mu(A)\nu(B)}^{(r)} \equiv P_{\mu(A)\nu(B)}^{(r)} - P_{\mu(A)\nu(B)}. \quad (3.9c)$$

Here $P_{\mu(A)}(P_{\mu(A)\nu(B)})$ is the electron density (bond order) defined in (2.10a).

Finally, we assume that $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)\nu(A)}^{(r)}\Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) give only negligible contributions to $E_{II}^{(r)}$, and that $P_3^{(r)}$ in (3.6a) can also be neglected. And on the assumptions and by replacing $\gamma_{\mu(A)\nu(B)}$ in (3.6b) with $\gamma_{s(A)s(B)}$ in (2.10c), we further approximate $E_{II}^{(r)}$ of (3.6b) to obtain

$$\begin{aligned} E_r \div & \sum_A \left\{ \sum_{\nu(A)} P_{\mu(A)}^{(r)} (\alpha_{\mu(A)} + P_{\mu(A)}^{(r)} \gamma_{\mu(A)} / 4) + \sum_{\mu(A) < \nu(A)} P_{\mu(A)}^{(r)} P_{\nu(A)}^{(r)} (\gamma_{\mu(A)\nu(A)} - \tilde{\gamma}_{\mu(A)\nu(A)} / 2) \right. \\ & - \sum_{\mu(A) < \nu(A)} [P_{\mu(A)\nu(A)}^{(r)}]^2 (\gamma_{\mu(A)\nu(A)} - 3\tilde{\gamma}_{\mu(A)\nu(A)}) / 2 \Big\} \\ & + 2 \sum_{A < B} \sum_{\mu(A)} \sum_{\nu(B)} P_{\mu(A)\nu(B)}^{(r)} (\beta_{\mu(A)\nu(B)} - P_{\mu(A)\nu(B)}^{(r)} \gamma_{s(A)s(B)} / 4) \\ & + \sum_{A \neq B} \sum_{\mu(A)} (P_B^{(r)} - 2Z_B) \sum_{\mu(A)} P_{\mu(A)}^{(r)} \gamma_{\mu(A)s(B)} / 2. \end{aligned} \quad (3.10)$$

Here it should be noted that the approximate expression (3.10) of E_r is identical in form with the total energy E_g of ground-state configuration $\psi(g)$ with the exception of $P_{\mu(A)}^{(r)}$, $P_{\mu(A)\nu(A)}^{(r)}$ and $P_{\mu(A)\nu(B)}^{(r)}$. In other words we can obtain the expression of E_g of $\psi(g)$ (note that $P_{\mu(A)}$ and $P_{\mu(A)\nu(B)}$ can be expressed in the same way as (3.4) by replacing Φ_r with $\psi(g)$), if we replace $(P_{\mu(A)}^{(r)}, P_{\mu(A)\nu(A)}^{(r)}, P_{\mu(A)\nu(B)}^{(r)})$ in (3.10) for Φ_r by $(P_{\mu(A)}, P_{\mu(A)\nu(A)}, P_{\mu(A)\nu(B)})$ for $\psi(g)$.

In the present section, the expectation value $E_r^{(r)}$ of Φ_r was first expressed as (3.2) in terms of the matrix elements between the orthonormal AOs $\lambda_{\mu(A)}$, and the electron density $P_{\mu(A)}^{(r)}$ and bond order $P_{\mu(A)\nu(B)}^{(r)}$ of Φ_r were defined as (3.4) in terms of the one-electron projection operator (3.3). Then, we expressed the expectation value $E_{II}^{(r)}$ as (3.5). And we applied the extended INDO approximation for (2.11) to $E_I^{(r)}$ and $E_{II}^{(r)}$, and we further simplified $E_{II}^{(r)}$ of (3.7b) under the assumptions that not only $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)\nu(A)}^{(r)}\Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) but also $P_3^{(r)}$ in (3.6b) give only negligible contributions to $E_{II}^{(r)}$. Thus, the approximate expression (3.10) of eigenvalue E_r for energy of Φ_r is obtained, of which the characteristic is that (3.10) is identical in form with that of ground-state configuration $\psi(g)$.

§4. Parametrization

The valence-state electron configuration of each constituent atom is affected by its interaction with surrounding atoms, so that all the molecular integrals in Fock matrix elements (2.11) are estimated in a different way from that by Pople *et al.*,⁷⁾ as functions of electron densities according to Sakuranaga *et al.*¹⁰⁾

Firstly, one-center core integral $\alpha_{s(H)}$ in (2.2a) for the 1s orbital of hydrogen atom is taken equal to the minus of ionization potential $I_{s(H)}$, following the definition of $\alpha_{s(H)}$. And $\alpha_{\mu(A)}$ for $\mu=(2s \text{ or } 2p)$ and $A=(C, N \text{ or } O)$ are estimated using the following relations:¹¹⁾

$$\alpha_{s(A)} = -I_{s(A)} - \gamma_{s(A)s(A)} - n_{p(A)}(\gamma_{s(A)p(A)} - \tilde{\gamma}_{s(A)p(A)}/2), \quad (4.1a)$$

$$\alpha_{p(A)} = -I_{p(A)} - 2(\gamma_{s(A)p(A)} - \tilde{\gamma}_{s(A)p(A)}/2) - (n_{p(A)} - 1)(\gamma_{p(A)p(A)} - \tilde{\gamma}_{p(A)p(A)}/2). \quad (4.1b)$$

Here s or p denotes the Slater-type orbital of $2s$ - or $2p$ -electron on core A , respectively; \bar{p} does another Slater-type orbital of $2p$ -electron of which the direction is perpendicular to that of $2p$; $I_{\mu(A)}$ is the valence-state ionization potential of the electron on $\mu(A)$; $n_{p(A)}$ is the number of $2p$ -electrons on the core.

Secondly, the effective nuclear charges Z'_A of Slater-type orbitals which are used for the calculation of overlap integrals are taken to be

$$Z'_H(Q_H) = Z_H(0) + 0.30Q_H, \quad (4.2a)$$

$$Z'_A(Q_A) = Z_A(0) + 0.35Q_A, \quad A=C, N \text{ or } O, \quad (4.2b)$$

following Slater's rule.¹⁰⁾ Here $Z_A(0)$ is the Slater value; Q_A denotes net charge ($Z_A - P_A$) of core A , where Z_A is the effective nuclear charge of the core (see (2.6b)) and P_A is the electron density on the core (see (2.10a)).

Thirdly, the one-center Coulomb repulsion integral $\gamma_{\mu(A)\nu(A)}$, the one-center exchange integral $\gamma_{\mu(A)\nu(A)}$ and the two-center Coulomb repulsion integral $\gamma_{\mu(A)\nu(B)}$ ($A \neq B$) are calculated using Z'_A (in place of Z'_A) which is assumed to be a linear function of total electron densities $P_{s(A)}^T$ and $P_{p(A)}^T$ of s - and p -electrons on core A .¹¹⁾ For example, Z'_O is taken as

$$Z'_O = 3.079 + 0.809(2 - P_{s(O)}^T) + 0.357(4 - P_{p(O)}^T). \quad (4.3)$$

Fourthly, the valence-state ionization potentials $I_{s(A)}$ and $I_{p(A)}$ in (4.1) are assumed to be quadratic functions of $P_{s(A)}^T$ and $P_{p(A)}^T$, respectively.¹⁰⁾ For example, $I_{s(O)}$ and $I_{p(O)}$ are taken in eV units to be

$$I_{s(O)} = -8.360 + 10.037D_{s(O)} + 1.047D_{s(O)}^2, \quad (4.4a)$$

$$I_{p(O)} = -16.463 + 6.801D_{p(O)} + 1.351D_{p(O)}^2. \quad (4.4b)$$

Here $D_{s(O)}$ (or $D_{p(O)}$) is the effective charge of oxygen atom for $2s$ - (or $2p$ -) electron, which is given by

$$D_{s(O)} = 3.079 + 0.809(2 - P_{s(O)}^T), \quad (4.5a)$$

$$D_{p(O)} = 3.079 + 0.357(4 - P_{p(O)}^T), \quad (4.5b)$$

Fifthly, $I_{s(A)}^*$ in (2.7) is taken equal to such $I_{s(A)}$ as (4.4a),¹⁰⁾ and $I_{p(A)}^*$ in (2.7) is assumed to have the same form as such $I_{p(A)}$ as (4.4b) provided $(n_{p(A)} - P_{p(A)}^T)$ in $D_{p(A)}$ is replaced by $(1 - P_{p(A)})$ [note that only the electrons in one $2p$ orbital on atom A are concerned with resonance integral $\beta_{\mu(A)\nu(B)}$, and that $(n_{p(A)} - P_{p(A)}^T) = \Sigma_{p(A)}(1 - P_{p(A)})$].¹⁰⁾ Here $P_{p(A)}$ is the electron density on $2p(A)$ (see (2.10a)).

The remaining one parameter, i.e. k_β in (2.7), had already been determined such that the calculated wavelength of the absorption maximum of formamide agrees with the ob-

served one of 171.7 nm¹¹⁾:

$$k_{\beta} = 1.325.^{10)} \quad (4.6)$$

In the present section, the molecular integrals in the Fock matrix elements of (2.11) were parametrized following Sakuranaga *et al*¹⁰⁾. The important point of the parametrization is that all the molecular integrals in the Fock matrix elements are improved as functions of electron densities in each stage of iteration process for solving MOs since the valence-state electron configuration of each constituent atom is affected by its interaction with surrounding atoms.

§5. Calculations of $E_{\Pi}^{(r)}$ for Oligoglycines

In order to show the validity of the approximate expression (3.10) of E_r , we must examine the contributions of $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)} \Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)} \Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) and $P_3^{(r)}$ of (3.7c) to $E_{\Pi}^{(r)}$ of (3.6b). For this purpose, we calculate $E_{\Pi}^{(r)}$ -part of (3.10) and $E_{\Pi}^{(r)}$ of (3.6b) for the cases of ground and first-excited states of oligoglycines with a planar or a helical configuration.

First, an oligoglycine with a planar configuraion is shown in Fig. 1. The structural parameters are taken according to the electron diffraction experiment for N-methylacetoamide¹²⁾ except for bond distance H-C₁ and bond angle \angle H-C₁-N₁: C_i=O_i=1.225Å, C_i-N_i=1.386Å, N_i-H=1.002Å, N_i-C_i^α=1.469Å, C_i^α-H=1.107Å and C_i^α-C_{i+1}=1.520Å; \angle O_i=C_i-N_i=121.8°, \angle C_i-N_i-H=110°, \angle C_i-N_i-C_i^α=119.7°, and \angle C_i-C_{i+1}^α-N_{i+1}=114.1°. Bond distance H-C₁ and bond angle \angle H-C₁-H₁ are taken according to the microwave spectroscopy experiment for formamide:¹⁴⁾ H-C₁=1.094Å, \angle H-C₁-N₁=103.9°. Bond angles \angle N_i-C_i^α-C_{i+1}, \angle N_i-C_i^α-H and \angle H-C_i^α-H are taken equal to the tetrahedral angle 109.5° of sp³-hybridization.

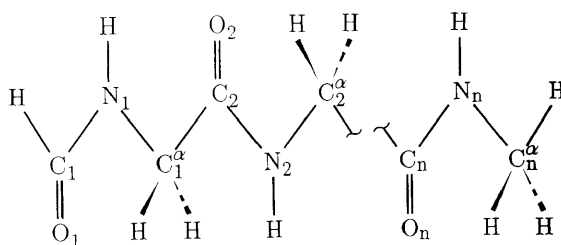


Fig. 1. A schematic representation of an oligoglycine with a planar configuration. On the structural parameters, see the letterpress.

The results of calculation for the monomer, the dimer and the trimer are shown in Table I. Here $E_{\Pi}^{(r)}(P^{(r)})(r=1,2)$ shows the results for $E_{\Pi}^{(r)}$ -part of (3.10); $E_{\Pi}^{(r)}(P^{(r)}, \Delta P^{(r)})$ is the energy including the contributions of $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)} \Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)} \Delta P_{\nu(B)}^{(r)}$, and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ (3.8) (note that this energy does not include the contribution

Table I $E_{II}^{(r)}(P^{(r)})$ of (3.10), $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)})$ (see the letterpress) and $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})$ of (3.6b) are calculated for the ground ($r=1$) and the first-excited state ($r=2$) of the monomer, the dimer or the trimer with the planar configuration shown in Fig. 1

State	Energy (eV)	Monomer	Dimer	Trimer
Ground State	$E_{II}^{(1)}(P^{(1)})$	2147.543	6024.828	10853.995
	$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)})$	2147.569	6024.836	10854.008
	$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)}, P_3^{(1)})$	2147.154	6024.915	10853.827
First-Excited State	$E_{II}^{(2)}(P^{(2)})$	2149.903	6029.776	10860.608
	$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)})$	2152.830	6033.117	10864.197
	$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})$	2140.829	6022.198	10852.545

of $P_3^{(r)}$ of (3.7c)); $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})$ indicates the results for $E_{II}^{(r)}$ of (3.6b) which were calculated by replacing $\gamma_{\mu(A)\nu(B)}$ in (3.6b) with $\gamma_{s(A)s(B)}$.

It is found from Table I that

$$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)})/E_{II}^{(1)}(P^{(1)})=1.000, \quad (5.1a)$$

$$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)}, P_3^{(1)})/E_{II}^{(1)}(P^{(1)})=1.000, \quad (5.1b)$$

$$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)})/E_{II}^{(2)}(P^{(2)})=1.001, \quad (5.2a)$$

$$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})/E_{II}^{(2)}(P^{(2)})=0.996 \quad (5.2b)$$

in the case of the monomer where the value of $E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})/E_{II}^{(2)}(P^{(2)})$ is smaller than those for the dimer and the trimer. We thus find that the contributions of $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) and $P_3^{(r)}$ of (3.7c) to $E_{II}^{(r)}$ of (3.6b) can be neglected.

Referring to the value of (5.2b) which is a little smaller than (5.1b), it should be noted that the first-excited state Φ_2 determined by the CI method of (2.12) is somewhat incorrect compared with the ground state Φ_1 because the MOs $\{\phi_j\}$ from which the various configurations in (2.12) are constructed are obtained by minimizing the total energy E_g of ground-state configuration $\psi(g)$. In other words, if we want to determine Φ_2 as correctly as Φ_1 , we will have to perform another CI calculation using such MOs that are obtained by minimizing the energy of the lowest excited-state configuration. For this reason, it would seem that $E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})/E_{II}^{(2)}(P^{(2)})$ has actually much the same value as $E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)}, P_3^{(1)})/E_{II}^{(1)}(P^{(1)})$ of (5.1b).

Secondly, we consider an oligoglycine with a helical configuration shown in Fig. 2. Here the bond distances and bond angles are identical to those of the oligoglycine with the planar configuration. The dihedral angles around the first and the third α -carbon are taken as $(\phi_1, \psi_1)=(\phi_3, \psi_3)=(-144^\circ, +132^\circ)$, and that around the second α -carbon as $(\phi_2, \psi_2)=(+104^\circ, -118^\circ)$, according to the left-handed $\beta^{6.3}$ helical conformation of gramicidin A¹⁴ (being a selective monovalent cation-channel^{15,16}) of a pentadeca-peptide consisted of alternating D and L amino acid residues). The definition of dihedral angles ϕ and ψ is the same as ref. 17.

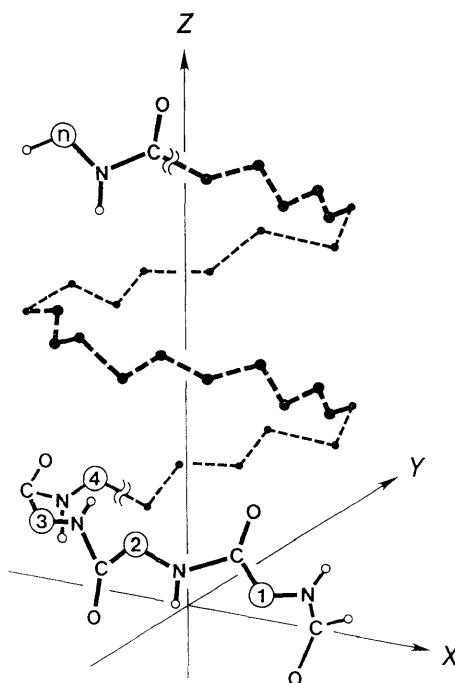


Fig. 2. A schematic representation of an oligoglycine with a helical configuration in Cartesian coordinate system (X, Y, Z). The encircled numbers represent α -carbons and the small circles denote hydrogen atoms. The first α -carbon is on the positive X-axis, and the axis of the helix is along Z-axis. See the letterpress on the details of the structural parameters.

The results of calculation for the dimer and the trimer with the helical configuration are shown in Table II, from which it is found that

$$E_{\text{II}}^{(1)}(P^{(1)}, \Delta P^{(1)})/E_{\text{II}}^{(1)}(P^{(1)}) = 1.000, \quad (5.3a)$$

$$E_{\text{II}}^{(1)}(P^{(1)}, \Delta P^{(1)}, P_3^{(1)})/E_{\text{II}}^{(1)}(P^{(1)}) = 1.000, \quad (5.3b)$$

$$E_{\text{II}}^{(2)}(P^{(2)}, \Delta P^{(2)})/E_{\text{II}}^{(2)}(P^{(2)}) = 1.001, \quad (5.4a)$$

$$E_{\text{II}}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})/E_{\text{II}}^{(2)}(P^{(2)}) = 0.999 \quad (5.4b)$$

in both the cases of the dimer and the trimer. It has thus been shown that the contributions of $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) and $P_3^{(r)}$ of (3.7c) to $E_{\text{II}}^{(r)}$ of (3.6b) ($r=1,2$) can also be neglected in the cases where the dimer and the trimer have the helical configuration.

In the present section, we considered the monomer, the dimer and the trimer of glycine with the planar (Fig. 1) or the helical configuration (Fig. 2) in order to confirm the validity of the approximate expression (3.10) of E_r , and we calculated their $E_{\text{II}}^{(r)}(P^{(r)})$, $E_{\text{II}}^{(r)}(P^{(r)}, \Delta P^{(r)})$ and $E_{\text{II}}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})$ (see Tables I and II). We thus found that $E_{\text{II}}^{(r)}(P^{(r)})$,

Table II $E_{II}^{(r)}(P^{(r)})$, $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)})$ and $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})$ are calculated for the ground ($r=1$) and the first-excited state ($r=2$) of the dimer or the trimer with the helical configuration shown in Fig. 2

State	Energy (eV)	Dimer	Trimer
Ground State	$E_{II}^{(1)}(P^{(1)})$	6052.973	11149.321
	$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)})$	6053.061	11149.456
	$E_{II}^{(1)}(P^{(1)}, \Delta P^{(1)}, P_3^{(1)})$	6050.953	11146.044
First-Excited State	$E_{II}^{(2)}(P^{(2)})$	6062.727	11155.847
	$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)})$	6070.750	11163.484
	$E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)})$	6053.633	11144.282

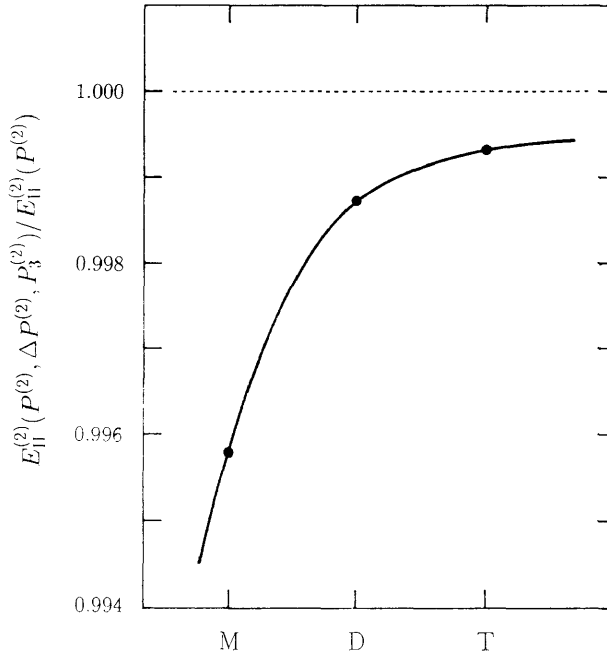


Fig. 3. The ratio (5.2b) is calculated for the monomer (M), the dimer (D) and the trimer (T) with the planar configuration.

$\Delta P^{(r)}/E_{II}^{(r)}(P^{(r)})$ and $E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})/E_{II}^{(r)}(P^{(r)})$ are 1.000 or almost 1.000 except for (5.2b) [see (5.1) to (5.4)], and hence that not only $[\Delta P_{\mu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(A)}^{(r)}$, $[\Delta P_{\mu(A)\nu(A)}^{(r)}]^2$, $\Delta P_{\mu(A)}^{(r)}\Delta P_{\nu(B)}^{(r)}$ and $[\Delta P_{\mu(A)\nu(B)}^{(r)}]^2$ in (3.8) but also $P_3^{(r)}$ in (3.6b) give only negligible contributions to $E_{II}^{(r)}$.

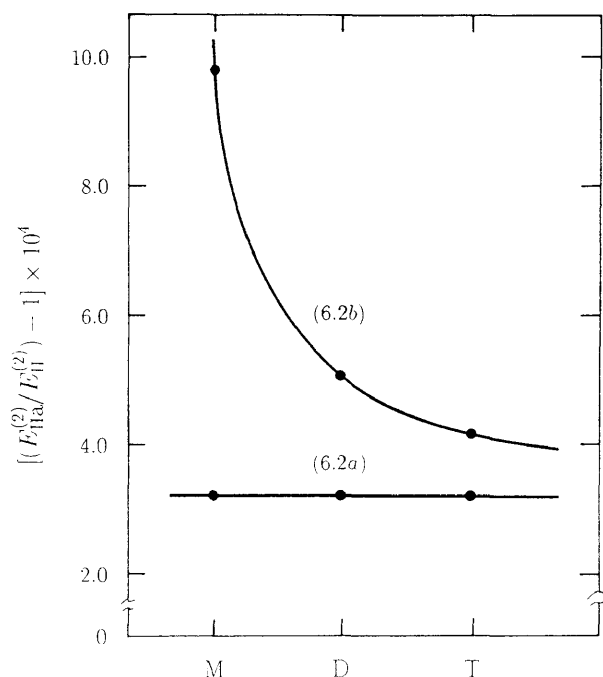


Fig. 4. The quantities (6.2a) and (6.2b) are calculated for the monomer (M), the dimer (D) and the trimer (T) with the planar configuration. The upper and lower lines show the results for (6.2b) and (6.2a), respectively.

§6. Concluding Remarks

We first discuss the contribution of $\psi(jj, mn)$ and $\psi(jk, mm)$ in (2.12). To do this, we calculate the same quantities as in Table I, using

$$\Phi_{ra} = C_r(g)\psi(g) + \sum_j \sum_m C_r(j, m)\psi(j, m) + \sum_j \sum_m C_r(jj, mm)\psi(jj, mm) \quad (6.1)$$

in place of (2.12). The results of calculation are shown in Fig. 3 for the quantities defined by

$$\{[E_{IIa}^{(r)}(P^{(r)}) / E_{II}^{(r)}(P^{(r)})] - 1\} \times 10^4, \quad (6.2a)$$

$$\{[E_{IIa}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)}) / E_{II}^{(r)}(P^{(r)}, \Delta P^{(r)}, P_3^{(r)})] - 1\} \times 10^4, \quad (6.2b)$$

where the suffix [a] of $E_{IIa}^{(r)}$ denotes that $E_{II}^{(r)}$ is calculated by using singlet state Φ_{ra} of (6.1). We can see from Fig. 3 that the doubly-excited configurations of types $\psi(jj, mn)$ and $\psi(jk, mm)$ give only a negligible contribution to the singlet states (2.12).

We must also examine how the ratio (5.2b) changes with the number of glycines. This change is shown in Fig. 4, indicating that (5.2b) approaches 1.000 as the number of glycines increases, and that $E_{II}^{(r)}(P^{(r)})$ is a good approximation to (3.6b). Needless to say, the result of Fig. 4 is consistent with Table I in which $[E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}) - E_{II}^{(2)}(P^{(2)})]$ increases gradually from 2.9 eV of the monomer to 3.6 eV of the trimer and $[E_{II}^{(2)}(P^{(2)}, \Delta P^{(2)}, P_3^{(2)}) - E_{II}^{(2)}(P^{(2)},$

$\Delta P^{(2)}]$ is nearly independent of the number of glycines and about 11.5 eV on average. In addition, much the same result as Fig. 4 is obtained for the helical configuration to show that (3.6b) can well be approximated by $E_{II}^{(r)}(P^{(r)})$ in both the cases of planar and helical configurations.

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