1968

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Recommended Citation

Silver, David Martin, "Quantum mechanics of diatomic molecules: overlap integrals, coulomb integrals and ab initio calculations on imidogen " (1968). *Retrospective Theses and Dissertations*. 3697.
https://lib.dr.iastate.edu/rtd/3697

SILVER, David Martin, 1941-
QUANTUM MECHANICS OF DIATOMIC MOLECULES:
OVERLAP INTEGRALS, COULOMB INTEGRALS AND
AB INITIO CALCULATIONS ON IMIDOGEN.

Iowa State University, Ph.D., 1968
Physics, molecular

University Microfilms, Inc., Ann Arbor, Michigan

QUANTUM MECHANICS OF DIATOMIC MOLECULES: OVERLAP INTEGRALS, COULOMB INTEGRALS AND *AB INITIO* CALCULATIONS ON IMIDOGEN

by

David Martin Silver

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Signature was redacted for privacy.

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Iowa State University
Ames, Iowa
1968

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CHAPTER I. SEPARATED PAIR WAVE FUNCTION, ELECTRON CORRELATION AND MOLECULAR PROPERTIES OF IMIDOGEN

INTRODUCTION

One of the goals of quantum chemistry is the ab initio calculation of molecular properties. Such calculations would, for example, be of particular value for species arising as reaction intermediates, which are of interest to the experimental chemist but which are not accessible to him for detailed study because of their short life-times. To achieve this objective, practical methods of obtaining suitably accurate wave functions for molecules and atoms must be developed. The recent self-consistent-field calculations by Cade and Huo (1) on the diatomic hydrides are an encouraging sign that the execution of such projects is within reach today, at least for small molecular systems. At the same time however, these results, which are very close to the exact Hartree-Fock solution for these systems, give systematically poor values for the dissociation energies which characterize the simple dissociation reactions of the hydrides and thus, point out the need for calculations, beyond the Hartree-Fock approximation, that will take into account the effects of electronic correlation. One approach in this direction is the method of separated pairs introduced by Hurley, Lennard-Jones, and Pople (2), which gives wave functions that are particularly amenable to intuitive interpretation while allowing for correlation effects within electron pairs or "geminals" (3).

The attainment of accurate results from separated pair calculations on the beryllium atomic systems (4) has stimulated an interest in the possibility of using this scheme to obtain similarly accurate results for molecular systems. The series of four-, six- and eight-electron diatomic hydrides, LiH, BH and NH, offers a means of testing this hypothesis on a set of increasingly more complicated molecules: LiH has two electrons forming a "K shell" geminal around the heavier nucleus and another two electrons forming a "bonding" geminal between the nuclei; BH has two additional electrons which form a "lone pair" geminal around the heavier nucleus; and in addition to these geminals, NH has two more electrons forming a "triplet" geminal about the heavy nucleus. The first two systems are the subject of a Ph.D. thesis being prepared by E. Mehler at Iowa State University and the imidogen, NH, molecule is the subject of this chapter.

Although the band spectra of the imidogen molecule had been observed in ammonia flames as early as 1893 by Eder (5) and in 1919 by Fowler and Gregory (6), the proper identification of these bands with NH did not come until the late 1920's (7-9). The imidogen molecule has been produced in the laboratory (10-26) by the thermal decomposition of hydrazoic acid N_3H (10,11), by the uv photochemical decomposition of N_3H (12), by passing an electrical discharge through N_3H (13), by the photolysis of N_3H (16-18), by decomposing hydrazine N_2H_4 (14, 19,20), by the photochemical decomposition of ammonia (15,21), and by photolysing isocyanic acid, HNCO (22,23). Imidogen has also been produced by shock wave studies of mixtures of nitrogen and hydrogen (24,25) and by the shock heating of ammonia (25,26). It has been proposed that NH exists on Ni and Fe surfaces during the chemisorption of N_2, H_2 and NH_3 (27), on Fe catalysts during NH_3 synthesis (28), and on Pt catalysts during NH_3 decomposition (29).

Imidogen has been studied in homogeneous electric fields (30,31). A study of the Stark effect by optical methods has allowed the determination of dipole moments for the NH excited states but no observations on the ground state could be made (31). Electron impact studies have yielded values for the NH ionization potential (32) and thermodynamic considerations have yielded heats of formation and dissociation energies (33-35). Analyses of the spectra of NH have produced values for the spectroscopic constants: k_e (36,37), ω_e (37-39), $\omega_e x_e$ (39), B_e (9,38), α_e (38) and R_e (9,37,40).

The chemistry of imidogen has been of interest in astrophysics since its spectral bands have been observed in the spectra of comets (41-44), in the solar spectrum (6,45), in the night sky afterglow (46), and in lightning (47). It has been suggested (48) that some of the colors on Jupiter may be due to condensed reactive species such as $(NH)_n$ since the conditions in Jupiter's atmosphere resemble those used in the laboratory to trap NH radicals at low temperatures (10,11,14,16-18). Work on the oxidation of hydrazines in liquid rocket fuel research has also stimulated an interest in imidogen and its halogenated derivatives (49). The reactions of imidogen in organic chemistry have been recently reviewed (50) and a general review article on imidogen chemistry has appeared (49, also see 51).

On the theoretical side, by interpreting the band spectra of diatomic molecules, and by correlating the electronic states of molecules with those of their isoelectronic united and separated atoms, Mulliken (52) predicted in 1932 the existence of six electronic states of NH which were all verified experimentally by 1945 (51). Later, in 1934, Lennard-Jones studied the correlation between the electronic states of NH with the isoelectronic states of oxygen and CH_2 using the molecular orbital method (53).

The earliest calculations on the NH ground state, $^3\Sigma^-$, were performed by Stehn in 1937 (54) and King in 1938 (55); these involved empirical methods for evaluating integrals. Further semi-empirical investigations were carried out by Moffitt in 1950 (56), by Companion and Ellison in 1960 (57) and by Lippencott and Dayhoff in 1960 (58).

The first non-empirical, ab initio calculation on the $^3\Sigma^-$ state of imidogen was performed by Higuchi in 1956 (59) using a basis set of Hartree-Fock atomic orbitals with the linear combination of atomic orbitals - molecular orbital - self consistent field (LCAO-MO-SCF) method. Further use of the LCAO-MO-SCF method was made in 1958 by Krauss (60) and

Boyd (61) using minimal basis sets of Slater-type atomic orbitals (STAO). Also, in 1958, Krauss and Wehner (62) extended their LCAO-MO-SCF wave function by the inclusion of higher configurations and Hurley (63) used the valence bond method including higher configurations to perform calculations using minimal STAO's. Configuration interaction calculations using Gaussian-type functions were performed by Reeves in 1963 (64) and by Reeves and Fletcher in 1965 (65). Calculations using STAO's on one center only were performed in 1963 by Bishop and Hoyland (66) and in 1965 by Lounsbury (67) and Joshi (68).

The calculations of Cade and Huo in 1967 (1), using an extended set of STAO's to build an LCAO-MO-SCF wave function for imidogen, are the most accurate and extensive of all the previous works. The current investigation goes beyond these results by using the separated pair approximation to study the effect of including some electron correlation in the wave function.

While explicit formulation of separated pairs in terms of natural orbitals for many-electron systems having a singlet spin state have been given repeatedly (2,4,69), the triplet spin case has been discussed only for two-electron systems (70,71). General expressions that are valid for any choice of spin state are therefore derived here for the many-electron separated pair wave function. The geminals are expanded in terms of their natural orbitals and a variational procedure is developed for their determination.

Within this framework, natural orbitals of the separated pair wave function for the $^3\Sigma^-$ ground state of the imidogen molecule are calculated, and in order to give a pictorial appreciation of their structures, contour maps have been drawn for them. Several physical properties are calculated, namely, the total energy, the dissociation energy, the equilibrium internuclear distance, the molecular potential energy curve, the spectroscopic constants, the molecular dipole and quadrupole moments, and various other one- and two-electron expectation values. Of greatest interest is the correlation energy recovered by the separated pair wave function and, for this reason, a detailed analysis of the correlation is given in terms of the geminals and the natural orbitals. This study reveals that the separated pair approximation provides a suitable description of part of the electronic correlation in NH, but, on the other hand, is too restrictive to yield a complete description of all the various electronic correlations in this molecular system. Nevertheless, the analysis does shed light on the nature of the omitted part of the correlation and suggests directions for future improvements.

FORMULATION OF THEORY

Geminals and Separated Pairs

The quantum mechanical properties of a pair of electrons can be described (70,71) by a geminal, Λ, which is a function of the spin and space coordinates of two particles. Geminals are normalized to unity in the sense,

$$\int d\tau_1 \int d\tau_2 \Lambda\ (1,2) \Lambda^*\ (1,2) = 1, \tag{1}$$

and are antisymmetric with respect to an interchange of the coordinations of the two electrons:

$$\Lambda(1,2) = -\Lambda(2,1). \tag{2}$$

An expansion in terms of natural spin orbitals (NSO), ψ_i, can be used to express the functional form of a geminal so that

$$\Lambda(1,2) = \sum_i c_i [\psi_{2i}(1)\ \psi_{2i+1}(2) - \psi_{2i+1}(1)\ \psi_{2i}(2)]/\sqrt{2}. \tag{3}$$

The natural orbitals are orthonormal functions,

$$\int d\tau_1\ \psi_m(1)\ \psi_n^*(1) = \delta_{mn}, \tag{4}$$

and therefore normalization of a geminal gives the occupation coefficients, c_i, the property,

$$\sum_i |\ c_i\ |^2 = 1. \tag{5}$$

The first order density matrix, γ, of a geminal thus takes the form,

$$\gamma(1|1') = 2\int d\tau_2\ \Lambda(1,2)\ \Lambda^*(1',2)$$

$$= \sum_i |c_i|^2[\psi_{2i}(1)\psi_{2i}^*(1')+\psi_{2i+1}(1)\psi_{2i+1}^*(1')]. \quad (6)$$

In this investigation, geminals are chosen to be eigenfunctions of the total spin angular momentum, S^2, and its z-component, S_z, thus the two electrons in a geminal can form a singlet or a triplet spin state. In the first case, the natural spin orbitals can be taken as:

$$\psi_{2i} = \phi_i\ \alpha$$

$$\psi_{2i+1} = \phi_i\ \beta \quad (7)$$

where the natural orbitals (NO), ϕ_i, are spatial functions only. This gives the singlet geminal a symmetric space function:

$$\Lambda(1,2) = \sum_i c_i \phi_i(1)\ \phi_i(2)\ [\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\ \sqrt{2.} \quad (8)$$

To obtain a triplet spin state with $S_z = +1$, the NSO can be expressed as:

$$\psi_{2i} = X_i = x_i\alpha$$

$$\psi_{2i+1} = Y_i = y_i\alpha. \quad (9)$$

The functions x and y are again spatial functions only, but the geminal now has an antisymmetric space representation:

$$\Lambda(1,2) = \sum_i c_i[x_i(1)y_i(2) - y_i(1)x_i(2)]\ \alpha(1)\alpha(2)/\ \sqrt{2.} \quad (10)$$

For the $S_z = -1$ component of the triplet, the functions α in Eq. 9 above would be replaced by β. The $S_z = 0$ component of the triplet can be handled by defining the NSO's as follows,

$$\begin{aligned}\psi_{4r} &= x_r\alpha \\ \psi_{4r+1} &= y_r\beta \\ \psi_{4r+2} &= x_r\beta \\ \psi_{4r+3} &= y_r\alpha, \end{aligned} \tag{11}$$

and by assuming the coefficients to be doubly degenerate,

$$\begin{aligned} c_{2r} &= c_{2r+1} \\ \sum_i |c_i|^2 &= 2\sum_r |c_{2r}|^2 = 1. \end{aligned} \tag{12}$$

Thereby, one obtains,

$$\begin{aligned}\Lambda(1,2) &= \sum_r c_{2r}\,[\psi_{4r}(1)\psi_{4r+1}(2) - \psi_{4r+1}(1)\psi_{4r}(2) \\ &\quad + \psi_{4r+2}(1)\psi_{4r+3}(2) - \psi_{4r+3}(1)\,\psi_{4r+2}(2)]/\sqrt{2} \\ &= \sum_r c_{2r}[x_r(1)y_r(2) - y_r(1)x_r(2)] \\ &\quad \cdot[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}. \end{aligned} \tag{13}$$

Thus, for any of the four possible spin eigenstates, Eq. 3 is applicable. This expression will therefore be used for the derivation of energy expressions.

In a many electron system, each distinct pair of electrons can be handled by means of a distinct geminal. Hurley, Lennard-Jones, and Pople (2) have used this concept of separated pairs to approximate the total wave function. They furthermore introduced the constraint that geminals for different pairs be "strongly" orthogonal:

$$\int d\tau_1\, \Lambda_\mu(1,2)\, \Lambda^*_\upsilon(1,3) = 0 \text{ if } \mu \neq \upsilon \tag{14}$$

which implies the "weak" orthogonality property:

$$\int d\tau_1 \int d\tau_2 \Lambda_\mu(1,2)\ \Lambda^*_\upsilon(1,2) = \delta_{\mu,\upsilon}. \tag{15}$$

It has been shown (72,73), that strong orthogonality between two geminals, Λ_μ and Λ_υ, implies orthogonality between the NSO's, $\psi_{\mu i}$ and $\psi_{\upsilon j}$, used in the expansion, Eq. 3, of the respective geminals:

$$\int d\tau_1 \; \psi_{\mu i}(1) \; \psi^*_{\upsilon j}(1) = \delta_{\mu\upsilon}\delta_{ij}. \qquad (16)$$

The imposition of strong orthogonality between various geminals represents a loss of generality from an unrestricted pair formulation but it does reduce the problem of finding energy and other expectation value expressions to a tractable form (74).

Total Many Electron Wave Function

In the approximation just referred to, a quantum mechanical state of a 2n-electron system is described by a wave function, Ψ, which is expressed as an antisymmetrized product of strongly orthogonal geminals:

$$\Psi(1,2,\ldots,2n) = \mathcal{A}[\Lambda_1(1,2)\;\Lambda_2(3,4)\;\ldots\Lambda_n\;(2n-1,2n)]. \qquad (17)$$

Because of the antisymmetry of the geminals themselves, a partial antisymmetrizer, $\mathcal{A}$, is sufficient to achieve a totally antisymmetric wave function as required to fulfill the Pauli exclusion principle:

$$\mathcal{A} = [2^n/(2n)!]^{1/2} \sum_P (-1)^P \; P \qquad (18)$$

where the permutation operator, P, only permutes the coordinates of electrons between different geminals.

In a system with an odd number of electrons, 2n electrons are described by n geminals as above and the remaining electron is described by an orbital, Z,

$$Z(1) = z_{n+1,0}(1)\ \alpha(1) \tag{19}$$

which is orthogonal to each of the geminals:

$$\int d\tau_1\ \Lambda_\mu(1,2)\ Z^*(1) = 0 \text{ for all } \mu. \tag{20}$$

The total wave function in this case is given by,

$$\Psi(1,2,\ldots 2n,2n+1) = \mathcal{A}[\Lambda_1(1,2)\ldots\ \Lambda_n(2n-1,2n)\ Z(2n+1)], \tag{21}$$

where

$$\mathcal{A} = [2^n/(2n+1)!]^{1/2} \sum_P (-1)^P\ P \tag{22}$$

and here the permutation operator, P, permutes the coordinates of electrons between the orbital and each of the geminals in addition to the intergeminal permutations as above. The constants multiplying the summation signs in Eqs. 18 and 22, insure that the total wave functions, Eqs. 17 and 21, respectively, be normalized to unity.

It is convenient to adopt the following convention for the case of 2n+1 electrons:

$$c_{n+1,i} = \delta_{i,0} \text{ and } \psi_{n+1,k} = Z\ \delta_{k,0}. \tag{23}$$

This allows the correct result to obtain from expressions involving summations over the geminal indices.

For an N-electron wave function of the above type, the second-order density matrix, Γ, can be easily calculated and easily expressed in terms of natural spin geminals (NSG). This expansion of the second-order density matrix is as follows:

$$\Gamma(1\ 2|1'2') = N(N-1) \int|\int d\tau_3 \ldots d\tau_N\ \Psi(1,2,\ldots,N)\ \Psi^*(1',2',\ldots,N)$$

$$= 2 \sum_{\mu} \Lambda_{\mu}(1,2)\ \Lambda^*_{\mu}(1',2')$$

$$+2 \sum_{\mu<\upsilon} \sum_{ij} |c_{\mu i}|^2\ |c_{\upsilon j}|^2\ A_{\mu i,\upsilon j}(1,2) A^*_{\mu i,\upsilon j}(1',2'). \tag{24}$$

The summation over μ runs over the number of geminals involved whereas the upper limit of the index, υ, will be n or n+1 for the even or odd electron case respectively. For $\upsilon = n+1$, the summation over j will reduce to the one term, $j=0$, due to Eq. 23. The first n NSG's are the geminals occurring in Eqs. 17 and 21. The remaining NSG are defined (69) as follows:

$$A_{\mu i,\upsilon j}(1,2) = [\psi_{\mu i}(1)\psi_{\upsilon j}(2) - \psi_{\upsilon j}(1)\psi_{\mu i}(2)]/\sqrt{2}. \tag{25}$$

The first order density matrix, γ, of the total wave function is given by

$$\gamma(1|1') = N\int|\int d\tau_2 \ldots d\tau_N\ \ \Psi(1,2,\ldots,N)\Psi^*(1',2,\ldots,N)$$

$$= (1/N-1)\ \ \int d\tau_2\ \Gamma(1\ 2\ |\ 1'2)$$

$$= \sum_{\mu} \gamma_{\mu}(1|1') + Z(1)Z^*(1')$$

$$= \sum_{\mu i} |c_{\mu i}|^2\ [\psi_{\mu,2i}(1)\psi^*_{\mu,2i}(1')+\psi_{\mu,2i+1}(1)\psi^*_{\mu,2i+1}(1')]. \tag{26}$$

Thus the NSO's of the geminals and the lone orbital form the NSO's of the total wave function.

Separated Pair Energy Expression

The energy, E, of a many electron system is given as the expectation value,

$$E = \int d\tau\ \Psi H \Psi^* \ / \int d\tau\ \Psi \Psi^* \qquad (27)$$

where H is the non-relativistic Hamiltonian operator in the Born-Oppenheimer approximation (75) expressed in atomic units (76):

$$H = \sum_{\alpha<\beta} V_{\alpha\beta} + \sum_{i} h(i) + \sum_{i<j} r_{ij}^{-1} \qquad (28)$$

where

$$V_{\alpha\beta} = Z_\alpha \cdot Z_\beta \cdot R_{\alpha\beta}^{-1} \qquad (29)$$

$$h(i) = T_i + \sum_{\alpha} V_{\alpha i} \qquad (30)$$

$$T_i = -1/2\ \nabla_i^2, \qquad (31)$$

$$V_{\alpha i} = -Z_\alpha r_{\alpha i}^{-1}. \qquad (32)$$

The indices, i and j, range over the number of electrons while the indices, α and β, range over the number of nuclei. The symbol, Z_α, is the charge on the α nucleus, $R_{\alpha\beta}$ is the distance between nuclear centers, $r_{\alpha i}$ is the distance from electron i to nucleus α, and r_{ij} is the distance between electrons i and j. Using the expression for the first and second-order density matrices given above, the total energy can be written as a sum over nuclear repulsion, intrageminal and intergeminal contributions:

$$E = \sum_{\alpha<\beta} V_{\alpha\beta} + \sum_{\mu} E(\mu) + \sum_{\mu<\upsilon} I(\mu,\upsilon) \qquad (33)$$

where

$$E(\mu) = \sum_{ij} c_{\mu i}\, c^*_{\mu j}\, E(\mu i,\mu j), \tag{34}$$

$$I(\mu,\upsilon) = \sum_{ij} |c_{\mu i}|^2\, |c_{\upsilon j}|^2\, I(\mu i,\upsilon j), \tag{35}$$

$$\begin{aligned} E(\mu i,\mu j) = {} & \delta_{ij}[(\mu,2i|h|\mu,2i) + (\mu,2i{+}1|h|\mu,2i{+}1)] \\ & +[\mu,2i\ \mu,2j|\mu,2j{+}1\ \mu,2i{+}i]-[\mu,2i{+}1\ \mu,2j|\mu,2j{+}1\ \mu,2i], \end{aligned} \tag{36}$$

$$\begin{aligned} I(\mu i,\upsilon j) = {} & [\mu,2i\ \mu,2i\,|\,\upsilon,2j\upsilon,2j]+[\mu,2i\ \mu,2i|\upsilon,2j{+}1\ \upsilon,2j{+}1] \\ & +[\mu,2i{+}1\ \mu,2i{+}1|\upsilon,2j\ \upsilon,2j]+[\mu,2i{+}1\ \mu,2i{+}1|\upsilon,2j{+}1\upsilon,\ 2j{+}1] \\ & -[\mu,2i\ \upsilon,2j|\mu,2i\ \upsilon,2j]-[\mu,2i\ \upsilon,2j{+}1|\mu,2i\ \upsilon,2j{+}1] \\ & -[\mu,2i{+}1\ \upsilon,2j|\mu,2i{+}1\ \upsilon,2j]-[\mu,2i{+}1\ \upsilon,2j{+}1|\mu,2i{+}1 \\ & \quad \upsilon,2j{+}1] \end{aligned} \tag{37}$$

and where the following conventions have been used:

$$(\kappa,k|h|\lambda,\ell) = \int d\tau_1\ \psi_{\kappa,k}(1)\ h(1)\ \psi^*_{\lambda,\ell}(1) \tag{38}$$

$$[\kappa,k\ \lambda,\ell|\mu,m\ \upsilon,n] = \int d\tau_1 \int d\tau_2 \psi^*_{\kappa,k}(1)\psi_{\lambda,\ell}(1)r_{12}^{-1}\psi_{\mu,m}(2)\psi^*_{\upsilon,n}(2). \tag{39}$$

The expression in Eqs. 36 and 37 can be simplified once the spin state of each geminal has been specified because the particular expansions in Eqs. 7 and 9 can then be inserted and the integration over the spin variables carried out. Here again, for the case of an odd number of electrons, the conventions adopted in Eq. 23 are used.

The quantities, $E(\mu)$, in Eq. 33 are derived from the presence of the first n natural spin geminals, Λ_μ, in the expansion of the second-order density matrix given in Eq. 24. The terms $I(\mu,\upsilon)$ in Eq. 33 result from the remaining natural spin geminals, $A_{\mu i,\upsilon j}$, occurring in the second-order density matrix. Thus, the energies, $E(\mu)$, arise when two electrons occupy the same geminal and the contributions, $I(\mu,\upsilon)$, arise when the electrons occupy different geminals. This justifies using the names, "intrageminal" and "intergeminal" to describe these energy terms. Partitioning the energy into these intrageminal and intergeminal contributions has been shown to be useful for a study of the correlation energy effects in the beryllium atom (4) and shall be further developed here in a later section.

For a real wave function, the NO's used for the symmetric spatial expansion of the singlet and for the antisymmetric spatial expansion of the triplet geminals can, without loss of generality, be chosen to be real. This choice of NO's forces the occupation coefficients, $c_{\mu i}$, to be real (70). The complex conjugation notation will therefore be dropped hereafter.

Parametrization of the Natural Orbitals

The spatial natural orbitals which have been given the symbols, ϕ,x,y,z, will hereafter be referred to by the generic symbol w. These functions are obtained as linear combinations of Slater-type atomic orbitals (AO),

$$\chi(n\ell m, \zeta) = (2\zeta)^{n+1/2} \, [(2n)!]^{-1/2} r_{\alpha}^{\,n-1} \, e^{-\zeta r_{\alpha}} \mathcal{Y}_{\ell m}(\Theta_{\alpha} \phi_{\alpha}), \quad (40)$$

where the normalized, real spherical harmonics are given by,

$$\mathcal{Y}_{\ell m}(\Theta \phi) = \mathcal{P}_{\ell}^{|m|} (\cos \Theta) \; \Phi_{m} (\phi) \qquad (41)$$

$$\Phi_m(\phi) = \begin{cases} \pi^{-1/2} \cos m\phi & m>0 \\ (2\pi)^{-1/2} & m=0 \\ \pi^{-1/2} \sin |m| \phi & m<0 \end{cases} \tag{42}$$

and $\mathcal{P}_\ell^{|m|}$ are the normalized associated Legendre functions. The subscript α implies that the coordinate variable is defined with respect to an axial system centered at the nucleus α. This basis set is non-orthogonal with the overlap matrix,

$$S_{ij} = \int d\tau\, \chi_i\, \chi_j . \tag{43}$$

The natural orbitals are written as

$$w_k = \sum_i \chi_i\, D_{ik} \tag{44}$$

where

$$D_{ik} = \sum_j S_{ij}^{-1/2}\, T_{jk} . \tag{45}$$

The matrix $\underline{\underline{S}}^{-1/2}$ performs a symmetric orthogonalization (77,78) on the basis set after which the orthogonal transformation matrix, $\underline{\underline{T}}$, generates the natural orbitals. The orthogonalizing matrix, $\underline{\underline{S}}^{-1/2}$, is obtained by letting the eigenvectors of $\underline{\underline{S}}$ form the columns of the orthogonal matrix $\underline{\underline{U}}$, constructing the diagonal matrix $\underline{\underline{\Lambda}}^{-1/2}$ from the positive inverse square roots of the corresponding eigenvalues, λ_i,

$$\Lambda_{ij}^{-1/2} = +\lambda_i^{-1/2}\, \delta_{ij} \tag{46}$$

and then forming

$$\underline{\underline{S}}^{-1/2} = \underline{\underline{U}} \cdot \underline{\underline{\Lambda}}^{-1/2} \cdot \underline{\underline{U}}^{\dagger} . \tag{47}$$

For a given set of M basis orbitals, χ_i, having the quantum numbers, $(n_i\ \ell_i\ m_i)$, and the orbital exponents, ζ_i, the degrees of freedom of the NO's are furnished by the M orbital exponents, ζ_i, and the M(M-1)/2 degrees of freedom of the orthogonal matrix $\underline{\underline{T}}$. For the latter, a parametrization is used (79) which expresses the M^2 elements of $\underline{\underline{T}}$ in terms of M(M-1)/2 angles, γ_{pq} (p=1...M, q=1...p), by means of the recursive procedure summarized below.

The orthogonal matrix $\underline{\underline{T}}$ of degree M is obtained as the M-th step in a recursive sequence of orthogonal matrices, $\underline{\underline{T}}^{(m)}$, i.e. $\underline{\underline{T}}=\underline{\underline{T}}^{(m)}$. The m-th matrix, $\underline{\underline{T}}^{(m)}$, is obtained from the (m-1)-st matrix $\underline{\underline{T}}^{(m-1)}$ by the following set of recursive steps:

$$T_{jk}^{(m)} = t_{jk}^{(m)} \cos\gamma_{jm} - s_{jk}^{(m)} \sin\gamma_{jm}$$

$$s_{j+1,k}^{(m)} = t_{jk}^{(m)} \sin\gamma_{jm} + s_{jk}^{(m)} \cos\gamma_{jm} \qquad (48)$$

where, for fixed k, one advances from j=1 to j=m using the definitions:

$$\underline{\underline{t}}^{(m)} = \begin{pmatrix} \underline{\underline{T}}^{(m-1)} & 0 \\ 0 & 1 \end{pmatrix}$$

$$s_{1k}^{(m)} = -\delta_{km}$$

$$\gamma_{mm} = \pi/2$$

$$\underline{\underline{T}}^{(1)} = 1. \qquad (49)$$

It should be noted that the matrix $\underline{\underline{D}}$ uniquely expresses the NO's in terms of the AO's regardless of the choice of orthogonalization procedure employed. For any particular basis-set orthogonalization-transformation, $\underline{\underline{V}}$, there would be a corresponding orthogonal matrix, $\underline{\underline{W}}$, such that the product $\underline{\underline{V}} \cdot \underline{\underline{W}}$ would still yield the same matrix $\underline{\underline{D}}$. Once $\underline{\underline{V}}$ is chosen however, the matrix $\underline{\underline{W}}$, and therefore its parametrization in terms of γ's would be sufficient to uniquely determine the NO's.

Variational Procedure

Variations of the energy with respect to the occupation coefficients with the constraint that Eq. 5 remains valid leads to the set of coupled eigenvalue equations for each geminal:

$$\sum_i c_{\mu i} H_{ij}(\mu) = \varepsilon_\mu c_{\mu j} \tag{50}$$

where

$$H_{ij}(\mu) = E(\mu i,\mu j) + \delta_{ij} \sum_{\upsilon(\neq\mu)} \sum_k |c_{\upsilon k}|^2 I(\mu i,\upsilon k). \tag{51}$$

For the ground state, the geminal energies, ε_μ, are taken to be the lowest eigenvalues of the matrices, $H(\mu)$, and the occupation coefficients are the components of the corresponding eigenvectors of $H(\mu)$. Since the solution of these equations for a given geminal depends on the occupation coefficients of the other geminals, the final set of geminal energies and coefficients are obtained through an iterative process. The geminal energies are also given by

$$\varepsilon_{\mu} = E(\mu) + \sum_{\upsilon(\neq\mu)} I(\mu,\upsilon) \tag{52}$$

and in turn the total energy can be expressed as

$$E = \sum_{\alpha<\beta} V_{\alpha\beta} + \sum_{\mu} \varepsilon_{\mu} - \sum_{\mu<\upsilon} I(\mu,\upsilon). \tag{53}$$

Variations of the energy with respect to the functional form of the NO's themselves with the constraint that they remain an orthonormal set of functions, leads to a set of coupled integrodifferential equations for the orbitals. These equations have been given previously (69,4), but as yet, have not been cast into an easily usable form because of the presence of off-diagonal Lagrangian multipliers. An alternative scheme is employed here for obtaining the NO's, namely to use the variational principle to determine optimal values for each of the parameters which enter the NO's discussed above.

The two sets of parameters, the ζ's and γ's, have values which are determined by a direct minimization of the total energy using a variational procedure known as conjugate directions (80). Solving the set of coupled eigenvalue equations constitutes a trivial phase of the calculation of the separated pair wave function and therefore these equations are solved iteratively for each trial choice of the ζ and γ parameters and Eq. 53 used to compute the total energy. Determination of the wave function is thus tantamount to finding an optimal set of ζ and γ values. The final wave function is a result of several stages of the variational procedure. Each stage corresponds to using a particular number of atomic orbitals as basis functions. For the first stage, a minimal basis set is employed and from this point on, the basis set is augmented by the systematic addition of new atomic orbitals.

In order to insure that the wave function at the beginning of each successive stage will be at least as good, in terms of the energy criterion, as the final result of the previous step, a procedure for adding orbitals has been developed. Suppose that the M-1 old NO's have the expansion,

$$w_i = \sum_{k=1}^{M-1} \chi_k D_{ki} \text{ (old)}. \tag{54}$$

Upon addition of a new basis orbital, M natural orbitals can be formed. These are defined by keeping the old NO's intact and Schmidt-orthogonalizing the M-th NO to them (78). The set of new NO's is then given by the MxM transformation matrix, $\underline{\underline{D}}$(new):

$$D_{ij}\text{(new)} = \begin{cases} D_{ij} \text{ (old)} & \text{for } i,j \neq M \\ 0 & \text{for } i=M,\ j\neq M \\ b_i B & \text{for } i\neq M,\ j=M \\ B & \text{for } i,j=M \end{cases} \tag{55}$$

where

$$b_i = \sum_{k=1}^{M-1} D_{ik}\text{(old)}\ a_k$$

$$B = \left[1 - \sum_{k=1}^{M-1} a_k^2\right]^{-1/2}$$

$$a_k = - \sum_{j=1}^{M-1} S_{Mj} D_{jk} \text{ (old)} \tag{56}$$

and S_{Mj} is the overlap integral between χ_M and χ_j.

In order to continue the minimization process using the parametrization of Eqs. 48 and 49, it is further necessary to decompose $\underline{\underline{D}}$ according to Eq. 45. Since the matrix $\underline{\underline{S}}$(new) is known, and $\underline{\underline{D}}$(new) has just been determined, the orthogonal matrix $\underline{\underline{T}}$ is obtained as

$$\underline{\underline{T}}(\text{new}) = \underline{\underline{S}}^{+1/2}(\text{new}) \cdot \underline{\underline{D}}(\text{new}) \tag{57}$$

where

$$\underline{\underline{S}}^{+1/2}(\text{new}) = \underline{\underline{U}}(\text{new}) \cdot \underline{\underline{\Lambda}}^{+1/2}(\text{new}) \cdot \underline{\underline{U}}^{\dagger}(\text{new}) \tag{58}$$

which is analogous to Eq. 47 for $\underline{\underline{S}}^{-1/2}$, except that here use is made of the diagonal matrix, $\underline{\underline{\Lambda}}^{+1/2}$, formed from the positive square roots of the overlap eigenvalues. Finally, the angles γ_{pq} corresponding to $\underline{\underline{T}}$(new) are readily found by minimizing the deviation,

$$\sum_{ij} |T_{ij}(\text{new}) - T_{ij}(\gamma_{pq})| \tag{59}$$

where $T_{ij}(\gamma_{pq})$ represents the functional dependence of $\underline{\underline{T}}$ upon the angles γ_{pq} described in connection with Eqs. 48 and 49. This minimization process is also carried out by the method of conjugate directions (80).

Computer Considerations

The execution of this project requires a heavy use of the electronic digital computer. A fully automatic computer program carries out the parameter searches according to the directions set forth by the minimization scheme employed until optimal values of the parameters are found. This implies the evaluation and the continued re-evaluation of the energy expression. The steps in this process will be briefly described.

For a given trial set of the ζ parameters, a set of integrals is required. The electron repulsion integrals needed are as follows: the one-center electron repulsion integrals, [NN|NN] and [HH|HH], the two-center Coulomb integrals (81), [NN|HH], the two-center exchange integrals (82), [NH|NH], and the two-center hybrid integrals (83), [NN|NH] and [HH|HN]. The N and H used in the integral designations here represent atomic orbitals, χ, centered at the N or H nucleus respectively. In addition the one- and two-center, one electron integrals (84) required are the overlap integrals, Eq. 43, the kinetic energy integrals, Eq. 31, and the nuclear attraction integrals, Eq. 32. From the overlap integrals, the matrix $\underline{\underline{S}}^{-1/2}$ is formed and at the same time the eigenvalues of $\underline{\underline{S}}$ are examined in order to determine the extent to which the basis set might have become linearly dependent (85,86). The complete set of integrals is saved on the computer's disc storage and reused if possible. Only in the cases where the minimization program has changed one or more ζ values, does this set of integrals need to be recomputed. All of these integrals are computed to an accuracy of at least 10^{-6} atomic units.

The matrix, $\underline{\underline{T}}$, is formed from the set of current γ values via Eqs. 48 and 49 and this is combined with the current $\underline{\underline{S}}^{-1/2}$ to form the matrix $\underline{\underline{D}}$, Eq. 45. This matrix is then used to transform the integrals over atomic orbitals into integrals over the natural orbitals, Eqs. 36 and 37.

Once the integrals over NO's are available the coupled eigenvalue equations are solved iteratively until the components of the eigenvectors (the occupation coefficients) have converged to 10^{-6} atomic units. The energy is finally obtained from Eq. 53.

Forming the matrix $\underline{\underline{T}}$ from the γ's, forming the matrix $\underline{\underline{D}}$, solving the eigenvalue equations, and obtaining the energy are phases of the calculation which require very little computer time. Computing the integrals over the atomic orbitals takes a substantial amount of computer time, but as mentioned above, they are recomputed only if variations within the set of M orbital exponents are encountered. The transformation from atomic orbital to natural orbital integrals is also time consuming; this phase however must be performed for each variation of ζ <u>or</u> γ values. Since there are about M(M-1)/2 different γ parameters, the transformation to NO integrals represents the heaviest burden in terms of computer time required.

The addition of new orbitals to the basis set constitutes a very important phase of the calculations. The computer time required for setting up a new orbital basis by the procedure described in Eqs. 54-59, is however minor. Moreover, this calculation is executed only once for any given atomic orbital basis set.

WAVE FUNCTION, ENERGY, CORRELATION

Orbitals for the Imidogen Molecule

A wave function for a diatomic molecule should be an eigenfunction of the z-component of the orbital angular momentum, L_z. The spectroscopic designation of the electronic ground state of the imidogen molecule is $^3\Sigma^-$ which means that the electrons form an overall triplet spin state, that the eigenvalue of L_z is zero and that the wave function is antisymmetric with respect to reflection in any plane containing the molecular axis. Four geminals are used to describe the eight electrons in the molecule and for descriptive purposes later, they are given the labels, K Shell, Lone Pair, Bonding, and Triplet. The first three of these are each built out of NSO's in such a way that they have the symmetry $^1\Sigma^+$. Thus, they are singlets, have L_z=0, are symmetric with respect to reflection in any plane containing the molecular axis and are expanded in NSO's according to Eq. 8. The remaining geminal will be a triplet with the symmetry, $^3\Sigma^-$, and thus Eq. 10 will represent its NSO expansion. Since the quantities of interest in this work are spin-independent, the particular choice made for the z-component of the triplet spin state is immaterial; however, S_z=+1 has been used. The product of these four geminals will then have the correct symmetry for the NH molecule.

Two coordinate systems are defined: one with its origin at the nitrogen nucleus, the other having its origin at the hydrogen nucleus. The two z-axes point toward each other along the molecular axis and the two x- and y-axes are parallel. A set of atomic orbitals is chosen on each of these centers and they form the basis set for expanding the natural orbitals. The symmetric orthogonalization, $\underline{\underline{S}}^{-1/2}$, preserves the cylindrical symmetry properties of this set of atomic orbitals and since the natural orbitals can be chosen to be symmetry adapted functions (87), the orthogonal transformation, $\underline{\underline{T}}$, is chosen so as to preserve this symmetry also. Thus, the angular quantum number, m, from the atomic orbitals, Eq. 40, can also be used to describe the symmetry of the NO's. Thus the symbol, w[m] implies that the NO has a definite functional form with respect to the variable ϕ as given by Eq. 42.

To obtain the required molecular symmetry, the basis functions have been chosen such that, if $m \neq 0$ for a particular atomic orbital, then a companion orbital will appear in the basis set: both will have the same values for n, ℓ and ζ but the remaining quantum number will be $+|m|$ in the one and $-|m|$ in the other orbital. Thus both w[m] and w[-m] will be available as NO's.

For the singlet geminals, if $\phi_i = w[m]$, $m \neq 0$, then $\phi_{i+1} = w[-m]$ and the term,

$$c\{w[m]\ (1)\ w[m]\ (2) + w[-m]\ (1)\ w[-m]\ (2)\} \qquad (60)$$

will appear in the expansion of the geminal. For the triplet geminal, all of the NO's designated x_i will be functions w[m], with m>0 only and the corresponding NO's, y_i, will be the functions, w[-m]. Thus each term of the geminal expansion will assume the spatial dependence,

$$c\{w[m]\ (1)\ w[-m]\ (2) - w[-m]\ (1)\ w[m]\ (2)\} \qquad (61)$$

in accord with Eq. 10. By this construction, each of the geminals will have the desired symmetry properties.

Orbitals for the Nitrogen Atom

For an atom, the wave function must be an eigenfunction of L^2 as well as L_z. The electronic ground state of the nitrogen atom has the spectroscopic designation, ^4S, denoting a quartet spin state being totally spherically symmetric. Three geminals plus one orbital are used to describe this seven electron system. Two of the geminals are used for the description of the "$1s^2$" and "$2s^2$" electron pairs and are labelled K and L respectively. These each have the symmetry, ^1S. The remaining geminal is again a triplet, as before, with $S_z=+1$ and the orbital is taken to have spin α. The product of this triplet geminal and orbital are used to provide the description of the $2p^3$ configuration.

In the atomic case, the spherical symmetry properties of the basis functions can be preserved on forming the NO's so that the latter will have a definite angular dependence as given by Eq. 41 and consequently the designation, w[ℓ,m].

To obtain the required atomic symmetry, the basis functions have been chosen such that, if $\ell \neq 0$, $2\ell+1$ atomic orbitals will appear in the basis set: each will have the same value for n, ℓ, and ζ but there will be one function with each of the allowed m values. Thus the complete set of NO's, $w[\ell,m]$, $(m=\ell, \ell-1, \ldots, -\ell+1, -\ell)$, will be available.

For the singlet geminals, if $\ell \neq 0$, the term,

$$c\left\{ \sum_{m=-\ell}^{\ell} w[\ell,m]\ (1)\ w[\ell,m]\ (2) \right\} \tag{62}$$

will appear in the expansion of the geminals. For the triplet geminal, the NSO expansion will be limited to one term where $X=w[+1,+1]\alpha$ and $Y=w[+1,-1]\alpha$. The lone orbital will be taken as $Z=w[+1,0]\alpha$ and therefore, this geminal-orbital product will appear as follows:

$$\left\{ w[+1,+1]\ (1)\ w[+1,-1]\ (2) - w[+1,-1]\ (1)\ w[+1,+1]\ (2) \right\} \cdot w[+1,0]\ (3) \cdot \alpha(1)\alpha(2)\alpha(3). \tag{63}$$

The partial antisymmetrizer, Eq. 22, will produce an overall quartet S state out of this product by properly permuting the three electrons between the geminal and orbital. The antisymmetrized, three particle geminal-orbital product will be equivalent to the singlet determinant,

$$\left| w[+1,+1]\ (1)\ w[+1,-1]\ (2)\ w[+1,0]\ (3) \right| \cdot \alpha(1)\alpha(2)\alpha(3). \tag{64}$$

The total atomic wave function has therefore been constructed essentially as an antisymmetrized product of strongly orthogonal group functions in the sense of McWeeny

(88). Here, two of these group functions are the two particle, ^1S geminals, K and L, while the remaining group function is the three particle, ^4S determinant, Eq. 64. This latter group function will be labelled Q and called the quartet group, by analogy to the naming of the triplet geminal of NH.

Atomic Orbital Basis Sets

The particular atomic orbitals comprising the basis sets for the imidogen molecule are given in Table 1. (For conciseness, the AO's with quantum number, $m<0$, have been omitted from the table.) The orbital exponents are functions of R and the table is arranged accordingly. For each value of R, the individual ζ's should be obtained by independent minimization procedures.

For R=1.9614 bohrs, a complete minimization with respect to the ζ parameters has been undertaken. For all other values of R, the minimization process has been carried out with respect to classes of ζ's in order to expedite the calculations. The division of AO's into classes is made on the basis of the expectation value of the distance from the AO origin, $\langle r_\alpha \rangle$,

$$\langle r_\alpha \rangle = \int dV \; \chi_i \; r_\alpha \; \chi_i . \tag{65}$$

From the values given in Table 1 for this quantity, the AO's are divided into three classes: inner nitrogen, outer nitrogen and hydrogen orbitals. The inner orbitals, with $\langle r_N \rangle$ less than 0.4 bohrs, are in fact the major contributors to the NO's which provide the K shell geminal description while the remaining orbitals are used mainly to describe the outer electron pairs.

This grouping of AO's into classes has been used to parametrize the ζ's in the following way. For each class of orbitals, an R-dependent scale parameter, $\eta(R,k)$, has been defined such that the value of a ζ for an AO in the k^{th} class for the distance R will be related to the value of the same AO ζ for R=1.9614 by the relation

$$\zeta(R) = \eta(R,k) \cdot \zeta(1.9614). \tag{66}$$

The three scale factors are found by minimizing the total energy with respect to these η's. In addition, an overall scale factor is used for each value of R which scales all of the ζ's by the same factor; the value of this parameter is found by the energy minimization procedure as well. Therefore, for each value of R, there are four orbital exponent scaling parameters and their effect on the orbital exponents can be seen in Table 1.

It is desirable to construct a basis set for the nitrogen atom such that the total wave functions of the atom and molecule will be of comparable accuracy. This is accomplished by choosing for the atomic basis set, the same twenty-two AO's centered on the nitrogen nucleus which are used for the molecular basis set. The individual ζ's for the atom, however, are found by an independent minimization procedure, the results of which are given in Table 1.

Natural Orbitals and Occupation Coefficients

The natural orbitals are obtained from the basis set by means of the transformation matrix, $\underline{\underline{D}}$, given in Eq. 45. The optimal values found for the parameters, γ, will be exhibited by means of $\underline{\underline{D}}$ rather than by tabulating the γ's themselves since Eqs. 57 and 59 allow the latter to be calculated from $\underline{\underline{D}}$ for any particular orthogonalization procedure desired.

Each natural orbital in Table 2 is given a label of four symbols. The first designates the geminal in which it is used, the second specifies the order of importance of the given NO within the geminal, the third indicates the symmetry type of the NO, and the fourth gives the order of importance of the NO within its symmetry type within its geminal. Thus, the NO label, "Bonding $3\pi 1$", denotes that NO of the bonding geminal, which has the third largest occupation coefficient, has pi symmetry and within this symmetry has the largest occupation coefficient. The numbering of the AO's on the left hand side of the table corresponds to the numbering of the AO basis functions given in Table 1. The occupation coefficient (OC) for each NO is given below the corresponding column of $\underline{\underline{D}}$ matrix coefficients in the table.

For each internuclear distance, R, of interest for the molecule, optimal values for the ζ and γ parameters must be found. The ζ variations, as a function of R, which have been discussed above, alter the basis set and in turn the natural orbitals. Changes in the γ's alter the form of the NO's only.

For R=1.9614 bohrs, the full minimization procedure was executed with respect to the individual γ's as well as the ζ's. In order to expedite the minimization problem with respect to the γ's for other values of R, a grouping of these parameters was employed wherein all γ's within a group were varied simultaneously rather than individually. Since there was a possibility that this grouping of terms might be too rigid, some overlapping of groups was allowed for in order to help offset the effects of this limitation. Since a particular angle, γ_{pq}, essentially governs the interaction between the NO's, p and q, the following groups were chosen: (1) the set of all γ's connecting σ orbitals with other σ orbitals; (2) the set of γ's connecting π with other π NO's; (3) all γ's connecting K shell NO's with other K shell NO's; (4) all γ's between the K shell and outer shell orbitals; (5) the γ's between the principal lone pair NO with all other NO's; (6) the γ's between the principal bonding NO with all other NO's.

Table 2 lists these data pertaining to the natural orbitals of NH for the internuclear distances, R=1.8, 1.9, 1.923, 1.9614, 2.0, 2.05, and 2.10 bohrs. For the nitrogen atom, the $\underline{\underline{D}}$ matrix was found by an independent minimization with respect to the individual γ's. This $\underline{\underline{D}}$ matrix and the nitrogen atom OC's are presented in Table 3.

Contour maps have been drawn to supplement the description of the natural orbitals given in Tables 2 and 3. They are drawn in a plane containing the molecular axis and perpendicular to the nodal plane of the π orbitals. A particular solid curve connects coordinates in the plane for which the orbital has a particular positive value. The dashed curves connect coordinates at which the orbital has particular negative values. The zero contour curves are drawn with dotted lines. The highest and lowest contour values drawn are ± 0.50 bohr$^{-3/2}$ and the increment used is 0.05 bohr$^{-3/2}$. The positions of the nuclei are indicated by the notches drawn along the borders of the map and by the labels along the right-hand side. For NH, the NO's correspond to the internuclear distance, R=1.9614 bohrs.

The principal natural orbitals are seen to be those having the least number of nodal surfaces cutting the contour plane. The energetically less important NO's have smaller occupation coefficients and more nodes in general. The influence of the hydrogen atom can be seen by comparing NO's in NH and the N atom. The K shell NO's of NH (see NO Contour Maps 1-4) show only a very slight asymmetric deviation when compared to the atomic K shell NO's (see NO Contour Maps 21-23) whereas the outer shell NO's are all influenced greatly by the H atom.

Because of the higher symmetry of the atom, certain NO's in the molecule will coalesce in the separated atom limit.

For instance, when $R \rightarrow \infty$, the K Shell $3\pi 1$ and K Shell $4\sigma 3$ natural orbitals in NO Contour Maps 3 and 4 will form the components of the nitrogen K 3p1 natural orbital given in NO Contour Map 23.

Energy

Correlation energy

The total electronic energy, E, calculated from the separated pair (SP) wave functions for imidogen as a function of R is given in Table 4. Also given is the energy of the Slater determinant obtained by using just the principal natural orbital (PNO) of each geminal:

$$E(\text{PNO}) = V_{NH} + \sum_{\mu} E(\mu 0,\mu 0) + \sum_{\mu<\upsilon} I(\mu 0,\upsilon 0) \qquad (67)$$

where these quantities have been defined in Eqs. 29, 36 and 37. This wave function and its energy are very close to those of the Hartree-Fock approximation (4,89) and the difference between the SP and PNO energies therefore essentially represents the correlation energy. It is listed in the third section of Table 4.

A decomposition of these energies is also contained in Table 4. In addition to the nuclear repulsion V_{NH}, it shows the contributions from the one- and two-electron operators which form the Hamiltonian for NH, viz; the nuclear-electronic attractions, V_N and V_H, electronic repulsion, V_{12}, and electronic kinetic energy, T. The new symbols are defined as the expectation values,

$$V_\alpha = \left\langle \sum_i V_{\alpha i} \right\rangle \tag{68}$$

$$V_{12} = \left\langle \sum_{i<j} r_{ij}^{-1} \right\rangle \tag{69}$$

$$T = \left\langle \sum_i T_i \right\rangle , \tag{70}$$

where the definitions of Eqs. 31 and 32 have been used. The decrease in V_{12} on going from the PNO to the full separated pair wave function represents the most important effect of correlating the wave function. As expected, the change in kinetic energy is the largest among the one-electron properties but the nuclear attraction energy changes are themselves significant.

Equilibrium distance

The virial theorem can be used to obtain an estimate of the equilibrium internuclear distance, R_e. It is written as follows:

$$T + E + R\frac{\partial E}{\partial R} + \sum_i p_i \frac{\partial E}{\partial p_i} = 0, \tag{71}$$

where p_i represents each of the independent variational parameters entering the wave function. On the assumption that all of the parameters, p_i, have been assigned optimal values, the last term in Eq. 71 is taken to be zero and thus,

$$\frac{\partial E}{\partial R} \simeq - (T + E) / R. \tag{72}$$

Values of this quantity are given in Table 4. In Graph 1, the negative of the kinetic energy is plotted along with the total energy for both the SP and PNO wave functions. The value of R corresponding to the intersection of the E and -T curves is taken to be R_e(virial). It has the value 1.965 bohrs for both cases, which deviates from the experimental R_e of 1.9614 bohrs by ~0.2%.

Dissociation energy

The separated pair dissociation energy of the molecule is obtained as the difference between the SP energy value of the separated atoms and the value at the minimum of the SP molecular energy curve and similarly for the PNO dissociation energy. The calculated values are as follows: D_e(SP) = 2.65eV and D_e(PNO) = 2.00eV. These are to be compared with the experimental dissociation energy corrected for zero-point energy. Cade and Huo (1) suggest D_e(exptl) = 3.80eV to be the most internally consistent of the experimental values (33-35,90).

The difference between the PNO and experimental dissociation energies for diatomic hydrides is due to the change in correlation energy between the molecule and its separated atoms. The improvement of D_e(SP) over D_e(PNO) represents about 36% of the PNO-experimental difference and it will be seen to be due to the inclusion of intrageminal correlation energy effects in the bonding geminal alone. The remaining error in D_e is judged to be due to intergeminal correlation energy changes within the valence shell of the molecule. This conjecture draws support from a similar conclusion of Bender and Davidson (91) who estimated that about one-third of the atom-molecule correlation change between F and HF is due to correlation within the HF bonding geminal and the remainder is due to inter-pair correlations.

Total energy

The total "experimental" energy of NH is calculated from the equation:

$$E(\text{exptl}) = \sum_{i=3}^{7} (\text{I.P.})_i + E(\text{calc}, N^{-5}) - 0.5 + D_e(\text{exptl}) + E(\text{rel}) \qquad (73)$$

where $(\text{I.P.})_i$ is the ionization potential of the i-th electron of the N atom; $E(\text{calc}, N^{-5})$ is the Pekeris (92,93) two-electron, N^{-5} atomic energy; -0.5 is the energy of the hydrogen atom; $D_e(\text{exptl})$ is the experimental dissociation energy mentioned above; and E(rel) is the sum of all pertinent relativistic energy effects. The accuracy of E(exptl) is limited by the accuracy with which $D_e(\text{exptl})$ is known: using their suggested value for $D_e(\text{exptl})$, Cade and Huo (1) recommend a value for E(exptl) of -55.252 hartrees. The separated pair energy of -55.03352 hartrees is clearly not within the range of chemical accuracy but the SP wave function nevertheless has its usefulness and moreover represents the most accurate of previous calculations (1,59-68) on the $^3\Sigma^-$ ground state of the NH molecule. For comparison, a list of previous theoretical investigations on the imidogen molecule has been prepared in Table 5. Only ab initio calculations have been tabulated and for those cases where the energy has been calculated at more than one value of R, only the lowest value of E obtained is given along with the corresponding value of R. The remarks given in the table are intended to briefly describe the various techniques and types of basis functions employed. The table does not include semi-empirical calculations (54-58).

Dependence upon internuclear distance

The calculations on NH reported by Cade and Huo (1), which are here referred to as the SCF results, are believed to be very close approximations to the true Hartree-Fock solutions and thus they have been used as a guide for judging the accuracy of the present work. In Graph 2, the total energy has been plotted as a function of R for the separated pair and PNO wave functions and for the Cade and Huo SCF wave function. The PNO and SCF energy curves should be grossly similar although they differ in detail.

A fair difference in curvature is seen in Graph 2 between the PNO and SCF curves and this is due to the choice of a non-perfect minimization procedure. The reason for this choice is that the results of the previous section as well as those of the subsequent section show that essential correlation energy contributions are not recovered by the SP wave function. Therefore, the efforts required to execute a more perfect minimization process are not justified.

For internuclear distances less than about 1.8 bohrs or greater than about 2.1 bohrs, a more complete minimization of individual parameters would seem to be necessary. Within these limits however, the parameters entering the separated pair wave function are expected to have close to optimal values. The NH orbital exponents given in Table 1 and the D matrices given in Table 2 as well as calculations of other properties of imidogen have therefore been restricted to this range of internuclear separations.

It is also true that the separated pair wave function does not dissociate into species with the required spin characteristics in the limit when $R \to \infty$. (The SCF function also dissociates improperly but its behavior for large R is not the same as the SP wave function.) In order to achieve the proper dissociation properties, the total SP wave function could be expressed as a linear combination of separated pair wave functions but such a procedure is beyond the scope of the present work. Even with a perfect minimization procedure, this dissociation problem would limit the range of internuclear distances over which the NH separated pair wave function will be adequate.

Correlation Energy Analysis

The improvement in the energy of the separated pair wave function over the SCF result is due to the inclusion of certain electron correlation effects. In general, the separated pair wave function furnishes a means of recovering intrageminal correlation but no direct facility is provided for recovering intergeminal correlations. The analysis which follows is intended to provide some insight in the separated pair approximation and its ability to handle the correlation effects which arise in NH. In Table 4, a decomposition was made of the "natural orbital correlation energy", ΔE, defined as the difference between the total SP energy and the PNO energy. The value of ΔE obtained with this definition differs from the correlation energy defined with respect to the SCF energy by 9% for wave functions corresponding to R=1.9614 bohrs.

Geminal analysis

The correlation energy is defined by:

$$\Delta E = E - E(\mathrm{PNO}) \qquad (74)$$

where E and E(PNO) are given by Eqs. 33 and 67 respectively. According to these equations, the correlation energy is decomposed,

$$\Delta E = \sum_{\mu} \Delta E(\mu) + \sum_{\mu<\upsilon} \Delta I(\mu,\upsilon), \qquad (75)$$

into intrageminal contributions, ΔE(μ),

$$\Delta E(\mu) = \sum_{ij} \Delta E(\mu i,\mu j), \qquad (76)$$

and intergeminal interactions, ΔI(μ,υ),

$$\Delta I(\mu,\upsilon) = \sum_{ij} \Delta I(\mu i,\upsilon j), \qquad (77)$$

where by virtue of Eqs. 33-35,

$$\Delta E(\mu i,\mu j) = c_{\mu i}\, c_{\mu j}[E(\mu i,\mu j) - \delta_{ij} E(\mu 0,\mu 0)] \qquad (78)$$

$$\Delta I(\mu i, \upsilon j) = c_{\mu i}^2 \; c_{\upsilon j}^2 [I(\mu i, \upsilon j) - I(\mu 0, \upsilon 0)]. \qquad (79)$$

According to the remarks in the paragraph beginning after Eq. 39, the energy lowering, $\Delta E(\mu)$, arises from correlation between two electrons within the μ-th geminal whereas, $\Delta I(\mu, \upsilon)$ represents an energy change due to an electron pair with one partner in geminal μ and the other in geminal υ.

Table 6 lists the triangular matrices of intrageminal and intergeminal contributions to the PNO energy, E(PNO), and those to the correlation energy, ΔE. The diagonal elements of the two matrices are $E(\mu 0, \mu 0)$ and $\Delta E(\mu)$; the corresponding off-diagonal elements are $I(\mu 0, \upsilon 0)$ and $\Delta I(\mu, \upsilon)$. The sum of these PNO and correlation terms plus the nuclear repulsion, V_{NH}, gives the total SP energy E.

Certain features of the geminal correlation energy matrices are to be noted. The diagonal elements are all negative whereas the off-diagonal elements are both positive and negative. For each of the NH and N wave functions, however, the sum of these intergeminal terms does give a net negative contribution to the correlation energy but it represents only 4.5 to 2.5% of the total ΔE. Therefore, the energy gains recovered by the SP wave function can indeed be classified as being derived almost entirely from intrageminal correlations. Furthermore, from Table 6, the source of the intrageminal energy lowerings can be ascribed principally to correlations within the K shell and bonding geminals. The triplet and lone pair geminals give only slight energy gains.

For the triplet, this is expected since the two electrons forming the geminal have parallel spins. For the lone pair, this result is contrary to expectations and therefore this situation will be further investigated below.

The changes in the diagonal terms, $\Delta E(\mu)$, as R increases are the smallest for the K shell and lone pair geminals. The changes in the triplet intrageminal term, although larger than the changes found in the K shell and lone pair terms, are also fairly small. Only the bonding intrageminal correlation energy contribution is substantially affected by increasing the internuclear distance. The change in this one term is more than an order of magnitude greater than the sum of the changes in all of the other intrageminal and all of the intergeminal terms combined. This is the result of the increasingly important role played by the secondary bonding NO's in the NH wave function as R becomes large. The reason for this dominating effect is not too clear at the present; perhaps it is due to the omission of correlations between the bonding, lone pair and triplet geminals.

In the nitrogen atom, the quartet group, which consists of the bonding orbital and triplet pair, is described by a single three-particle determinant and thus there is no intragroup correlation energy available from this source. The nitrogen K and L geminals have intrageminal correlation energies which are larger than those present in the molecule and intergeminal correlations which are negative but smaller in magnitude than their molecular counterparts.

Natural orbital analysis

A further decomposition of the correlation energy exhibits natural orbital correlation effects. The total intrageminal correlation energy contribution of the μ-th geminal is decomposed as follows:

$$\Delta E(\mu) = \sum_{i(\neq 0)} \Delta E(\mu i) \tag{80}$$

where the contribution of the μi-th NO is defined as

$$\Delta E(\mu i) = \Delta E(\mu i,\mu 0) + \sum_{j} \Delta E(\mu j,\mu i). \tag{81}$$

[This differs from the definition used by Miller and Ruedenberg (4, see Eq. 64).] For all secondary NO's in the K shell, lone pair and triplet geminals of NH, this quantity can be approximated to an accuracy of 10^{-5} hartrees by the following:

$$\Delta E(\mu i) \simeq \Delta E(\mu i,\mu 0)+[\Delta E(\mu 0,\mu i) + \Delta E(\mu i,\mu i)] \tag{82}$$

where the second term in brackets is the NO self-energy and the other terms are the exchange interactions with the principal NO of the geminal. For NO's in the bonding geminal, this relationship holds true to an accuracy of only 10^{-4} hartrees because of the exchange interactions involving the strongly occupied secondary Bonding $2\sigma 2$ natural orbital. For most of the NO's, the two terms in brackets in Eq. 82 are about equal in magnitude but opposite in sign and therefore the remaining exchange integral governs the intrageminal correlation gain. Both $\Delta E(\mu i,\mu 0)$ and $\Delta E(\mu i)$ are given in Table 7 and the principal exceptions to the rule are seen to be the Lone Pair $2\sigma 2$, Bonding $2\sigma 2$, Bonding $3\pi 1$ and Bonding $4\sigma 3$ secondary NO's.

The total intergeminal contribution arising from the μi-th NO is defined by

$$\Delta I(\mu i) = \sum_{\upsilon(\neq\mu)} \sum_{j} \Delta I(\mu i,\upsilon j), \tag{83}$$

and for the NH wave functions, this quantity can be approximated by

$$\Delta I(\mu i) \simeq \sum_{\upsilon(\neq\mu)} \Delta I(\mu i,\upsilon 0) \tag{84}$$

since all secondary-secondary intergeminal interactions are less than 10^{-6} hartrees. From Table 7, only four secondary NO's are seen to have substantial values for $\Delta I(\mu i)$ and these are the same NO's mentioned above. Three of these, Lone Pair $2\sigma 2$, Bonding $3\pi 1$ and Bonding $4\sigma 3$, contribute more energy from intergeminal sources than they do from intrageminal sources.

The total contribution, $\Delta(\mu i)$, from the μi-th NO to the correlation energy is defined as the sum of its total intrageminal and intergeminal contributions:

$$\Delta(\mu i) = \Delta E(\mu i) + \Delta I(\mu i). \tag{85}$$

From the tabulated values of this quantity and from the occupation coefficients listed, it can be seen that within each geminal, the NO's which are energetically more important have occupation coefficients with larger magnitudes.

The energetically most important secondary NO is the Bonding $2\sigma 2$ function. The K Shell $2\sigma 2$ natural orbital is next in importance and gives an energy lowering that is only half as large. Next, the K Shell $3\pi 1$, K Shell $4\sigma 3$ and Triplet $2\pi 2$ secondary NO's give correlation gains that are about one-fourth that of the Bonding $2\sigma 2$. The Lone Pair $2\sigma 2$, Bonding $3\pi 1$ and Bonding $4\sigma 3$ orbitals, which are next in importance, give about one-eighth the gain of the Bonding $2\sigma 2$ orbital. The NO's mentioned here are the principal sources of the energy lowering in the SP wave function; the remaining NO's give relatively unimportant contributions to the total energy lowering.

Assignment of natural orbitals to geminals

There exists an "exclusion principle" for NO's between geminals because of the strong orthogonality condition and in some cases, it is not obvious in which geminal, certain NO's will be most effective. In order to determine the amount of correlation energy which different NO's can recover in different geminals, calculations were performed in which all of the secondary natural orbitals were placed successively in each of the geminals. In each case the eigenvalue equations, 50 , were solved for the occupation coefficients and all of the orbital correlation energy quantities given in Table 7 were recomputed. The results are given in Table 8. Here, the NO's are still identified, in the left-hand column, by the labels they have in Table 2.

The first section of Table 8 lists the results of a calculation where all secondary NO's are placed in the K shell geminal. It shows that only the NO's with labels "K Shell" are effective in correlating this geminal. The second section of the table lists the results of a calculation where all the secondary NO's are used in the lone pair geminal. Likewise, the third and fourth sections contain the results of calculations with all of the secondary NO's being assigned to the bonding and triplet geminals, respectively. It should be mentioned that the energy lowering, $\Delta(\mu i)$, for any particular natural orbital, μi, is essentially independent of which other NO's are present in the geminal, since only the interactions of the μi-th NO with the PNO are substantial.

From the table, it can be seen that the NO's giving large correlation energy lowerings in one geminal usually do not give significant gains in other geminals. This is especially true of the NO's: K Shell $2\sigma 2$, K Shell $3\pi 1$, K Shell $4\sigma 3$, Lone Pair $2\sigma 2$, Bonding $2\sigma 2$, Bonding $3\pi 1$, Bonding $4\sigma 3$ and Triplet $2\pi 2$. Thus, the use of geminal names for labelling these NO's seems justified. The only exception is the Lone Pair $3\delta 1$ natural orbital which gives a larger correlation gain when placed in the triplet geminal instead of the lone pair geminal. It is nevertheless associated with the lone pair in order to build wave functions having nearly similar properties for the molecule and atom, and in the latter, the set of 3d atomic orbitals are used for the L geminal description and are prohibited from being used in the triplet atomic geminal.

The total correlation energy recovered within each geminal in this way is given in the table. It might be possible to achieve slightly larger gains in each geminal if further minimization of the γ and ζ parameters would be carried out with the different arrangements of NO's, but the investment of computer time required for such a project was not considered warrented.

Limitations of the separated pair approximation

The most remarkable feature of the correlation energy analysis given above is the uniform inability of the separated pair wave function to provide for correlation in the lone pair geminal in NH. This is illuminated by examining the correlation situation in the L geminal of the beryllium atom (4). The total intrageminal correlation of the L geminal of Be was found to be -0.04928 hartrees, 96% of which was derived from the use of the L2p NO. This correlation arises from the near degeneracy (4,94,95) between the L2s and L2p NO's which results in the large occupation coefficient of the L2p NO and the consequent strong interaction with the L2s PNO. If this L2p NO is removed from the L geminal, the L shell intrageminal correlation energy in Be drops to less than -0.002 hartrees.

In the N atom, a set of L2p NO's do exist (see NO Contour Map 30) but they constitute the quartet group PNO. Being thus occupied, the constraint of strong orthogonality precludes the use of these NO's in any other geminal. In NH, the x and y components of the L2p NO form the triplet PNO (see NO Contour Map 18) while the z component of the L2p shares in the formation of the bonding PNO (see NO Contour Map 10). Again strong orthogonality renders these NO's unavailable for usage in the lone pair geminal. It is this unavailability of the L2p orbitals for the lone pair geminal that depresses its intrageminal correlation energy contributions in N as well as NH.

One might consider placing the L2p NO's in the lone pair geminal and then, for strong orthogonality reasons, dropping them from being used as PNO's in the other geminals. A calculation with a wave function of this type was performed where the Triplet $1\pi 1$ and Triplet $1\bar{\pi}1$ NO's were removed from the triplet geminal and placed in the lone pair geminal. The eigenvalue equations, 50, were solved and a correlation analysis made. The gain in lone pair intrageminal correlation was found to be -.03240 hartrees which agrees closely with the expected gain of (2/3)·(0.96)·(-0.04928) hartrees (only two out of three 2p components were used). However, the triplet geminal, which now had to use its $2\pi 2$ NO's as its PNO's, suffered a loss of over 2.7 hartrees and thus the use of the Triplet $1\pi1$ NO's in any other geminal but the triplet was found to be prohibited.

Strong orthogonality is thus seen to be a severe handicap in handling intrageminal correlation energy effects in cases where the necessary correlating NO's must be occupied as PNO's in some other geminal or where a particular secondary NO can be useful for correlation in several different geminals. For NH, a relaxation of the strong orthogonality condition between the three outer shell geminals might prove sufficient to relieve this situation. In addition some of the pair correlation energy gains presented in Table 8 might prove to be additive with the strong orthogonality constraint removed. However, even with the most optimistic estimates for the total intrageminal correlation energy gains, there is still a substantial amount of correlation energy unrecovered. For instance, assuming that ~1 eV were available as intrageminal correlation in each of the singlet geminals and ~0.3 eV in the triplet geminal, there would still remain 6.8 -3.3 = 3.5 eV to be accounted for. It must be concluded that the source of this energy difference has to be attributed to intergeminal correlation effects.

Limited-Configuration Separated Pair Approximations

Recently, attention has been drawn to the utility of wave functions containing only a limited number of configurations beyond the principal term (96-100). In this regard, it is of interest to study the effect on the molecular energy curve for NH of omitting certain secondary natural orbitals from the full separated pair wave function.

From the discussion of the correlation energy, it is realized that only the K shell and bonding geminals are significantly enhanced by the inclusion of secondary NO's in the SP geminals. Thus one limited wave function consists of the PNO's and the K Shell $2\sigma 2$, K Shell $3\pi 1$, K Shell $4\sigma 3$, and Bonding $2\sigma 2$ secondary natural orbitals. This wave function is denoted "K + B" and has a comparable nitrogen atom wave function consisting of the PNO's and the K 2s2 and K 3p1 secondary NO's. These NH and N wave functions both have equally correlated K shells and only the Bonding $2\sigma 2$ function, which has no counterpart in the atom, has been added to the molecule. An even simpler set of wave functions denoted by "B" is obtained by using only the PNO's for the atom and augmenting this with the Bonding $2\sigma 2$ natural orbital for the molecule.

Table 9, lists the energy results corresponding to the SP, K + B, B, and PNO wave functions of the NH molecule and the nitrogen atom. For each of the approximations, the sum of the hydrogen atom energy plus the corresponding nitrogen atom energy is subtracted from the molecular energy to give the binding energies.

In Graph 3, it is seen that the B and PNO curves are not parallel. This behavior is due of course to the inclusion of the single correlating NO in the bonding geminal. Since the SP, K + B, and B curves have quite similar curvatures, it is concluded that the R-dependence of these curves is governed essentially by the PNO's and the Bonding $2\sigma 2$ function. Although the shape of the SP energy curve is retained by the B and K + B wave functions, the absolute values of the total energy and binding energy are affected. For the B and K + B approximations, the total energy loss amounts to 1.11 eV and 0.45 eV respectively and the loss of the binding energy is 0.11 eV and 0.30 eV for the two wave functions respectively.

OTHER PROPERTIES

Spectroscopic Analysis

In order to relate the calculated potential energy curve to spectroscopic results, the analysis of Dunham (101) is the most practical approach. It involves fitting the potential curve by a polynomial of which the terms of order higher than the fourth are expected to be negligible. The first four terms are written in the form,

$$E(R) = E(R_e) + a_0\rho^2 (1 + a_1\rho + a_2\rho^2) \tag{86}$$

where

$$\rho = (R - R_e) / R_e . \tag{87}$$

Then the standard spectroscopic constants, B_e(rotational constant), α_e(rotational anharmonicity), k_e(force constant), ω_e(vibrational frequency), and $\omega_e x_e$(vibrational anharmonicity), can be simply calculated from a_0, a_1 and a_2 (101, Eq. 15).

In the present case, the seven points between R=1.8 and 2.1 bohrs have been chosen to determine the polynomial constants, a_0, a_1 and a_2. This is accomplished by finding the least-mean-square fit of the points on the energy curve to a fourth-order polynomial, determining R_e, the R value for which this quartic has its minimum, and then carrying out a transformation to the reduced variable ρ of Eq. 87. This gives the desired power series expansion of E about the equilibrium point R_e. The resulting spectroscopic constants are listed in Table 10; caution should be used in judging them however, since their reliability is limited by the fact that the number of points used for the determination of the fourth-order fit is relatively small. A self-consistency check is provided by comparing the equilibrium internuclear distances obtained from the Dunham analyses with those predicted using the virial theorem. The quantities, R_e(virial) and R_e(Dunham), agree to 0.03 and 0.8% for the SP and PNO wave functions respectively.

The accuracy of the rotational constant, B_e, is due to the close agreement of R_e(Dunham) with the experimental value. The three constants, α_e, k_e and ω_e, depend strongly on the curvature of the E versus R curve as well as on R_e. Since a full minimization of all wave function parameters could be executed for only one value of R, namely R = 1.9614 bohrs, whereas for all other R values, the minimization process was systematically restricted as described in a previous section, the resulting SP and PNO energy curves are expected to rise more sharply than the true energy curves as the distance from R = 1.9614 bohrs increases. This effect is especially noticeable for the constants k_e and ω_e which depend on R_e and a_0 only. The extremely close agreement of the SP value obtained for the constant $\omega_e x_e$, which depends upon the anharmonicity terms a_1 and a_2 as well as the distance R_e, is probably due to a fortuitous cancellation of errors in the coefficients a_1 and a_2. The energy, E_e, quoted in

Table 10 is that obtained from the Dunham polynomial with the given coefficients and thus corresponds to $E(R_e)$ in Eq. 86.

For comparison purposes, an "experimental" energy curve for NH has been constructed by finding that polynomial in the reduced variable ρ which, when expanded about the point R_e(exptl), gives the experimental values for the other spectroscopic constants. The resulting "Dunham polynomial" is plotted in Graph 4 with the SP and PNO Dunham functions. As expected, close agreement is obtained for the minimum of the curves but further minimization of wave function parameters is necessary in order to obtain closer agreement for the shape of the curves.

Since the systematic deviations in E(R), introduced by the choice of minimization technique, increase as the distance from R_e increase, one might expect to obtain better results by limiting oneself to a closer range on the E(R) curve. There is, however, a practical limit to such a narrowing of the range because any polynomial fit based on a number of points on the E(R) curve can be meaningful only to a degree n given by the condition that the n-th order differences, Δ_n, remain larger than the numerical inaccuracies in the values of E(R) available at the given points. Because of this, it is not possible to determine the higher expansion coefficients if all points are chosen too close to R_e. Therefore, it is necessary to include points of E(R) taken over a certain minimum range around R_e in the polynomial fit. In the case of NH, the range, R = 1.8 to 2.1 bohrs, was considered to be the best compromise.

One-Electron Expectation Values

The one-electron properties of a wave function provide information about the electronic structure present in the molecule. For the separated pair wave function, the expectation value of a one-electron operator, p(1), is obtained from the first order density matrix given in Eq. 26:

$$P(SP) = N^{-1} \int d\tau_1 \, p(1)\gamma(1|1) \tag{88}$$

whence

$$P(SP) = \sum_{\mu i} c_{\mu i}^{2} P(\mu i) \tag{89}$$

with

$$P(\mu i) = (\mu,2i|p|\mu,2i) + (\mu,2i+1|p|\mu,2i+1) \tag{90}$$

(see Eq. 38). The geminal one-electron property, $P(\mu)$, is obtained by summing only over i for fixed μ in Eq. 89. The PNO property is defined as

$$P(PNO) = \sum_{\mu} P(\mu 0). \tag{91}$$

The total effect of correlation on the value of the property is then given by

$$P(CORR) = \sum_{\mu} \Delta P(\mu), \tag{92}$$

where the geminal correlation property, $\Delta P(\mu)$, is

$$\Delta P(\mu) = \sum_{i} c_{\mu i}^{2} \left[P(\mu i) - P(\mu 0)\right]. \tag{93}$$

The quantities, $P(\mu 0)$, $\Delta P(\mu)$ and $P(\mu)$, for each geminal as well as the total quantities, P(PNO), P(CORR) and P(SP), are given in Table 11 for a selection of twenty one-electron operators. This decomposition refers to the wave function at the experimental equilibrium distance $R_e(\text{exptl}) = 1.9614$ bohrs. The column labeled % contains the percentage of P(SP) contributed by P(CORR). Most of the expectation values are self-explanatory since the corresponding operators are simple functions of spherical polar coordinates, $(r\ \Theta\ \phi)$, cartesian coordinates, $(x\ y\ z)$, or elliptic coordinates, $(\xi\ \eta\ \phi)$, defined with respect to axial systems with origins located at the nitrogen and hydrogen nuclei. The only exceptions are d and Q, which represent the intrinsic molecular dipole and quadrupole moments respectively. To avoid geometrical multipole effects, these quantities are defined with respect to an origin situated at the center of charge of the molecule. Due to the cylindrical symmetry of NH, the center of charge lies on the molecular axis and is located between the nuclei at the distance c from the nitrogen atom given by

$$c = (R_{NH} + \sum_i \langle z_{Ni} \rangle)/16 \qquad (94)$$

where z_{Ni} is the component along the molecular axis of the radius vector from the nitrogen nucleus to the i-th electron. Using a cartesian system located at c with its z-axis pointing toward the hydrogen atom, d and Q are given by the following standard definitions:

$$d = \left| \sum_{\alpha} Z_{\alpha} \cdot \vec{z}_{c\alpha} - \sum_{i} \langle \vec{z}_{ci} \rangle \right| \tag{95}$$

$$Q = \sum_{\alpha} Z_{\alpha} \cdot 2z_{c\alpha}^{2} - \sum_{i} [3\langle z_{ci}^{2} \rangle - \langle r_{ci}^{2} \rangle] \tag{96}$$

in which Z_{α} is the charge on the α nucleus, $\vec{z}_{c\alpha}$ and $\vec{z}_{ci}$ are the vector distances along the molecular axis from the center of charge to the α nucleus and the i-th electron respectively, and r_{ci} is the radial distance from c to the electron i. For the NH wave functions given here, the intrinsic quadrupole moment tensor is diagonal and has the form:

$$\underline{\underline{Q}} = Q \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{97}$$

For the decomposition of d and Q into geminal contributions, the nuclear charges have been divided amongst the geminals in the following way. The K shell, lone pair and triplet geminals are each associated with two nitrogen protons. The remaining nitrogen proton and the hydrogen proton are assigned to the bonding geminal. For the four resulting "geminal" charge distributions, d and Q are calculated with respect to the same center of charge, c, given in Eq. 94. For d, one obtains intrinsic geminal dipole moments because each of the charge distributions consists of an equal number of positive and negative charges. For Q, one obtains geometrical geminal quadrupole moments; however, because of the common origin at c, the four geminal moments can be added to give the total intrinsic molecular quadrupole moment.

The role played by the secondary natural orbitals is that of augmenting the description of the geminal furnished by the PNO. For the K shell, lone pair, and triplet geminals, the effect of correlation is practically nil for all of the properties listed. The bonding geminal is the one that is influenced most by its secondary NO's, especially in terms of the bonding dipole and quadrupole moments. The percentage change in the property value due to correlation is quite small in general but it is to be remembered that even the correlation energy recovered by the SP wave function represents only about 0.11% of the total energy.

In Table 12, the R dependence of P(PNO), P(CORR), and P(SP) is displayed for each of the properties over the restricted range of internuclear separations. Graph 5 gives P(PNO) and P(SP) for the properties, d and Q, as functions of internuclear distance. The remaining properties are plotted against R in Graphs 6-9 but since P(CORR) is so small for these quantities, only P(SP) is given.

Two-Electron Expectation Values

The two-electron properties of a many electron system are those influenced most by the inclusion of correlation in the wave function. Although the separated pair approximation takes account of only a limited amount of correlation, it is of interest to examine the changes which are produced in the values of some two-electron expectation values for the wave functions. The four operators to be studied here are

r_{12}^{-1}, r_{12}^{2}, $\cos \Theta_{12,N}$ and $\cos \Theta_{12,H}$ where

$$r_{12} = |\vec{r}_{1\alpha} - \vec{r}_{2\alpha}| \tag{98}$$

$$\cos \Theta_{12,\alpha} = \vec{r}_{1\alpha} \cdot \vec{r}_{2\alpha} \,/\, |\vec{r}_{1\alpha}| \; |\vec{r}_{2\alpha}| \tag{99}$$

and $\vec{r}_{i\alpha}$ is the distance vector from nucleus α to electron i. The first two operators give a measure of the expected distance between any two electrons and the latter two give a measure of the angular correlation of two electrons.

The expectation value of a two-electron operator, G(1,2), is found to be

$$\langle G\rangle = \sum_{\mu}\sum_{ij} c_{\mu i}\, c_{\mu j}\, E_G(\mu i,\mu j) + \sum_{\mu<\upsilon}\sum_{ij} c_{\mu i}^{2}\, c_{\upsilon j}^{2}\, I_G(\mu i,\upsilon j) \tag{100}$$

where the quantities E_G and I_G can be thought of as being defined by Eqs. 36 and 37 if the following two changes are made: the one electron integrals, $(\kappa k|h|\lambda \ell)$, are dropped from Eq. 36 and the two electron integrals in those equations are taken to be defined by

$$[\kappa,k\lambda,\ell|\mu,m\;\upsilon,n] = 2/N(N-1) \int d\tau_1 \int d\tau_2\, \psi_{\kappa,k}^{*}(1)\psi_{\lambda,\ell}(1)$$

$$G(1,2)\psi_{\mu,m}(2)\psi_{\upsilon,n}^{*}(2) \tag{101}$$

with N being the total number of electrons. The factor involving N is used in order to give values for <G> that represent a single pair interaction within the N-electron system.

One can decompose <G> by

$$\langle G\rangle = \langle G(\mathrm{PNO})\rangle + \Delta G, \qquad (102)$$

which is analogous to Eq. 74, where <G(PNO)> arises from the principal natural orbitals and ΔG is the correlation correction due to the secondary NO's. These quantities are given by

$$\langle G(\mathrm{PNO})\rangle = \sum_{\mu} E_G(\mu 0,\mu 0) + \sum_{\mu<\upsilon} I_G(\mu 0,\upsilon 0) \qquad (103)$$

$$\Delta G = \sum_{\mu} \Delta E_G(\mu) + \sum_{\mu<\upsilon} \Delta I_G(\mu,\upsilon) \qquad (104)$$

where $\Delta E_G(\mu)$ and $\Delta I_G(\mu,\upsilon)$ can be defined by subscripting G onto each E and I in Eqs. 76 and 77.

These properties are exhibited in Table 13 by means of geminal matrices which are analogous to those presented in Table 6. Listed are the triangular matrices of intrageminal and intergeminal contributions to the PNO property, <G(PNO)>, and those to the correlation correction, ΔG, for each of the four two-electron operators. The diagonal elements of the two matrices for each property are $E_G(\mu 0,\mu 0)$ and $\Delta E_G(\mu)$, the corresponding off-diagonal elements are $I_G(\mu 0,\upsilon 0)$ and $\Delta I_G(\mu,\upsilon)$. The sum of the PNO and correlation matrix elements gives the total expectation value, <G>.

The lone pair and triplet geminal properties are seen to be the least affected by the inclusion of correlation. The K shell description appears to be changed mostly by angular effects as measured by $\langle \cos \theta_{12,N} \rangle$. The largest correlation effects are seen in the bonding geminal where both the interelectronic distance and angular dependence are greatly influenced by the secondary NO's.

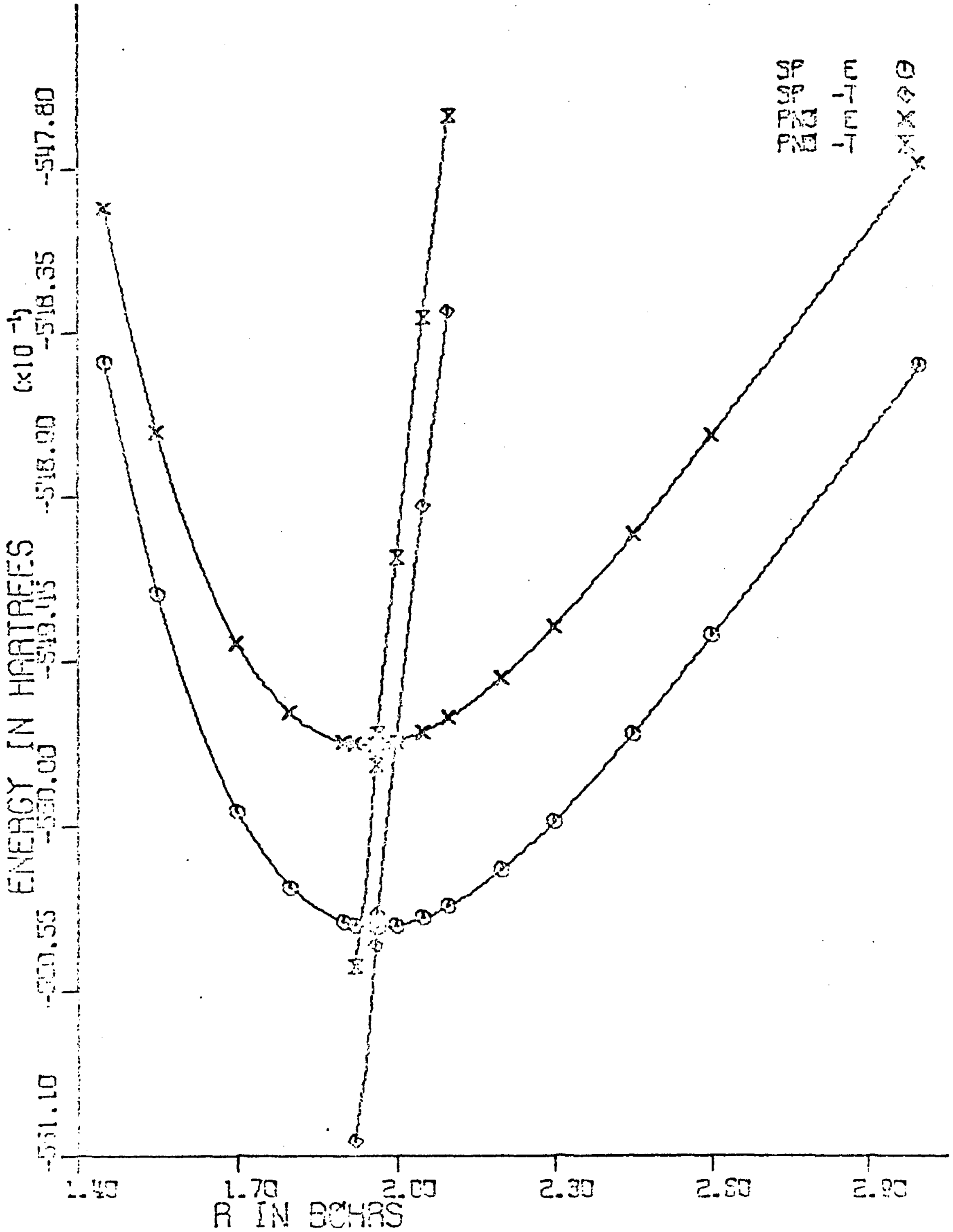
The R dependence of the two-electron properties is given in Table 14 and plotted in Graph 10. Since the SP wave function dissociates into the neutral species, N and H, one of the NH electrons will position itself about the hydrogen atom while all others will remain associated with the nitrogen atom. Thus, as R increases, the pair property, r_{12}^{2} (r_{12}^{-1}), will increase (decrease) for each of the pair interactions involving the "H atom electron". These interactions are averaged with all other pair interactions in the molecule by computing the expectation value and therefore one sees a very strong R-dependence in the quantities r_{12}^{2} and r_{12}^{-1}.

The angular functions have values which are very sensitive to the distance between the reference origin (the N or H nuclear center) and the centroid of the average pair. The centroid of the average pair is given by $\langle r_\alpha \rangle$ of Table 12 when measured with respect to the α nucleus. As $\langle r_\alpha \rangle$ increases, $\theta_{12,\alpha}$ decreases and thus $\langle \cos \theta_{12,\alpha} \rangle$ increases. From Table 12 and Graph 6, $\langle r_H \rangle$ is seen to increase much more strongly than $<r_N>$ as R increases and thus the strong R dependence of $<\cos \Theta_{12,H}>$ can be understood. The PNO value for $<\cos \Theta_{12,N}>$ increases slightly with increasing R as expected, but so slowly that the decrease in the correlation contribution (increase in magnitude) eventually dominates and gives the expectation value the R-dependence seen in Table 14.

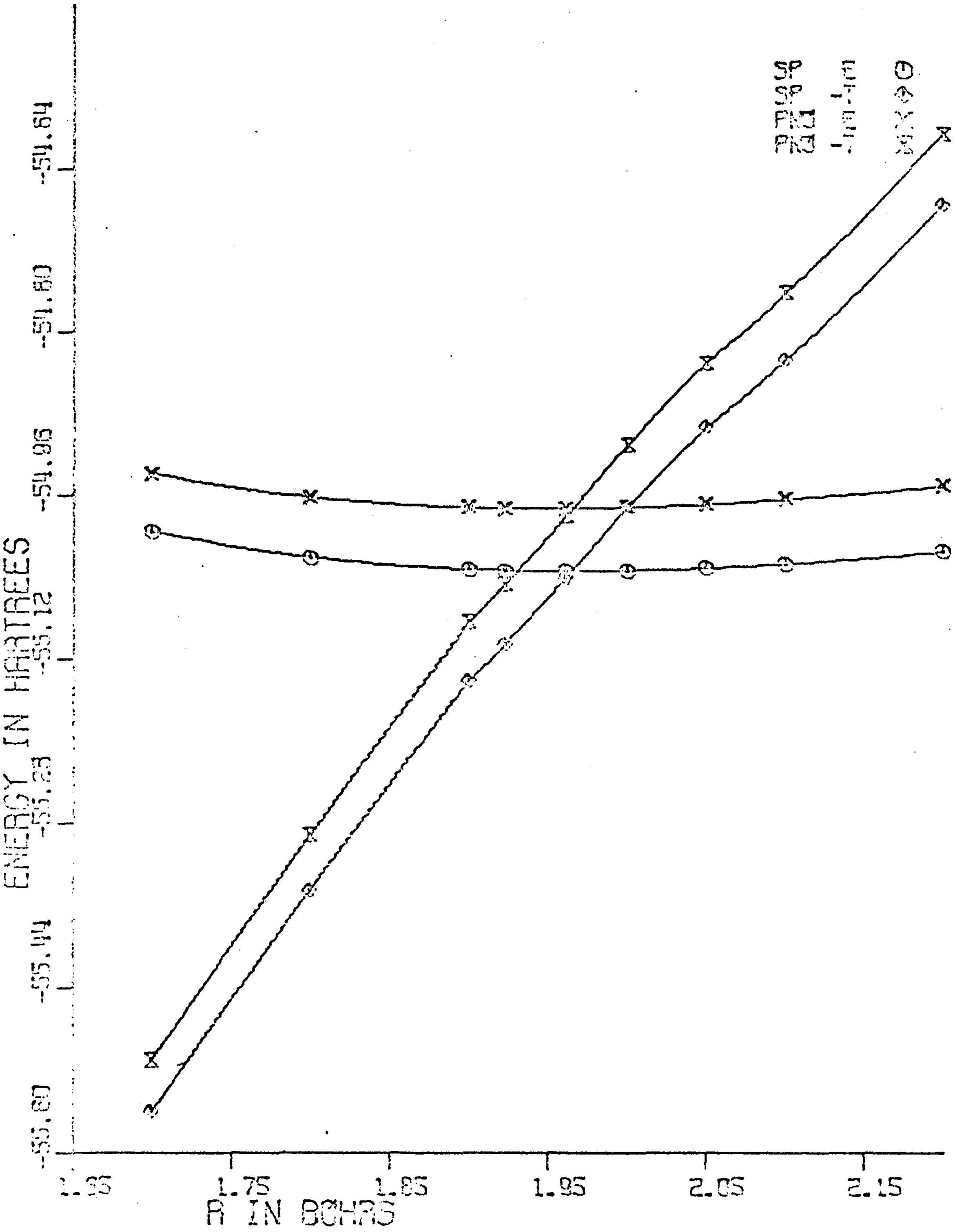
SUMMARY

A general formulation of the separated pair approximation has been presented and used to calculate a wave function for the $^3\Sigma^-$ ground state of the imidogen molecule. Although the energy obtained with this wave function is better than any previously calculated result, the amount of correlation energy recovered has been found to be severely limited due to the constraint imposed by the strong orthogonality conditions and the omission of intergeminal correlations. Nevertheless, an understanding of the correlation problem in NH is achieved and the limitations of the separated pair method are documented. From the experience gained here, it must be concluded that a more general scheme for handling electron correlation must be employed if more than two outer-shell electrons are involved.

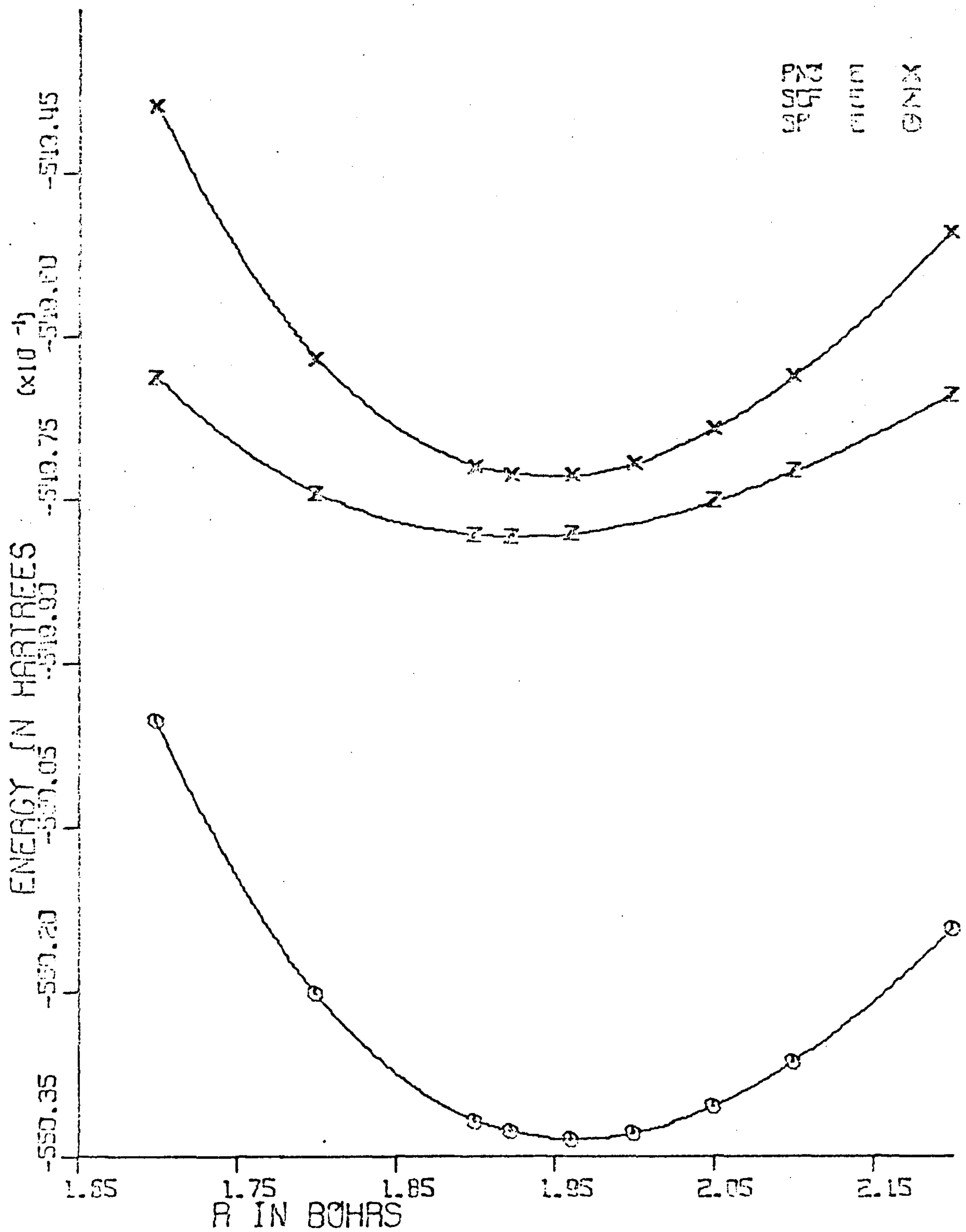
APPENDIX: GRAPHS, TABLES, NATURAL ORBITAL CONTOUR MAPS



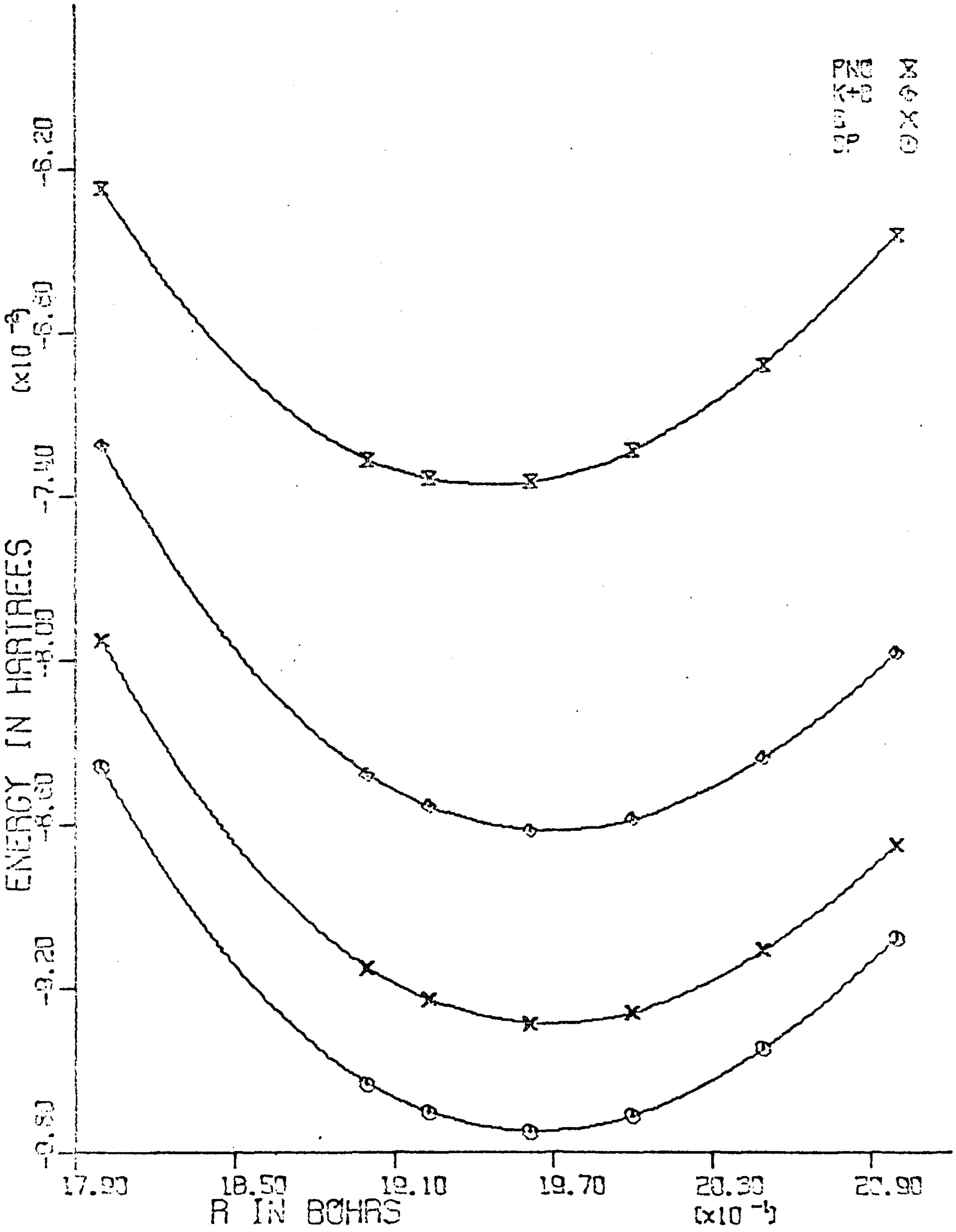
GRAPH 1A. TØTAL AND KINETIC ENERGIES ØF IMIDØGEN



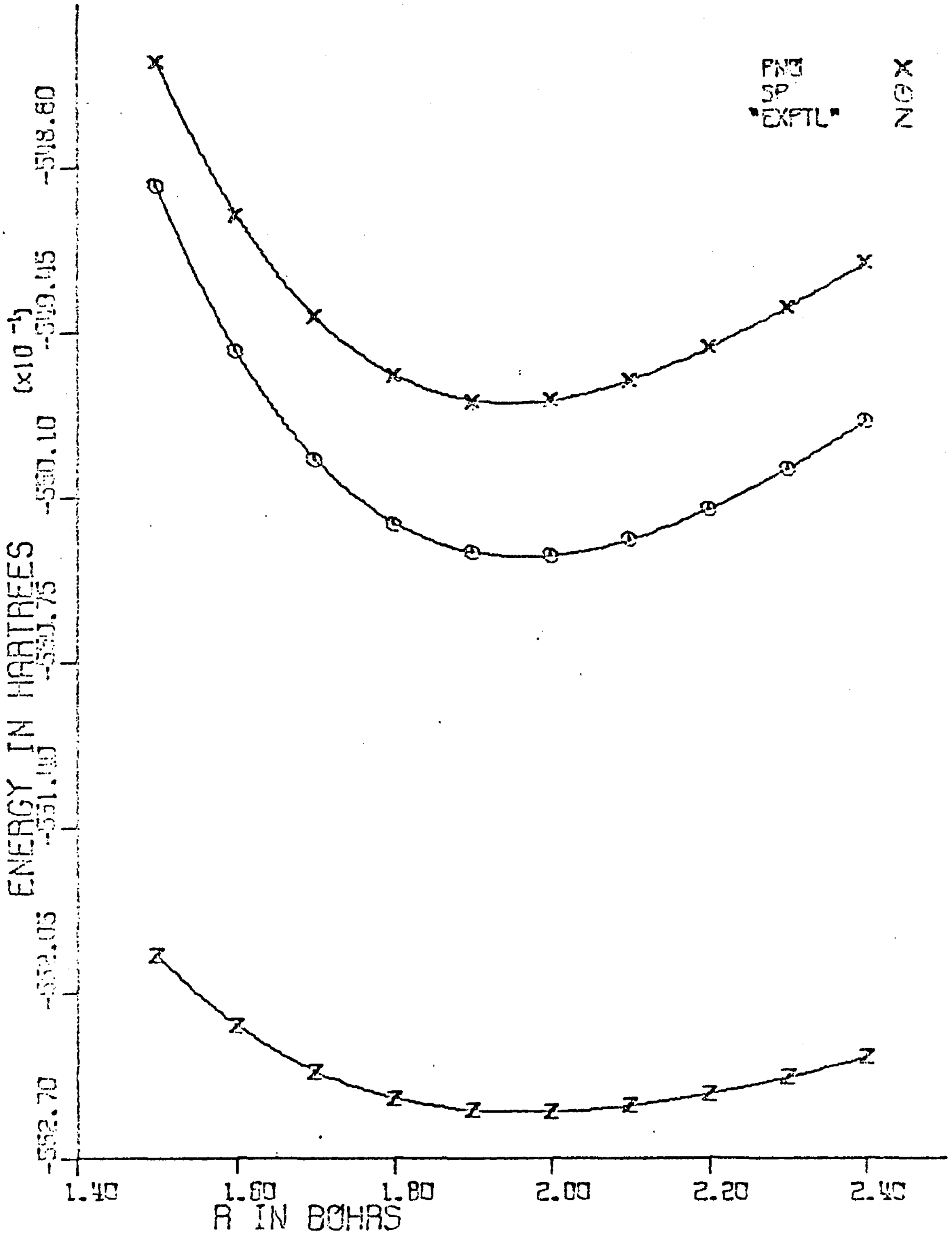
GRAPH 1B. DETAIL OF THE INTERSECTION OF E AND -T FOR IMIDOGEN



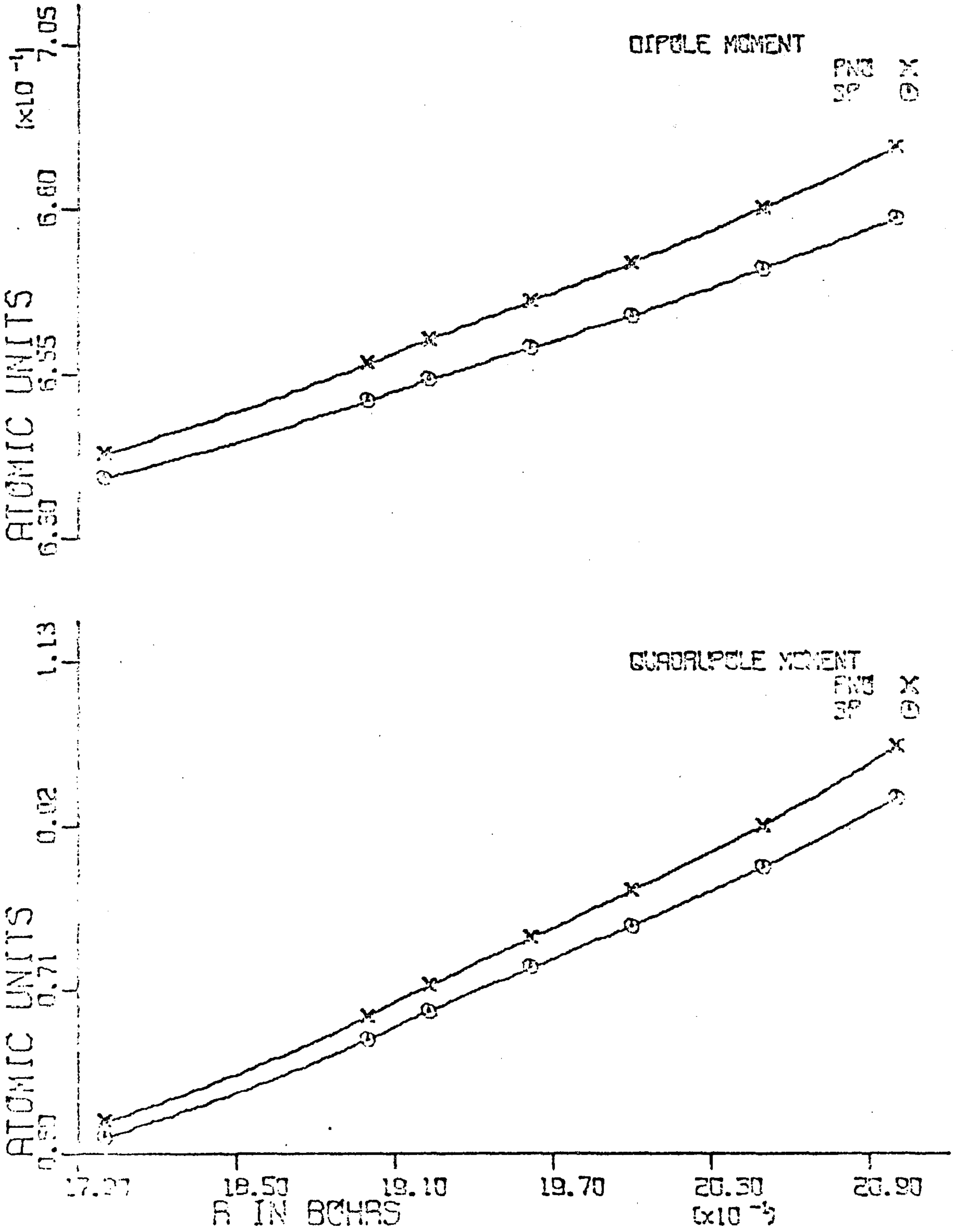
GRAPH 2. POTENTIAL ENERGY COMPARISON
WITH SCF CURVE FOR IMIDOGEN



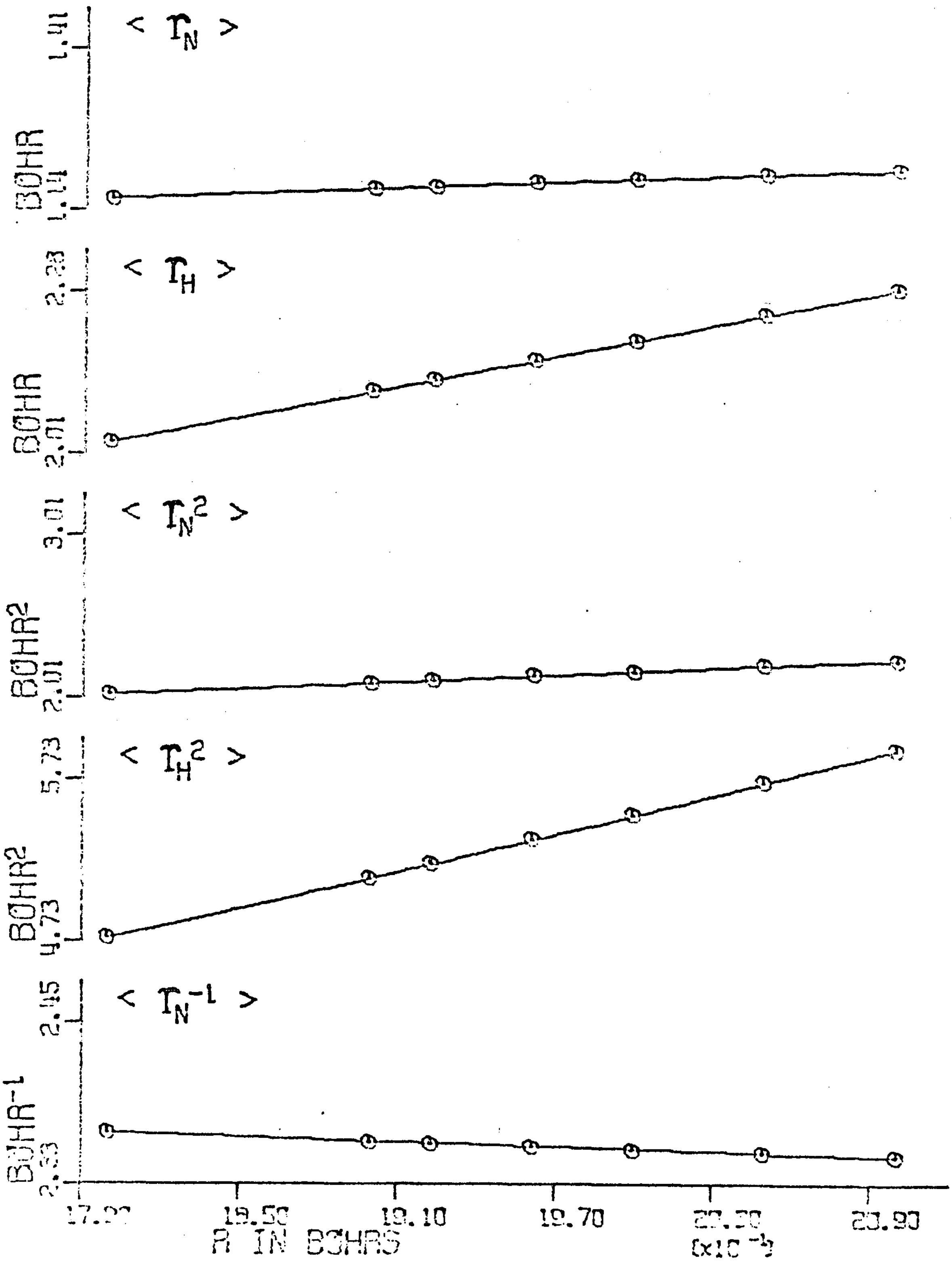
GRAPH 3. BINDING ENERGIES OF IMIDOGEN
FROM VARIOUS WAVE FUNCTIONS



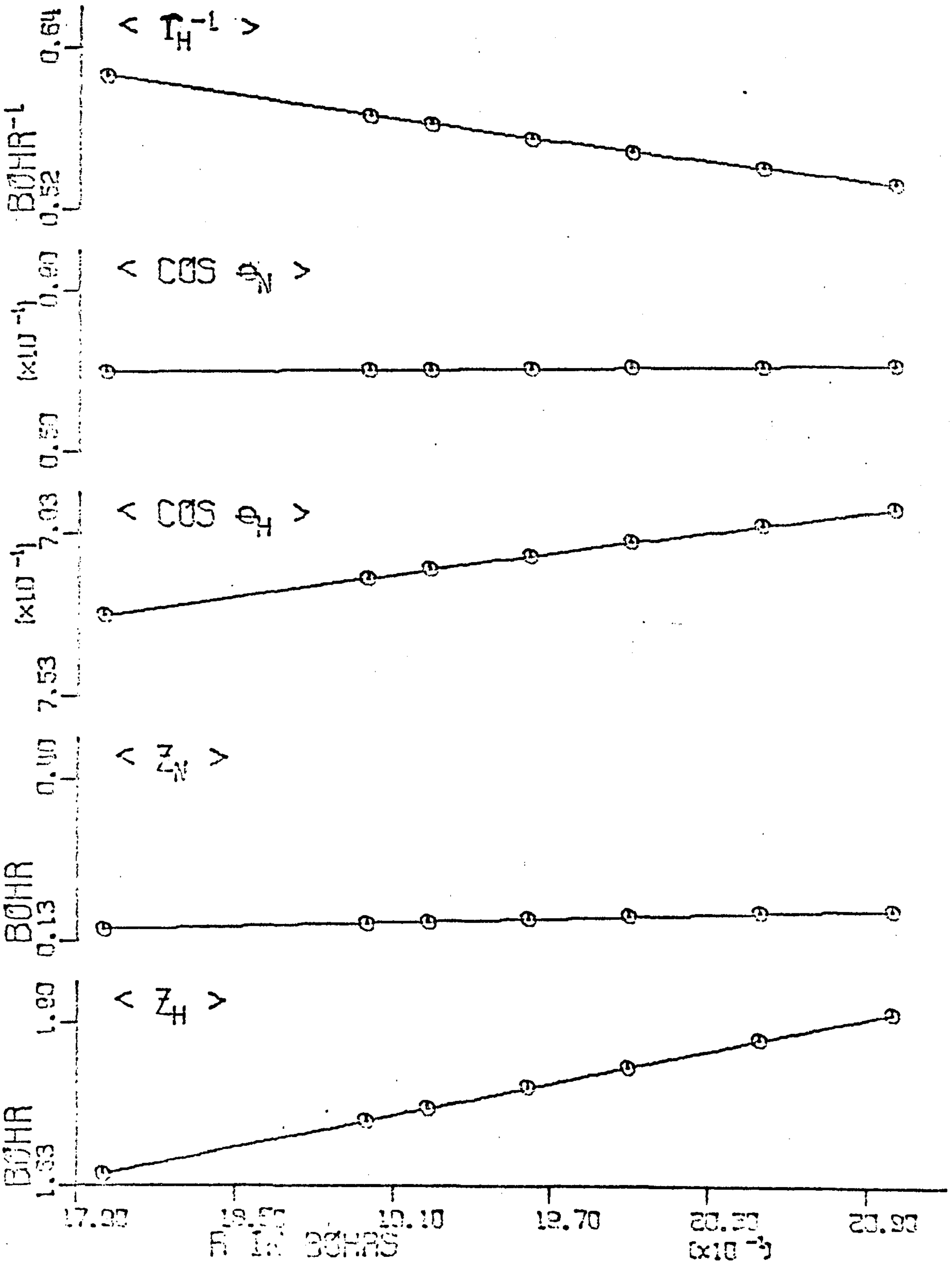
GRAPH 4. NH POTENTIAL ENERGY CURVES FROM THE ANALYSIS OF DUNHAM



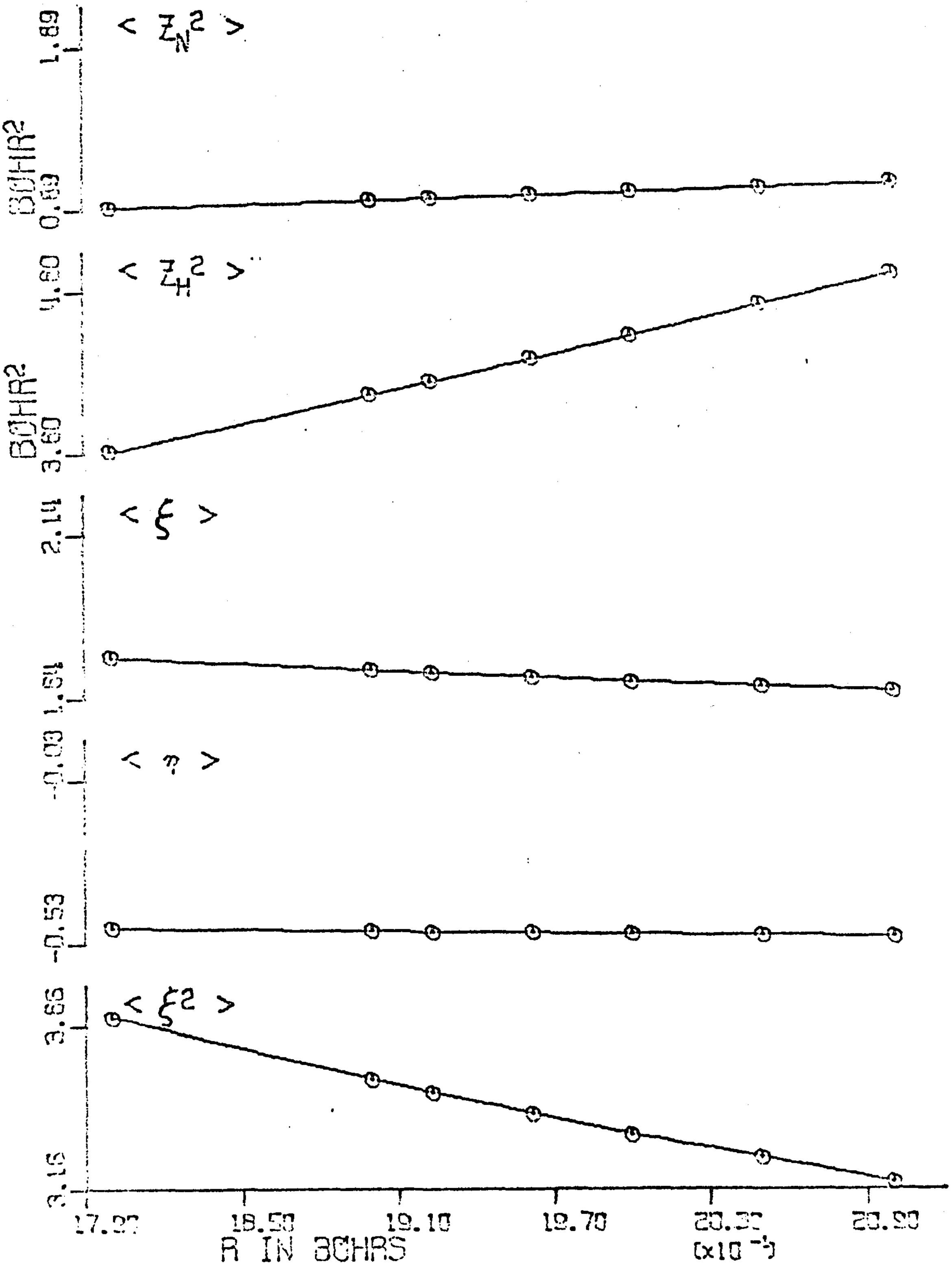
GRAPH 5. DIPOLE AND QUADRUPOLE MOMENTS OF IMIDOGEN



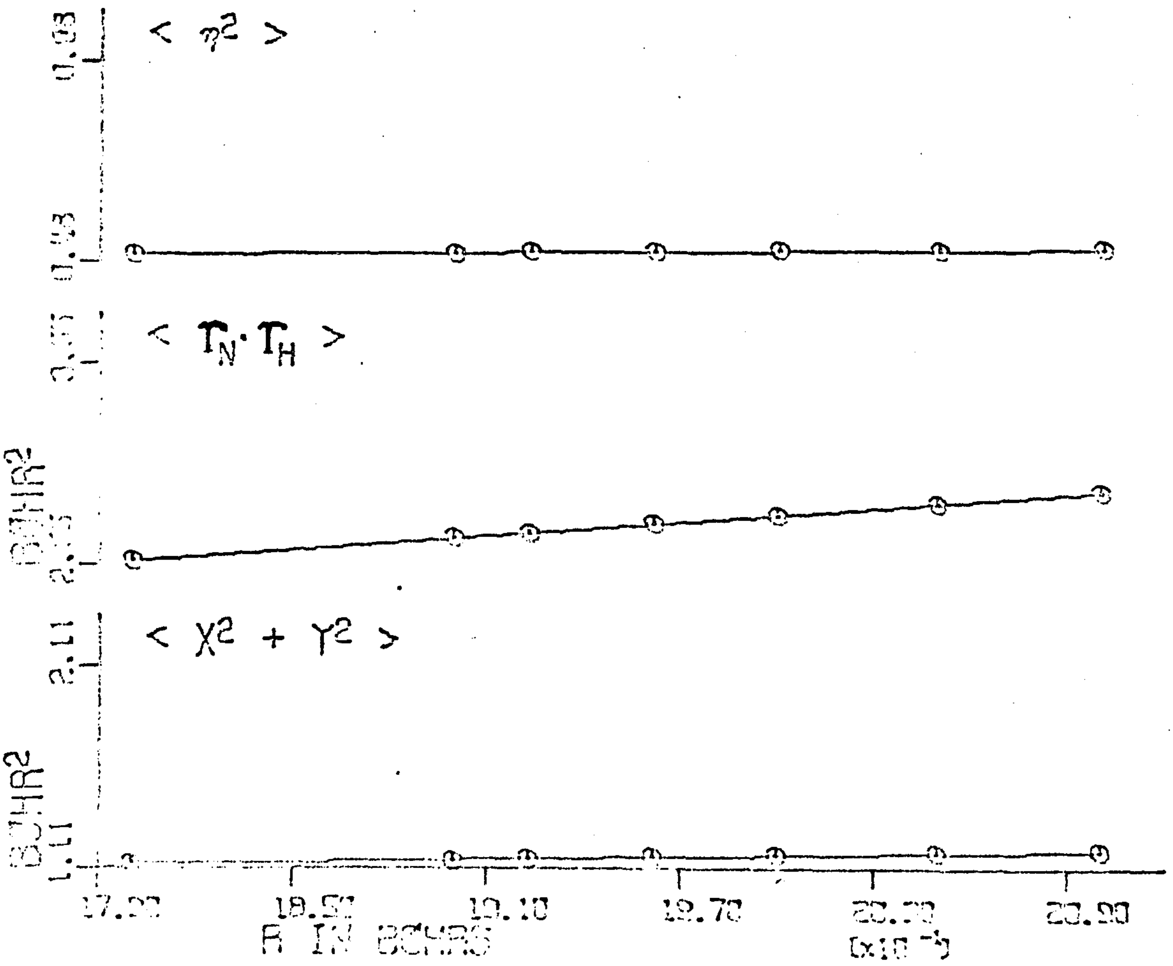
GRAPH 6. <ONE-ELECTRON> VALUES FOR NH



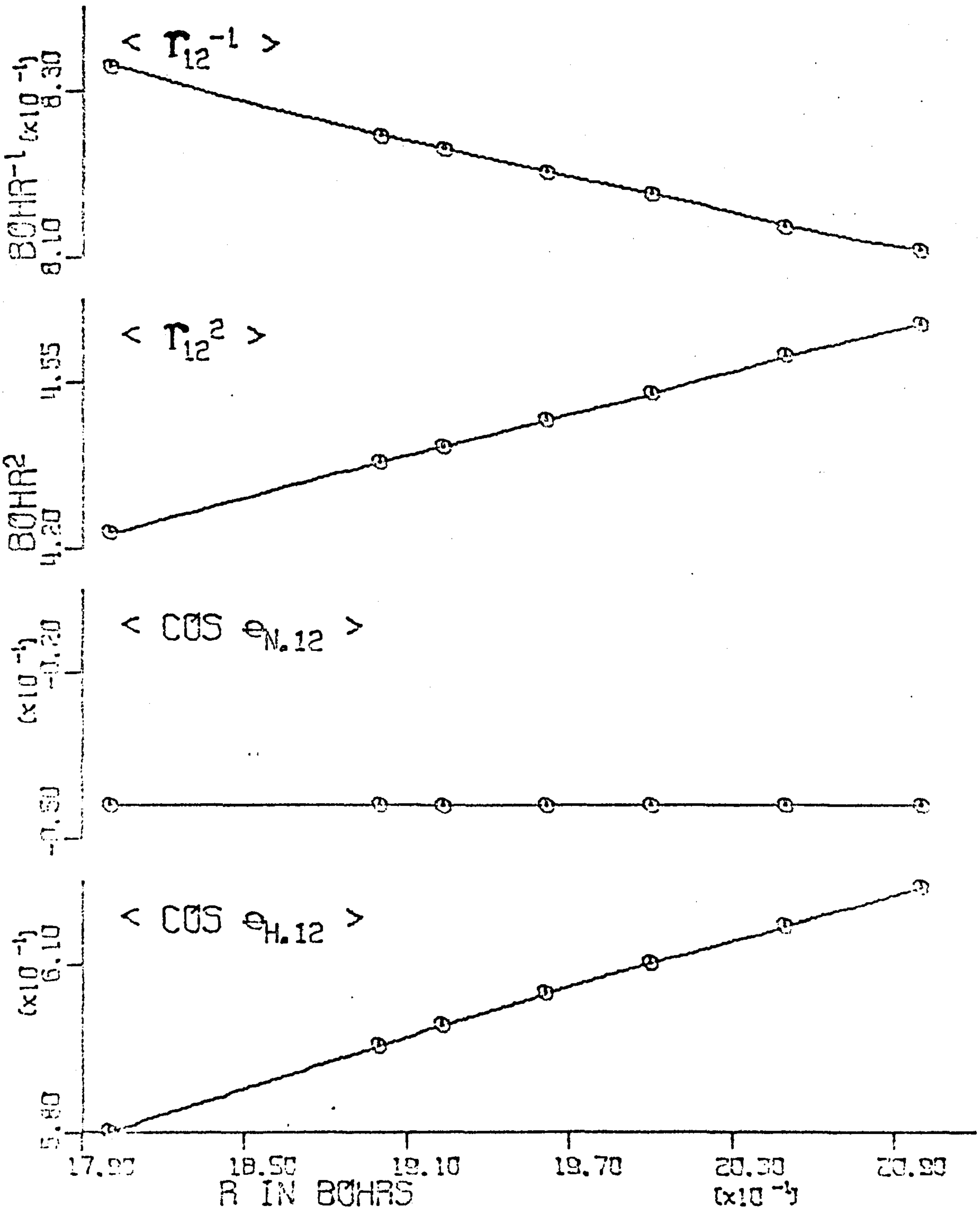
GRAPH 7. <ONE-ELECTRON> VALUES FOR NH



GRAPH 8. <ONE-ELECTRON> VALUES FOR NH



GRAPH 9. <ONE-ELECTRON> VALUES FOR NH



GRAPH 10. TWØ-ELECTRØN EXPECTATIØN VALUES FØR IMIDØGEN

TABLE 1. ATOMIC ORBITAL BASIS SETS

N ATOM

AO	NLM	NH, R = 1.8000 ZETA	$\langle r_N \rangle$	NH, R = 1.9000 ZETA	$\langle r_N \rangle$	NH, R = 1.9230 ZETA	$\langle r_N \rangle$	NH, R = 1.9614 ZETA	$\langle r_N \rangle$
1	100	6.23887	0.24	6.23584	0.24	6.23430	0.24	6.23302	0.24
2	200	7.00044	0.36	6.99704	0.36	6.99531	0.36	6.99388	0.36
3	210	7.52337	0.33	7.51972	0.33	7.51786	0.33	7.51632	0.33
4	211	7.08395	0.35	7.08051	0.35	7.07876	0.35	7.07731	0.35
5	200	1.15207	2.17	1.14252	2.19	1.14100	2.19	1.13781	2.20
6	200	2.04880	1.22	2.03180	1.23	2.02909	1.23	2.02343	1.24
7	210	1.12714	2.22	1.11779	2.24	1.11630	2.24	1.11318	2.25
8	211	1.48111	1.69	1.46882	1.70	1.46686	1.70	1.46277	1.71
9	210	2.59182	0.96	2.57032	0.97	2.56689	0.97	2.55973	0.98
10	211	2.97545	0.84	2.95077	0.85	2.94684	0.85	2.93862	0.85
11	300	2.50403	1.40	2.48326	1.41	2.47995	1.41	2.47303	1.42
12	310	1.63311	2.14	1.61957	2.16	1.61741	2.16	1.61290	2.17
13	311	1.98409	1.76	1.96764	1.78	1.96501	1.78	1.95953	1.79
14	320	2.18191	1.60	2.16381	1.62	2.16093	1.62	2.15490	1.62
15	321	2.28853	1.53	2.26955	1.54	2.26653	1.54	2.26020	1.55
16	322	2.56072	1.37	2.53948	1.38	2.53609	1.38	2.52902	1.38

H ATOM

AO	NLM	ZETA	$\langle r_H \rangle$	ZETA	$\langle r_H \rangle$	ZETA	$\langle r_H \rangle$	ZETA	$\langle r_H \rangle$
17	100	1.41948	1.06	1.34660	1.11	1.32856	1.13	1.30295	1.15
18	200	1.58862	1.57	1.50706	1.66	1.48687	1.68	1.45820	1.71
19	210	1.81543	1.38	1.72223	1.45	1.69916	1.47	1.66640	1.50
20	211	1.80215	1.39	1.70962	1.46	1.68672	1.48	1.65420	1.51

TABLE 1. (CONT.)

		NH, R = 2.0000		NH, R = 2.0500		NH, R = 2.1000		NITROGEN ATOM	
N ATOM									
AO	NLM	ZETA	$\langle r_N \rangle$	ZETA	$\langle r_N \rangle$	ZETA	$\langle r_N \rangle$	ZETA	$\langle r_N \rangle$
1	100	6.23062	0.24	6.23046	0.24	6.22793	0.24	5.98635	0.25
2	200	6.99118	0.36	6.99100	0.36	6.98816	0.36	7.20686	0.35
3	210	7.51343	0.33	7.51323	0.33	7.51018	0.33	7.56232	0.33
4	211	7.07458	0.35	7.07440	0.35	7.07153	0.35	7.56232	0.33
5	200	1.13570	2.20	1.13119	2.21	1.12874	2.21	0.95092	2.63
6	200	2.01968	1.24	2.01166	1.24	2.00730	1.25	2.04691	1.22
7	210	1.11112	2.25	1.10671	2.26	1.10431	2.26	1.01464	2.46
8	211	1.46006	1.71	1.45426	1.72	1.45111	1.72	1.01464	2.46
9	210	2.55499	0.98	2.54484	0.98	2.53932	0.98	1.93575	1.29
10	211	2.93317	0.85	2.92152	0.86	2.91519	0.86	1.93575	1.29
11	300	2.46845	1.42	2.45864	1.42	2.45331	1.43	2.68240	1.30
12	310	1.60990	2.17	1.60351	2.18	1.60003	2.19	2.58502	1.35
13	311	1.95590	1.79	1.94813	1.80	1.94391	1.80	2.58502	1.35
14	320	2.15090	1.63	2.14236	1.63	2.13772	1.64	2.50539	1.40
15	321	2.25601	1.55	2.24705	1.56	2.24218	1.56	2.50539	1.40
16	322	2.52433	1.39	2.51430	1.39	2.50885	1.40	2.50539	1.40

H ATOM							
AO	NLM	ZETA	$\langle r_H \rangle$	ZETA	$\langle r_H \rangle$	ZETA	$\langle r_H \rangle$
17	100	1.27847	1.17	1.24806	1.20	1.21692	1.23
18	200	1.43081	1.75	1.39677	1.79	1.36193	1.84
19	210	1.63509	1.53	1.59620	1.57	1.55638	1.61
20	211	1.62312	1.54	1.58452	1.58	1.54499	1.62

TABLE 2. D MATRICES AND OCCUPATION COEFFICIENTS FOR NH

NH, R = 1.8000 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11481	-2.30521	0.0	-0.02122	-0.24635	0.20111	0.0
2	-0.13851	2.81536	0.0	0.02476	-0.02527	0.03811	0.0
3	-0.00003	0.00069	0.0	1.27782	-0.00771	-0.01876	0.0
4	0.0	0.0	1.45803	0.0	0.0	0.0	0.0
5	0.01082	0.47548	0.0	-0.04558	0.16290	1.51718	0.0
6	0.07319	-1.09783	0.0	-0.13762	1.03063	-1.77507	0.0
7	-0.00553	-0.04861	0.0	-2.14106	-0.14037	-0.23655	0.0
8	0.0	0.0	-1.48166	0.0	0.0	0.0	0.0
9	-0.00027	-0.00435	0.0	-0.83431	-0.11081	0.31966	0.0
10	0.0	0.0	-0.96117	0.0	0.0	0.0	0.0
11	-0.04843	0.03560	0.0	-0.01277	-0.09353	0.17590	0.0
12	0.01177	-0.08651	0.0	2.42947	0.04648	-0.18977	0.0
13	0.0	0.0	1.78797	0.0	0.0	0.0	0.0
14	0.00453	-0.05427	0.0	-0.04650	0.02090	-0.11851	0.0
15	0.0	0.0	-0.05737	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	-0.00831	0.06768	0.0	-0.10508	0.02646	-0.26391	0.0
18	-0.01345	0.17028	0.0	0.26643	-0.11431	0.45492	0.0
19	-0.01121	0.06615	0.0	0.16464	-0.01170	0.21182	0.0
20	0.0	0.0	0.05523	0.0	0.0	0.0	0.0
OC	0.99982	-0.01119	-0.00871	-0.00860	0.99926	-0.03187	-0.01243

TABLE 2. (CONT.)

NH, R = 1.8000 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.46501	-0.03330	0.06392	0.0	0.00624	0.04603
2	0.0	3.17478	-0.00456	0.03066	0.0	0.00125	-0.05647
3	0.0	-0.01417	0.01118	0.02684	0.0	-0.01326	0.02917
4	0.05744	0.0	0.0	0.0	0.00801	0.0	0.0
5	0.0	-0.94972	-0.09435	-0.17010	0.0	0.48616	0.70175
6	0.0	-11.00612	0.07960	-0.72858	0.0	-0.14800	0.04300
7	0.0	0.07280	0.02968	0.12461	0.0	2.68907	0.49728
8	6.79164	0.0	0.0	0.0	3.96919	0.0	0.0
9	0.0	-0.00896	0.42991	-0.85624	0.0	-0.94400	-0.23369
10	-1.37147	0.0	0.0	0.0	-0.71620	0.0	0.0
11	0.0	11.48753	-0.00468	-0.00842	0.0	0.00328	-0.08616
12	0.0	0.30002	0.30141	-0.42480	0.0	-1.28640	0.39236
13	-5.38810	0.0	0.0	0.0	-3.03523	0.0	0.0
14	0.0	0.18726	0.05220	-0.11521	0.0	-0.16779	1.25953
15	1.08328	0.0	0.0	0.0	-0.35858	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.30593	0.45451	1.26270	0.0	-0.95639	-1.47015
18	0.0	-0.32325	-0.00661	0.19163	0.0	0.31227	0.18622
19	0.0	-0.05192	0.02424	0.11378	0.0	0.12202	0.11517
20	-0.95124	0.0	0.0	0.0	-0.85577	0.0	0.0
OC	-0.00872	-0.00114	0.99540	-0.08124	-0.02783	-0.02865	-0.01016

TABLE 2. (CONT.)

NH, R = 1.8000 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11231	0.02199	0.16423	0.0	0.0	0.0
2	0.18304	0.01818	-0.86900	0.0	0.0	0.0
3	-0.12313	-0.02013	0.12739	0.0	0.0	0.0
4	0.0	0.0	0.0	0.00886	0.14383	-0.35575
5	-2.29872	0.65089	-2.77691	0.0	0.0	0.0
6	-1.13699	-0.10361	2.51158	0.0	0.0	0.0
7	-4.12430	-7.86602	2.22671	0.0	0.0	0.0
8	0.0	0.0	0.0	1.02643	2.11977	14.85654
9	0.78104	0.24962	-0.85232	0.0	0.0	0.0
10	0.0	0.0	0.0	0.26052	-1.67094	-1.70984
11	1.55509	0.21530	-5.16117	0.0	0.0	0.0
12	2.26518	8.48796	-5.57010	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.25553	-0.79042	-13.90383
14	-0.26377	0.24221	-1.49115	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02729	-0.15834	-0.32112
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.88655	-0.52031	0.98412	0.0	0.0	0.0
18	4.18992	-0.65129	5.41730	0.0	0.0	0.0
19	-0.08810	-0.07760	2.93385	0.0	0.0	0.0
20	0.0	0.0	0.0	0.01876	0.14874	0.51316
OC	-0.00811	-0.00574	-0.00368	0.99930	-0.03741	-0.00175

TABLE 2. (CONT.)

NH, R = 1.9000 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11587	-2.29825	0.0	-0.01823	-0.24620	0.20573	0.0
2	-0.14208	2.80539	0.0	0.02311	-0.02506	0.04273	0.0
3	0.00072	-0.00283	0.0	1.26590	-0.00549	-0.02261	0.0
4	0.0	0.0	1.44772	0.0	0.0	0.0	0.0
5	0.00536	0.51421	0.0	-0.05729	0.14730	1.63382	0.0
6	0.08369	-1.07029	0.0	-0.11663	1.03651	-1.76357	0.0
7	0.00025	-0.03670	0.0	-2.17502	-0.12476	-0.21270	0.0
8	0.0	0.0	-1.48904	0.0	0.0	0.0	0.0
9	-0.00293	0.00734	0.0	-0.79956	-0.11808	0.33776	0.0
10	0.0	0.0	-0.94666	0.0	0.0	0.0	0.0
11	-0.06697	0.05682	0.0	0.01386	-0.12592	0.26006	0.0
12	-0.00238	-0.04602	0.0	2.46400	0.00266	-0.07744	0.0
13	0.0	0.0	1.79254	0.0	0.0	0.0	0.0
14	0.00038	-0.03062	0.0	-0.03688	0.00707	-0.06554	0.0
15	0.0	0.0	-0.05495	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	-0.00268	0.04833	0.0	-0.14926	0.04296	-0.30929	0.0
18	-0.00248	0.08694	0.0	0.27459	-0.07765	0.24867	0.0
19	-0.00217	0.03646	0.0	0.12453	0.00367	0.10733	0.0
20	0.0	0.0	0.04981	0.0	0.0	0.0	0.0
OC	0.99982	-0.01124	-0.00873	-0.00862	0.99924	-0.03242	-0.01250

TABLE 2. (CONT.)

NH, R = 1.9000 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.45778	-0.03173	0.06988	0.0	0.00869	0.04385
2	0.0	3.13201	-0.00819	0.03056	0.0	0.00979	-0.05035
3	0.0	-0.00797	0.01100	0.00810	0.0	-0.01280	0.03884
4	0.06331	0.0	0.0	0.0	0.01389	0.0	0.0
5	0.0	-1.01076	-0.12053	-0.13135	0.0	0.63978	0.76431
6	0.0	-10.88193	0.09613	-0.69513	0.0	-0.14605	0.03853
7	0.0	0.03049	0.03052	0.10662	0.0	2.75446	0.54568
8	6.83517	0.0	0.0	0.0	3.99153	0.0	0.0
9	0.0	-0.01818	0.43826	-0.79520	0.0	-0.95418	-0.26620
10	-1.39356	0.0	0.0	0.0	-0.73454	0.0	0.0
11	0.0	11.33929	-0.02011	0.08098	0.0	0.05671	-0.10780
12	0.0	0.26122	0.27096	-0.33412	0.0	-1.19299	0.38372
13	-5.43039	0.0	0.0	0.0	-3.04957	0.0	0.0
14	0.0	0.15082	0.04616	-0.06210	0.0	-0.11721	1.25269
15	1.06673	0.0	0.0	0.0	-0.36529	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.30870	0.46603	1.20978	0.0	-1.00486	-1.47090
18	0.0	-0.16791	0.02267	0.05269	0.0	0.10233	0.15497
19	0.0	-0.05242	0.03291	0.04459	0.0	0.02316	0.06560
20	-0.93933	0.0	0.0	0.0	-0.86192	0.0	0.0
OC	-0.00894	-0.00116	0.99442	-0.09267	-0.02788	-0.02740	-0.01063

TABLE 2. (CONT.)

NH, R = 1.9000 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11444	0.01530	0.17761	0.0	0.0	0.0
2	0.18676	0.01372	-0.84477	0.0	0.0	0.0
3	-0.12481	-0.01518	0.07740	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01247	0.13990	-0.34632
5	-2.48846	0.49395	-2.94773	0.0	0.0	0.0
6	-1.13990	-0.11082	2.61537	0.0	0.0	0.0
7	-4.42627	-7.95990	1.97148	0.0	0.0	0.0
8	0.0	0.0	0.0	1.01528	2.13583	14.89249
9	0.83417	0.24371	-0.62837	0.0	0.0	0.0
10	0.0	0.0	0.0	0.26012	-1.67070	-1.72999
11	1.65865	0.13091	-4.85796	0.0	0.0	0.0
12	2.47752	8.39052	-5.28820	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.24716	-0.79578	-13.89723
14	-0.27013	0.16651	-1.40439	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02552	-0.14991	-0.29049
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.87874	-0.54554	0.97659	0.0	0.0	0.0
18	4.31435	-0.29141	5.09748	0.0	0.0	0.0
19	-0.02788	-0.05100	2.93583	0.0	0.0	0.0
20	0.0	0.0	0.0	0.02395	0.13052	0.45529
OC	-0.00803	-0.00600	-0.00370	0.99926	-0.03831	-0.00179

TABLE 2. (CONT.)

NH, R = 1.9230 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11646	-2.29678	0.0	-0.01739	-0.24609	0.20620	0.0
2	-0.14332	2.80385	0.0	0.02252	-0.02560	0.04510	0.0
3	0.00056	-0.00347	0.0	1.26396	-0.00546	-0.02302	0.0
4	0.0	0.0	1.44633	0.0	0.0	0.0	0.0
5	0.00421	0.52620	0.0	-0.06115	0.14479	1.66871	0.0
6	0.08643	-1.06475	0.0	-0.11161	1.03927	-1.76443	0.0
7	0.00213	-0.03081	0.0	-2.18534	-0.12001	-0.20100	0.0
8	0.0	0.0	-1.48807	0.0	0.0	0.0	0.0
9	-0.00304	0.00931	0.0	-0.79240	-0.11872	0.33948	0.0
10	0.0	0.0	-0.94509	0.0	0.0	0.0	0.0
11	-0.07065	0.06126	0.0	0.01951	-0.13290	0.28003	0.0
12	-0.00587	-0.03778	0.0	2.47376	-0.00737	-0.05215	0.0
13	0.0	0.0	1.79177	0.0	0.0	0.0	0.0
14	-0.00037	-0.02488	0.0	-0.03494	0.00460	-0.05234	0.0
15	0.0	0.0	-0.05444	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	-0.00133	0.04431	0.0	-0.15888	0.04638	-0.32086	0.0
18	-0.00082	0.06486	0.0	0.27852	-0.07204	0.19607	0.0
19	-0.00045	0.02793	0.0	0.11557	0.00606	0.07963	0.0
20	0.0	0.0	0.04847	0.0	0.0	0.0	0.0
OC	0.99982	-0.01126	-0.00873	-0.00862	0.99923	-0.03249	-0.01251

TABLE 2. (CONT.)

NH, R = 1.9230 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.45751	-0.03163	0.07050	0.0	0.00883	0.04314
2	0.0	3.12625	-0.00899	0.03142	0.0	0.01263	-0.04858
3	0.0	-0.00636	0.01051	0.00471	0.0	-0.01197	0.04122
4	0.06448	0.0	0.0	0.0	0.01484	0.0	0.0
5	0.0	-1.03014	-0.12850	-0.12280	0.0	0.68545	0.78367
6	0.0	-10.86444	0.09894	-0.69117	0.0	-0.14797	0.03775
7	0.0	0.01655	0.03079	0.10384	0.0	2.77861	0.56101
8	6.84977	0.0	0.0	0.0	4.00163	0.0	0.0
9	0.0	-0.01976	0.44072	-0.78352	0.0	-0.95951	-0.27429
10	-1.39935	0.0	0.0	0.0	-0.73905	0.0	0.0
11	0.0	11.31311	-0.02276	0.10104	0.0	0.06898	-0.11364
12	0.0	0.25119	0.26250	-0.31576	0.0	-1.17323	0.38068
13	-5.44320	0.0	0.0	0.0	-3.05705	0.0	0.0
14	0.0	0.14080	0.04455	-0.05066	0.0	-0.10407	1.25181
15	1.06313	0.0	0.0	0.0	-0.36687	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.30880	0.46935	1.19968	0.0	-1.01894	-1.47334
18	0.0	-0.12468	0.03073	0.02374	0.0	0.04779	0.14548
19	0.0	-0.04837	0.03617	0.02984	0.0	-0.00400	0.05257
20	-0.93765	0.0	0.0	0.0	-0.86391	0.0	0.0
OC	-0.00899	-0.00116	0.99418	-0.09529	-0.02789	-0.02706	-0.01075

TABLE 2. (CONT.)

NH, R = 1.9230 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11553	0.01338	0.17988	0.0	0.0	0.0
2	0.18855	0.01322	-0.83974	0.0	0.0	0.0
3	-0.12526	-0.01394	0.06614	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01287	0.13939	-0.34478
5	-2.54411	0.44811	-2.99891	0.0	0.0	0.0
6	-1.14469	-0.11286	2.63434	0.0	0.0	0.0
7	-4.51104	-7.99732	1.90812	0.0	0.0	0.0
8	0.0	0.0	0.0	1.01586	2.14061	14.90615
9	0.84894	0.24531	-0.57739	0.0	0.0	0.0
10	0.0	0.0	0.0	0.25970	-1.67143	-1.73518
11	1.68978	0.11514	-4.78546	0.0	0.0	0.0
12	2.53692	8.37689	-5.22174	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.24802	-0.79786	-13.90064
14	-0.27127	0.14783	-1.38292	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02501	-0.14810	-0.28319
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.87489	-0.55256	0.98390	0.0	0.0	0.0
18	4.35084	-0.19857	5.02816	0.0	0.0	0.0
19	-0.01019	-0.04140	2.94138	0.0	0.0	0.0
20	0.0	0.0	0.0	0.02517	0.12608	0.44123
OC	-0.00801	-0.00606	-0.00369	0.99926	-0.03847	-0.00180

TABLE 2. (CONT.)

NH, R = 1.9614 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11677	-2.29456	0.0	-0.01664	-0.24614	0.20760	0.0
2	-0.14437	2.80071	0.0	0.02228	-0.02546	0.04631	0.0
3	0.00074	-0.00430	0.0	1.26040	-0.00490	-0.02319	0.0
4	0.0	0.0	1.44299	0.0	0.0	0.0	0.0
5	0.00183	0.54368	0.0	-0.06710	0.13714	1.71787	0.0
6	0.08975	-1.05704	0.0	-0.10752	1.04121	-1.76249	0.0
7	0.00344	-0.02277	0.0	-2.20344	-0.11706	-0.18192	0.0
8	0.0	0.0	-1.49870	0.0	0.0	0.0	0.0
9	-0.00375	0.01134	0.0	-0.78142	-0.12036	0.33995	0.0
10	0.0	0.0	-0.93880	0.0	0.0	0.0	0.0
11	-0.07626	0.06742	0.0	0.03021	-0.14303	0.30144	0.0
12	-0.01039	-0.02566	0.0	2.49011	-0.02150	-0.02126	0.0
13	0.0	0.0	1.79971	0.0	0.0	0.0	0.0
14	-0.00175	-0.01675	0.0	-0.03261	-0.00020	-0.03524	0.0
15	0.0	0.0	-0.05396	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	0.00038	0.03667	0.0	-0.17347	0.05199	-0.33717	0.0
18	0.00300	0.03585	0.0	0.28582	-0.05811	0.12729	0.0
19	0.00286	0.01567	0.0	0.10229	0.01268	0.04094	0.0
20	0.0	0.0	0.04762	0.0	0.0	0.0	0.0
OC	0.99982	-0.01128	-0.00873	-0.00863	0.99923	-0.03259	-0.01254

TABLE 2. (CONT.)

NH, R = 1.9614 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.45500	-0.03101	0.07228	0.0	0.00944	0.04242
2	0.0	3.11093	-0.01000	0.03155	0.0	0.01519	-0.04700
3	0.0	-0.00415	0.01039	-0.00089	0.0	-0.01069	0.04483
4	0.06666	0.0	0.0	0.0	0.01753	0.0	0.0
5	0.0	-1.06389	-0.13965	-0.10495	0.0	0.74746	0.80684
6	0.0	-10.81909	0.10414	-0.68431	0.0	-0.14856	0.03781
7	0.0	-0.00709	0.02805	0.10049	0.0	2.81653	0.58233
8	6.86737	0.0	0.0	0.0	4.00760	0.0	0.0
9	0.0	-0.02173	0.44459	-0.76612	0.0	-0.96908	-0.28716
10	-1.40703	0.0	0.0	0.0	-0.74604	0.0	0.0
11	0.0	11.25689	-0.02626	0.13117	0.0	0.07776	-0.12686
12	0.0	0.23557	0.25380	-0.28523	0.0	-1.15424	0.37174
13	-5.46150	0.0	0.0	0.0	-3.06031	0.0	0.0
14	0.0	0.12473	0.04272	-0.03259	0.0	-0.08855	1.24794
15	1.05675	0.0	0.0	0.0	-0.36947	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.30403	0.47371	1.18068	0.0	-1.03654	-1.47240
18	0.0	-0.05903	0.04157	-0.02166	0.0	-0.02062	0.13730
19	0.0	-0.03905	0.04030	0.00473	0.0	-0.04093	0.03522
20	-0.93267	0.0	0.0	0.0	-0.86632	0.0	0.0
OC	-0.00907	-0.00117	0.99377	-0.09961	-0.02787	-0.02652	-0.01091

TABLE 2. (CONT.)

NH, R = 1.9614 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11633	0.01114	0.18430	0.0	0.0	0.0
2	0.19059	0.01177	-0.83002	0.0	0.0	0.0
3	-0.12579	-0.01295	0.04875	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01439	0.13848	-0.34108
5	-2.61549	0.37652	-3.04732	0.0	0.0	0.0
6	-1.14911	-0.11452	2.65584	0.0	0.0	0.0
7	-4.63231	-8.06014	1.82439	0.0	0.0	0.0
8	0.0	0.0	0.0	1.00677	2.14703	14.93053
9	0.86951	0.25012	-0.50200	0.0	0.0	0.0
10	0.0	0.0	0.0	0.26055	-1.67177	-1.74504
11	1.73562	0.09399	-4.66060	0.0	0.0	0.0
12	2.62778	8.36312	-5.11457	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.24048	-0.80037	-13.90741
14	-0.27298	0.12043	-1.34847	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02481	-0.14540	-0.27282
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.86970	-0.55694	0.97646	0.0	0.0	0.0
18	4.39072	-0.06698	4.90337	0.0	0.0	0.0
19	0.01376	-0.02686	2.93581	0.0	0.0	0.0
20	0.0	0.0	0.0	0.02653	0.12050	0.41972
OC	-0.00797	-0.00617	-0.00369	0.99925	-0.03875	-0.00182

TABLE 2. (CONT.)

NH, R = 2.0000 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11738	-2.29295	0.0	-0.01584	-0.24598	0.20870	0.0
2	-0.14583	2.79916	0.0	0.02210	-0.02597	0.04845	0.0
3	0.00074	-0.00497	0.0	1.25796	-0.00440	-0.02292	0.0
4	0.0	0.0	1.44110	0.0	0.0	0.0	0.0
5	-0.00036	0.56268	0.0	-0.07285	0.12873	1.76957	0.0
6	0.09402	-1.05258	0.0	-0.10383	1.04446	-1.76362	0.0
7	0.00590	-0.01318	0.0	-2.22310	-0.11441	-0.15900	0.0
8	0.0	0.0	-1.49801	0.0	0.0	0.0	0.0
9	-0.00392	0.01251	0.0	-0.77189	-0.12149	0.33820	0.0
10	0.0	0.0	-0.93653	0.0	0.0	0.0	0.0
11	-0.08224	0.07414	0.0	0.04108	-0.15369	0.32113	0.0
12	-0.01561	-0.01475	0.0	2.50861	-0.03551	0.00587	0.0
13	0.0	0.0	1.79908	0.0	0.0	0.0	0.0
14	-0.00301	-0.00885	0.0	-0.03032	-0.00490	-0.01902	0.0
15	0.0	0.0	-0.05341	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	0.00270	0.02889	0.0	-0.18743	0.05804	-0.35319	0.0
18	0.00540	0.00747	0.0	0.29298	-0.04422	0.06083	0.0
19	0.00579	0.00293	0.0	0.08890	0.01984	0.00163	0.0
20	0.0	0.0	0.04604	0.0	0.0	0.0	0.0
OC	0.99982	-0.01130	-0.00874	-0.00864	0.99923	-0.03263	-0.01256

TABLE 2. (CONT.)

NH, R = 2.0000 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.45391	-0.03068	0.07389	0.0	0.01009	0.04189
2	0.0	3.10146	-0.01089	0.03245	0.0	0.01761	-0.04568
3	0.0	-0.00197	0.00979	-0.00557	0.0	-0.00871	0.04851
4	0.06804	0.0	0.0	0.0	0.01876	0.0	0.0
5	0.0	-1.10271	-0.15189	-0.08344	0.0	0.81273	0.83026
6	0.0	-10.79131	0.10808	-0.68082	0.0	-0.14956	0.03854
7	0.0	-0.03513	0.02375	0.09884	0.0	2.86220	0.60703
8	6.88929	0.0	0.0	0.0	4.02306	0.0	0.0
9	0.0	-0.02272	0.44885	-0.75094	0.0	-0.98131	-0.30037
10	-1.41465	0.0	0.0	0.0	-0.75230	0.0	0.0
11	0.0	11.21576	-0.02796	0.16300	0.0	0.08233	-0.14243
12	0.0	0.22047	0.24671	-0.25327	0.0	-1.14260	0.35843
13	-5.48371	0.0	0.0	0.0	-3.07375	0.0	0.0
14	0.0	0.10762	0.04077	-0.01389	0.0	-0.07383	1.24336
15	1.04983	0.0	0.0	0.0	-0.37290	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.29682	0.47818	1.16077	0.0	-1.05433	-1.47012
18	0.0	0.00959	0.05249	-0.06870	0.0	-0.08729	0.12985
19	0.0	-0.02627	0.04465	-0.02193	0.0	-0.07888	0.01779
20	-0.92755	0.0	0.0	0.0	-0.86797	0.0	0.0
OC	-0.00914	-0.00118	0.99335	-0.10388	-0.02784	-0.02596	-0.01107

TABLE 2. (CONT.)

NH, R = 2.0000 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11718	0.00913	0.18868	0.0	0.0	0.0
2	0.19356	0.01043	-0.82047	0.0	0.0	0.0
3	-0.12614	-0.01165	0.03171	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01489	0.13779	-0.33880
5	-2.68709	0.29839	-3.08745	0.0	0.0	0.0
6	-1.15682	-0.11651	2.67635	0.0	0.0	0.0
7	-4.75855	-8.13568	1.74507	0.0	0.0	0.0
8	0.0	0.0	0.0	1.00742	2.15454	14.95796
9	0.89020	0.25696	-0.42847	0.0	0.0	0.0
10	0.0	0.0	0.0	0.26017	-1.67289	-1.75428
11	1.78732	0.07720	-4.53147	0.0	0.0	0.0
12	2.72547	8.35899	-5.00349	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.24201	-0.80445	-13.91818
14	-0.27430	0.09290	-1.31190	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02379	-0.14335	-0.26222
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.86359	-0.55950	0.96519	0.0	0.0	0.0
18	4.42706	0.06616	4.77037	0.0	0.0	0.0
19	0.03854	-0.01008	2.92613	0.0	0.0	0.0
20	0.0	0.0	0.0	0.02920	0.11515	0.39834
OC	-0.00792	-0.00629	-0.00369	0.99924	-0.03899	-0.00183

TABLE 2. (CONT.)

NH, R = 2.0500 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11773	-2.29000	0.0	-0.01512	-0.24596	0.21053	0.0
2	-0.14702	2.79422	0.0	0.02176	-0.02507	0.04802	0.0
3	0.00096	-0.00551	0.0	1.25356	-0.00385	-0.02172	0.0
4	0.0	0.0	1.43600	0.0	0.0	0.0	0.0
5	-0.00332	0.58593	0.0	-0.08090	0.11821	1.83082	0.0
6	0.09865	-1.04239	0.0	-0.10029	1.04642	-1.75919	0.0
7	0.00736	-0.00033	0.0	-2.24865	-0.11280	-0.12832	0.0
8	0.0	0.0	-1.49675	0.0	0.0	0.0	0.0
9	-0.00436	0.01284	0.0	-0.75907	-0.12234	0.33312	0.0
10	0.0	0.0	-0.93019	0.0	0.0	0.0	0.0
11	-0.08899	0.07758	0.0	0.05336	-0.16346	0.33334	0.0
12	-0.02064	-0.00313	0.0	2.53073	-0.05050	0.03176	0.0
13	0.0	0.0	1.79656	0.0	0.0	0.0	0.0
14	-0.00452	0.00026	0.0	-0.02838	-0.01026	-0.00163	0.0
15	0.0	0.0	-0.05298	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	0.00483	0.01917	0.0	-0.20283	0.06497	-0.37157	0.0
18	0.00906	-0.02478	0.0	0.30374	-0.02898	-0.01068	0.0
19	0.00957	-0.01283	0.0	0.07399	0.02818	-0.04312	0.0
20	0.0	0.0	0.04468	0.0	0.0	0.0	0.0
OC	0.99982	-0.01132	-0.00874	-0.00865	0.99922	-0.03266	-0.01259

TABLE 2. (CONT.)

NH, R = 2.0500 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.44903	-0.02988	0.07614	0.0	0.01087	0.04119
2	0.0	3.07686	-0.01215	0.03167	0.0	0.01934	-0.04449
3	0.0	0.00039	0.00971	-0.01134	0.0	-0.00648	0.05267
4	0.06953	0.0	0.0	0.0	0.02033	0.0	0.0
5	0.0	-1.15628	-0.16629	-0.05790	0.0	0.88925	0.85627
6	0.0	-10.71626	0.11456	-0.67364	0.0	-0.14762	0.04083
7	0.0	-0.07351	0.01729	0.09828	0.0	2.92048	0.63619
8	6.91495	0.0	0.0	0.0	4.04084	0.0	0.0
9	0.0	-0.02260	0.45396	-0.73476	0.0	-0.99745	-0.31605
10	-1.42313	0.0	0.0	0.0	-0.75956	0.0	0.0
11	0.0	11.13173	-0.03069	0.19316	0.0	0.07875	-0.16331
12	0.0	0.20259	0.23991	-0.21903	0.0	-1.13703	0.34057
13	-5.51022	0.0	0.0	0.0	-3.08945	0.0	0.0
14	0.0	0.08599	0.03898	0.00668	0.0	-0.05873	1.23715
15	1.04161	0.0	0.0	0.0	-0.37706	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.28495	0.48345	1.13807	0.0	-1.07432	-1.46670
18	0.0	0.09497	0.06461	-0.11870	0.0	-0.15835	0.12377
19	0.0	-0.00520	0.05003	-0.05228	0.0	-0.12256	-0.00159
20	-0.92133	0.0	0.0	0.0	-0.86982	0.0	0.0
OC	-0.00922	-0.00119	0.99279	-0.10928	-0.02778	-0.02527	-0.01126

TABLE 2. (CONT.)

NH, R = 2.0500 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11767	0.00684	0.19375	0.0	0.0	0.0
2	0.19577	0.00874	-0.80711	0.0	0.0	0.0
3	-0.12639	-0.01154	0.01223	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01621	0.13542	-0.33416
5	-2.76881	0.20132	-3.12398	0.0	0.0	0.0
6	-1.16184	-0.11704	2.68296	0.0	0.0	0.0
7	-4.90782	-8.23678	1.65975	0.0	0.0	0.0
8	0.0	0.0	0.0	1.00721	2.16420	14.99152
9	0.91437	0.26927	-0.34674	0.0	0.0	0.0
10	0.0	0.0	0.0	0.25938	-1.67273	-1.76793
11	1.84613	0.06225	-4.36820	0.0	0.0	0.0
12	2.84429	8.36491	-4.87329	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.24272	-0.81093	-13.93117
14	-0.27541	0.06124	-1.26800	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02271	-0.14128	-0.25035
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.85494	-0.55908	0.94878	0.0	0.0	0.0
18	4.46360	0.21834	4.61109	0.0	0.0	0.0
19	0.06768	0.01159	2.91037	0.0	0.0	0.0
20	0.0	0.0	0.0	0.03223	0.10956	0.37351
OC	-0.00786	-0.00644	-0.00368	0.99922	-0.03940	-0.00184

TABLE 2. (CONT.)

NH, R = 2.1000 BOHRS

AO	K SHELL 1 SIGMA 1	K SHELL 2 SIGMA 2	K SHELL 3 PI 1	K SHELL 4 SIGMA 3	LONE PAIR 1 SIGMA 1	LONE PAIR 2 SIGMA 2	LONE PAIR 3 DELTA 1
1	1.11850	-2.28801	0.0	-0.01419	-0.24556	0.21140	0.0
2	-0.14871	2.79201	0.0	0.02117	-0.02590	0.05039	0.0
3	0.00085	-0.00579	0.0	1.25113	-0.00371	-0.02000	0.0
4	0.0	0.0	1.43376	0.0	0.0	0.0	0.0
5	-0.00591	0.61424	0.0	-0.09083	0.10824	1.90447	0.0
6	0.10384	-1.03618	0.0	-0.09612	1.05207	-1.76063	0.0
7	0.01019	0.01757	0.0	-2.27942	-0.10984	-0.08703	0.0
8	0.0	0.0	-1.50439	0.0	0.0	0.0	0.0
9	-0.00425	0.01191	0.0	-0.74816	-0.12218	0.32470	0.0
10	0.0	0.0	-0.92586	0.0	0.0	0.0	0.0
11	-0.09541	0.08120	0.0	0.06536	-0.17494	0.34622	0.0
12	-0.02656	0.00608	0.0	2.55741	-0.06618	0.05458	0.0
13	0.0	0.0	1.80241	0.0	0.0	0.0	0.0
14	-0.00580	0.00959	0.0	-0.02681	-0.01505	0.01681	0.0
15	0.0	0.0	-0.05266	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	1.00000
17	0.00734	0.00955	0.0	-0.21734	0.07195	-0.39217	0.0
18	0.01101	-0.06024	0.0	0.31668	-0.01602	-0.08897	0.0
19	0.01280	-0.03088	0.0	0.05937	0.03592	-0.09395	0.0
20	0.0	0.0	0.04388	0.0	0.0	0.0	0.0
OC	0.99982	-0.01134	-0.00875	-0.00865	0.99922	-0.03263	-0.01262

TABLE 2. (CONT.)

NH, R = 2.1000 BOHRS

AO	LONE PAIR 4 PI 1	LONE PAIR 5 SIGMA 3	BONDING 1 SIGMA 1	BONDING 2 SIGMA 2	BONDING 3 PI 1	BONDING 4 SIGMA 3	BONDING 5 SIGMA 4
1	0.0	-1.44757	-0.02930	0.07748	0.0	0.01132	0.04044
2	0.0	3.06427	-0.01328	0.03265	0.0	0.02184	-0.04322
3	0.0	0.00262	0.00881	-0.01573	0.0	-0.00288	0.05730
4	0.07133	0.0	0.0	0.0	0.02246	0.0	0.0
5	0.0	-1.22187	-0.18309	-0.03085	0.0	0.98041	0.88866
6	0.0	-10.67623	0.11967	-0.67162	0.0	-0.14686	0.04480
7	0.0	-0.12317	0.01049	0.09923	0.0	2.99397	0.67253
8	6.94577	0.0	0.0	0.0	4.05892	0.0	0.0
9	0.0	-0.01973	0.46026	-0.72096	0.0	-1.01845	-0.33319
10	-1.43269	0.0	0.0	0.0	-0.76792	0.0	0.0
11	0.0	11.07890	-0.03113	0.22483	0.0	0.07088	-0.18818
12	0.0	0.18686	0.23213	-0.18572	0.0	-1.13787	0.31850
13	-5.54132	0.0	0.0	0.0	-3.10446	0.0	0.0
14	0.0	0.06221	0.03727	0.02721	0.0	-0.04244	1.23105
15	1.03324	0.0	0.0	0.0	-0.38118	0.0	0.0
16	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	0.0	-0.27096	0.48969	1.11610	0.0	-1.09873	-1.46507
18	0.0	0.19054	0.07722	-0.16733	0.0	-0.23546	0.11565
19	0.0	0.02276	0.05666	-0.08293	0.0	-0.17250	-0.02324
20	-0.91547	0.0	0.0	0.0	-0.87270	0.0	0.0
OC	-0.00932	-0.00120	0.99221	-0.11458	-0.02771	-0.02452	-0.01145

TABLE 2. (CONT.)

NH, R = 2.1000 BOHRS

AO	BONDING 6 SIGMA 5	BONDING 7 SIGMA 6	BONDING 8 SIGMA 7	TRIPLET 1 PI 1	TRIPLET 2 PI 2	TRIPLET 3 PI 3
1	-0.11899	0.00417	0.19806	0.0	0.0	0.0
2	0.20018	0.00785	-0.79464	0.0	0.0	0.0
3	-0.12675	-0.01079	-0.00721	0.0	0.0	0.0
4	0.0	0.0	0.0	0.01713	0.13491	-0.33095
5	-2.86439	0.08650	-3.16746	0.0	0.0	0.0
6	-1.17558	-0.11988	2.68951	0.0	0.0	0.0
7	-5.07857	-8.36679	1.57191	0.0	0.0	0.0
8	0.0	0.0	0.0	1.00287	2.17446	15.03946
9	0.94197	0.28607	-0.26458	0.0	0.0	0.0
10	0.0	0.0	0.0	0.25981	-1.67441	-1.78239
11	1.92049	0.05564	-4.19995	0.0	0.0	0.0
12	2.98157	8.38839	-4.73655	0.0	0.0	0.0
13	0.0	0.0	0.0	-0.23981	-0.81684	-13.95638
14	-0.27556	0.02750	-1.22001	0.0	0.0	0.0
15	0.0	0.0	0.0	0.02206	-0.13896	-0.23831
16	0.0	0.0	0.0	0.0	0.0	0.0
17	-1.84225	-0.55707	0.93882	0.0	0.0	0.0
18	4.50409	0.38474	4.44547	0.0	0.0	0.0
19	0.10162	0.03955	2.89623	0.0	0.0	0.0
20	0.0	0.0	0.0	0.03461	0.10370	0.34667
OC	-0.00780	-0.00661	-0.00367	0.99921	-0.03966	-0.00186

TABLE 3. D MATRIX AND OCCUPATION COEFFICIENTS FOR NITROGEN

	K	K	K	L	L
AO	1 S 1	2 S 2	3 P 1	1 S 1	2 D 1
1	1.20416	-2.74018	0.0	-0.21523	0.0
2	-0.20030	3.31292	0.0	-0.02030	0.0
3	0.0	0.0	-1.46320	0.0	0.0
5	0.00164	-0.06637	0.0	0.09135	0.0
6	-0.12799	-1.95653	0.0	1.08466	0.0
7	0.0	0.0	-0.21587	0.0	0.0
9	0.0	0.0	4.14811	0.0	0.0
11	0.07832	1.54725	0.0	-0.10646	0.0
12	0.0	0.0	-3.48826	0.0	0.0
14	0.0	0.0	0.0	0.0	1.00000
OC	0.99979	-0.01156	-0.00980	0.99946	-0.01326

	L	L	L	L	Q
AO	3 P 1	4 S 2	5 P 2	6 S 3	1 P 1
1	0.0	-1.69779	0.0	-0.55715	0.0
2	0.0	3.62446	0.0	1.61998	0.0
3	0.19557	0.0	-1.25075	0.0	0.00996
5	0.0	1.15624	0.0	-0.94765	0.0
6	0.0	-14.61596	0.0	-9.48276	0.0
7	1.61414	0.0	-0.33947	0.0	0.19905
9	-1.47059	0.0	13.22597	0.0	1.29766
11	0.0	12.97813	0.0	9.82230	0.0
12	0.02757	0.0	-12.69782	0.0	-0.46889
14	0.0	0.0	0.0	0.0	0.0
OC	-0.00802	-0.00171	-0.00169	-0.00158	1.00000

TABLE 4. ENERGY DECOMPOSITION OF NH AS A FUNCTION OF INTERNUCLEAR DISTANCE

R	V_{NH}	V_N	V_H	V_{12}	T	E	$\partial E/\partial R$
SEPARATED PAIR WAVE FUNCTION (ENERGIES IN HARTREES)							
1.8000	3.8889	-132.6091	-4.9716	23.3267	55.3450	-55.02019	-0.1804
1.9000	3.6842	-132.2051	-4.7414	23.0895	55.1409	-55.03178	-0.0574
1.9230	3.6401	-132.1306	-4.6901	23.0428	55.1050	-55.03281	-0.0375
1.9614	3.5689	-131.9978	-4.6085	22.9643	55.0396	-55.03352	-0.0031
2.0000	3.5000	-131.8668	-4.5294	22.8916	54.9717	-55.03293	0.0306
2.0500	3.4146	-131.6911	-4.4299	22.7824	54.8934	-55.03047	0.0669
2.1000	3.3333	-131.5561	-4.3341	22.7027	54.8277	-55.02643	0.0946
PRINCIPAL NATURAL ORBITAL WAVE FUNCTION (ENERGIES IN HARTREES)							
1.8000	3.8889	-132.6166	-4.9702	23.4441	55.2917	-54.96207	-0.1831
1.9000	3.6842	-132.2102	-4.7392	23.2096	55.0836	-54.97200	-0.0587
1.9230	3.6401	-132.1354	-4.6878	23.1635	55.0468	-54.97269	-0.0386
1.9614	3.5689	-132.0017	-4.6059	23.0861	54.9798	-54.97281	-0.0036
2.0000	3.5000	-131.8698	-4.5265	23.0143	54.9104	-54.97166	0.0306
2.0500	3.4146	-131.6929	-4.4266	22.9064	54.8300	-54.96850	0.0676
2.1000	3.3333	-131.5571	-4.3305	22.8280	54.7624	-54.96381	0.0959
CORRELATION ENERGY (ENERGIES IN EV)							
1.8000		0.2041	-0.0397	-3.1941	1.4484	-1.5814	
1.9000		0.1401	-0.0593	-3.2665	1.5591	-1.6266	
1.9230		0.1295	-0.0639	-3.2842	1.5828	-1.6358	
1.9614		0.1067	-0.0716	-3.3120	1.6250	-1.6519	
2.0000		0.0808	-0.0789	-3.3381	1.6690	-1.6671	
2.0500		0.0501	-0.0887	-3.3726	1.7251	-1.6862	
2.1000		0.0258	-0.0980	-3.4083	1.7765	-1.7039	

TABLE 5. COMPARISON WITH PREVIOUS INVESTIGATIONS

E(HARTREE)	R(BOHR)	YEAR	REFERENCE	DESCRIPTION[a]
...	1.908	1956	HIGUCHI (59)	APPROXIMATE LCAO-MO-SCF HARTREE-FOCK AO BASIS SET
-53.8215	2.0	1963	REEVES (64)	GENERAL CI (63 CONFIGURATIONS) EXTENDED GTF BASIS SET
-54.5409	2.0	1965	REEVES AND FLETCHER (65)	GENERAL CI (56 CONFIGURATIONS) EXTENDED GTF BASIS SET
-54.55581	1.9614	1965	LOUNSBURY (67)	ONE-CENTER LCAO-MO-SCF MINIMAL STAO BASIS SET
-54.68909	1.9735	1963	BISHOP AND HOYLAND (66)	ONE-CENTER VB (1 CONFIGURATION) STAO BASIS SET WITH NON-INTEGRAL QUANTUM NUMBERS
-54.7827	1.9614	1958	BOYD (61)	LCAO-MO-SCF MINIMAL STAO BASIS SET

[a] THE ABBREVIATIONS USED ARE AS FOLLOWS...
LCAO-MO-SCF = LINEAR COMBINATION OF ATOMIC ORBITALS - MOLECULAR ORBITAL - SELF CONSISTENT FIELD METHOD
CI = CONFIGURATION INTERACTION
VB = VALENCE BOND METHOD
GTF = GAUSSIAN-TYPE FUNCTIONS
STAO = SLATER-TYPE ATOMIC ORBITALS

TABLE 5. (CONT.)

E(HARTREE)	R(BOHR)	YEAR	REFERENCE	DESCRIPTION
-54.785	1.9614	1958	KRAUSS (60)	LCAO-MO-SCF MINIMAL STAO BASIS SET
-54.805	1.9614	1958	HURLEY (63)	VB-CI (5 CONFIGURATIONS) MINIMAL STAO BASIS SET
-54.810	1.9614	1958	KRAUSS AND WEHNER (62)	LCAO-MO-SCF-CI (9 CONFIGURATIONS) MINIMAL STAO BASIS SET
-54.90638	1.9	1965	JOSHI (68)	ONE-CENTER LCAO-MO-SCF EXTENDED STAO BASIS SET
-54.97281	1.9614	1968	THIS WORK	PRINCIPAL NATURAL ORBITAL - SINGLE DETERMINANT OF THE SEPARATED PAIR APPROXIMATION EXTENDED STAO BASIS SET
-54.97838	1.923	1967	CADE AND HUO (1)	LCAO-MO-SCF EXTENDED STAO BASIS SET
-55.03352	1.9614	1968	THIS WORK	SEPARATED PAIR - NATURAL ORBITAL EXTENDED STAO BASIS SET

TABLE 6. GEMINAL ENERGY MATRICES

NH, R = 1.8000

PNO MATRIX

	K	L	B	T
K	-45.835451			
L	3.784619	-10.804800		
B	3.114357	2.097825	-9.554925	
T	3.689466	2.387884	2.229892	-9.959823

CORR MATRIX

	K	L	B	T
K	-0.024126			
L	-0.001687	-0.002214		
B	0.000616	-0.000607	-0.024758	
T	0.000448	-0.000629	-0.000715	-0.004454

NH, R = 1.9000

PNO MATRIX

	K	L	B	T
K	-45.777345			
L	3.752242	-10.715599		
B	3.065353	2.061451	-9.385478	
T	3.664772	2.365469	2.193017	-9.880096

CORR MATRIX

	K	L	B	T
K	-0.024156			
L	-0.001726	-0.002171		
B	0.001069	-0.000620	-0.026629	
T	0.000475	-0.000645	-0.000807	-0.004566

TABLE 6. (CONT.)

NH, R = 1.9230

PNO MATRIX

	K	L	B	T
K	-45.764578			
L	3.746647	-10.698150		
B	3.055536	2.054294	-9.349793	
T	3.659789	2.361335	2.185497	-9.863417

CORR MATRIX

	K	L	B	T
K	-0.024159			
L	-0.001733	-0.002162		
B	0.001147	-0.000639	-0.026969	
T	0.000483	-0.000646	-0.000848	-0.004591

NH, R = 1.9614

PNO MATRIX

	K	L	B	T
K	-45.743882			
L	3.735399	-10.665887		
B	3.039359	2.041575	-9.290578	
T	3.653257	2.354097	2.173268	-9.838302

CORR MATRIX

	K	L	B	T
K	-0.024169			
L	-0.001739	-0.002155		
B	0.001288	-0.000664	-0.027567	
T	0.000486	-0.000650	-0.000917	-0.004617

TABLE 6. (CONT.)

NH, R = 2.0000

PNO MATRIX

	K	L	B	T
K	-45.723962			
L	3.726333	-10.637871		
B	3.024169	2.030267	-9.233193	
T	3.646089	2.347786	2.161516	-9.812799

CORR MATRIX

	K	L	B	T
K	-0.024177			
L	-0.001740	-0.002151		
B	0.001427	-0.000694	-0.028134	
T	0.000497	-0.000648	-0.000994	-0.004654

NH, R = 2.0500

PNO MATRIX

	K	L	B	T
K	-45.699167			
L	3.711144	-10.595374		
B	3.003496	2.013853	-9.157843	
T	3.633048	2.336684	2.144490	-9.773467

CORR MATRIX

	K	L	B	T
K	-0.024195			
L	-0.001739	-0.002146		
B	0.001594	-0.000741	-0.028792	
T	0.000517	-0.000643	-0.001105	-0.004718

TABLE 6. (CONT.)

NH, R = 2.1000

PNO MATRIX

	K	L	B	T
K	-45.675284			
L	3.700843	-10.561372		
B	2.987248	2.000687	-9.091361	
T	3.626511	2.329884	2.131402	-9.745705

CORR MATRIX

	K	L	B	T
K	-0.024208			
L	-0.001736	-0.002146		
B	0.001682	-0.000825	-0.029254	
T	0.000523	-0.000640	-0.001265	-0.004751

NITROGEN ATOM

PNO MATRIX

	K	L	B	T
K	-44.701701			
L	3.708872	-9.915854		
B	1.868965	1.197551	-4.827409	
T	3.737930	2.395102	1.194688	-9.057473

CORR MATRIX

	K	L	B	T
K	-0.031333			
L	-0.000679	-0.004676		
B	-0.000022	-0.000060	0.0	
T	-0.000045	-0.000119	0.0	0.0

TABLE 7. SECONDARY NATURAL ORBITAL CORRELATION ENERGY CONTRIBUTIONS

NH, R = 1.9614 BOHRS

NATURAL ORBITAL	$\Delta E(\mu i,\mu 0)$	$\Delta E(\mu i)$	$\Delta I(\mu i)$	$\Delta(\mu i)$	OC
K SHELL 2 SIGMA 2	-0.00980	-0.00972	-0.00008	-0.00980	-0.01128
K SHELL 3 PI 1	-0.00489	-0.00485	-0.00003	-0.00488	-0.00873
K SHELL 4 SIGMA 3	-0.00479	-0.00474	-0.00005	-0.00479	-0.00863
LONE PAIR 2 SIGMA 2	-0.00250	0.00010	-0.00261	-0.00251	-0.03259
LONE PAIR 3 DELTA 1	-0.00079	-0.00076	-0.00003	-0.00079	-0.01254
LONE PAIR 4 PI 1	-0.00045	-0.00034	-0.00011	-0.00045	-0.00907
LONE PAIR 5 SIGMA 3	-0.00005	-0.00005	0.0	-0.00005	-0.00117
BONDING 2 SIGMA 2	-0.01883	-0.02383	0.00472	-0.01911	-0.09961
BONDING 3 PI 1	-0.00234	-0.00099	-0.00137	-0.00236	-0.02787
BONDING 4 SIGMA 3	-0.00180	-0.00045	-0.00137	-0.00182	-0.02652
BONDING 5 SIGMA 4	-0.00074	-0.00079	0.00005	-0.00074	-0.01091
BONDING 6 SIGMA 5	-0.00045	-0.00026	-0.00018	-0.00044	-0.00797
BONDING 7 SIGMA 6	-0.00017	-0.00009	-0.00008	-0.00017	-0.00617
BONDING 8 SIGMA 7	-0.00017	-0.00016	-0.00001	-0.00017	-0.00369
TRIPLET 2 PI 2	-0.00409	-0.00461	0.00052	-0.00409	-0.03875
TRIPLET 3 PI 3	-0.00002	-0.00001	-0.00001	-0.00002	-0.00182
TOTAL GAIN		-0.06311	-0.00167	-0.06478	

TABLE 7. (CONT.)

NITROGEN ATOM

NATURAL ORBITAL	$\Delta E(\mu i,\mu 0)$	$\Delta E(\mu i)$	$\Delta I(\mu i)$	$\Delta(\mu i)$	OC
K 2 S 2	-0.01160	-0.01154	-0.00006	-0.01160	-0.01156
K 3 P 1	-0.00661	-0.00660	-0.00002	-0.00662	-0.00980
L 2 D 1	-0.00088	-0.00083	-0.00005	-0.00088	-0.01326
L 3 P 1	-0.00023	-0.00004	-0.00019	-0.00023	-0.00802
L 4 S 2	-0.00013	-0.00014	0.00001	-0.00013	-0.00171
L 5 S 3	-0.00007	-0.00008	0.00001	-0.00007	-0.00169
L 6 S 4	-0.00003	-0.00002	0.0	-0.00002	-0.00158
TOTAL GAIN		-0.03585	-0.00092	-0.03677	

TABLE 8. PAIR CORRELATION ENERGIES FOR EACH GEMINAL OF NH AT R=1.9614 BOHRS

PAIR CORRELATION OF THE K SHELL GEMINAL

NATURAL ORBITAL	ΔE(μi,μ0)	ΔE(μi)	ΔI(μi)	Δ(μi)	OC
K SHELL 2 SIGMA 2	-0.00979	-0.00971	-0.00008	-0.00979	-0.01126
K SHELL 3 PI 1	-0.00488	-0.00485	-0.00003	-0.00488	-0.00873
K SHELL 4 SIGMA 3	-0.00479	-0.00474	-0.00005	-0.00479	-0.00862
LONE PAIR 2 SIGMA 2	-0.00005	-0.00005	-0.0	-0.00005	-0.00124
LONE PAIR 3 DELTA 1	-0.0	-0.0	-0.0	-0.0	-0.00008
LONE PAIR 4 PI 1	-0.0	-0.0	-0.0	-0.0	-0.00005
LONE PAIR 5 SIGMA 3	-0.00021	-0.00020	-0.0	-0.00020	-0.00175
BONDING 2 SIGMA 2	-0.00004	-0.00004	-0.0	-0.00004	-0.00108
BONDING 3 PI 1	-0.0	-0.0	-0.0	-0.0	-0.00001
BONDING 4 SIGMA 3	-0.00001	-0.00001	-0.0	-0.00001	-0.00045
BONDING 5 SIGMA 4	-0.0	-0.0	-0.0	-0.0	-0.00006
BONDING 6 SIGMA 5	-0.0	-0.0	-0.0	-0.0	-0.00006
BONDING 7 SIGMA 6	-0.00002	-0.00002	-0.0	-0.00002	-0.00071
BONDING 8 SIGMA 7	-0.0	-0.0	-0.0	-0.0	-0.00011
TRIPLET 2 PI 2	-0.00008	-0.00007	-0.0	-0.00007	-0.00145
TRIPLET 3 PI 3	-0.0	-0.0	-0.0	-0.0	-0.00013
TOTAL GAIN		-0.02460	-0.00025	-0.02484	

TABLE 8. (CONT.)

PAIR CORRELATION OF THE LONE PAIR GEMINAL

NATURAL ORBITAL	ΔE(μi,μ0)	ΔE(μi)	ΔI(μi)	Δ(μi)	OC
K SHELL 2 SIGMA 2	-0.00013	-0.00015	0.00002	-0.00013	-0.00149
K SHELL 3 PI 1	-0.00002	-0.00002	0.0	-0.00002	-0.00059
K SHELL 4 SIGMA 3	-0.00002	-0.00002	0.0	-0.00002	-0.00064
LONE PAIR 2 SIGMA 2	-0.00242	0.00002	-0.00245	-0.00243	-0.03158
LONE PAIR 3 DELTA 1	-0.00077	-0.00075	-0.00003	-0.00078	-0.01224
LONE PAIR 4 PI 1	-0.00043	-0.00033	-0.00010	-0.00043	-0.00868
LONE PAIR 5 SIGMA 3	-0.00005	-0.00005	0.0	-0.00005	-0.00110
BONDING 2 SIGMA 2	-0.00072	-0.00070	-0.00003	-0.00073	-0.01578
BONDING 3 PI 1	-0.00014	-0.00007	-0.00008	-0.00015	-0.00587
BONDING 4 SIGMA 3	-0.00012	-0.00002	-0.00010	-0.00012	-0.00586
BONDING 5 SIGMA 4	-0.00066	-0.00059	-0.00007	-0.00066	-0.01061
BONDING 6 SIGMA 5	-0.0	-0.0	-0.0	-0.0	-0.00017
BONDING 7 SIGMA 6	-0.00007	-0.00002	-0.00005	-0.00007	-0.00408
BONDING 8 SIGMA 7	-0.00001	-0.00001	-0.0	-0.00001	-0.00092
TRIPLET 2 PI 2	-0.00033	-0.00035	0.00003	-0.00032	-0.00896
TRIPLET 3 PI 3	-0.00003	-0.00002	-0.00001	-0.00003	-0.00204
TOTAL GAIN		-0.00461	-0.00305	-0.00766	

TABLE 8. (CONT.)

PAIR CORRELATION OF THE BONDING GEMINAL

NATURAL ORBITAL	ΔE(μi,μ0)	ΔE(μi)	ΔI(μi)	Δ(μi)	OC
K SHELL 2 SIGMA 2	-0.0	-0.0	0.0	-0.0	-0.00019
K SHELL 3 PI 1	-0.0	-0.0	0.0	-0.0	-0.00010
K SHELL 4 SIGMA 3	-0.00003	-0.00003	0.0	-0.00003	-0.00075
LONE PAIR 2 SIGMA 2	-0.00013	-0.00007	-0.00006	-0.00013	-0.00671
LONE PAIR 3 DELTA 1	-0.00002	-0.00002	0.0	-0.00002	-0.00142
LONE PAIR 4 PI 1	-0.00027	-0.00025	-0.00001	-0.00026	-0.00651
LONE PAIR 5 SIGMA 3	-0.00001	-0.00001	0.0	-0.00001	-0.00032
BONDING 2 SIGMA 2	-0.01872	-0.02367	0.00468	-0.01899	-0.09902
BONDING 3 PI 1	-0.00231	-0.00099	-0.00134	-0.00233	-0.02756
BONDING 4 SIGMA 3	-0.00178	-0.00046	-0.00134	-0.00180	-0.02625
BONDING 5 SIGMA 4	-0.00074	-0.00079	0.00005	-0.00074	-0.01082
BONDING 6 SIGMA 5	-0.00045	-0.00026	-0.00018	-0.00044	-0.00793
BONDING 7 SIGMA 6	-0.00016	-0.00009	-0.00007	-0.00016	-0.00604
BONDING 8 SIGMA 7	-0.00017	-0.00016	-0.00001	-0.00017	-0.00366
TRIPLET 2 PI 2	-0.00005	-0.00006	0.00001	-0.00005	-0.00297
TRIPLET 3 PI 3	-0.00001	-0.0	-0.0	-0.0	-0.00086
TOTAL GAIN		-0.02819	0.00037	-0.02782	

TABLE 8. (CONT.)

PAIR CORRELATION OF THE TRIPLET GEMINAL

NATURAL ORBITAL	ΔE(μi,μ0)	ΔE(μi)	ΔI(μi)	Δ(μi)	OC
K SHELL 3 PI 1	-0.00003	-0.00004	0.00001	-0.00003	-0.00087
LONE PAIR 3 DELTA 1	-0.00387	-0.00373	-0.00014	-0.00387	-0.03080
LONE PAIR 4 PI 1	-0.00025	-0.00018	-0.00008	-0.00026	-0.00762
BONDING 3 PI 1	-0.00035	-0.00005	-0.00030	-0.00035	-0.01134
TRIPLET 2 PI 2	-0.00403	-0.00454	0.00050	-0.00404	-0.03821
TRIPLET 3 PI 3	-0.00002	-0.00001	-0.00001	-0.00002	-0.00185
TOTAL GAIN		-0.00854	-0.00003	-0.00857	

TABLE 9. BINDING ENERGIES OF NH FROM VARIOUS WAVE FUNCTIONS

NH MOLECULAR BINDING ENERGY

R	SP	K+B	B	PNO
1.7000	-0.05904	-0.04687	-0.05401	-0.03955
1.8000	-0.08393	-0.07216	-0.07928	-0.06274
1.9000	-0.09551	-0.08420	-0.09128	-0.07267
1.9230	-0.09655	-0.08534	-0.09242	-0.07336
1.9614	-0.09725	-0.08623	-0.09330	-0.07348
2.0000	-0.09667	-0.08582	-0.09288	-0.07233
2.0500	-0.09421	-0.08357	-0.09062	-0.06917
2.1000	-0.09017	-0.07977	-0.08680	-0.06448
2.2000	-0.07804	-0.06805	-0.07506	-0.05115

N ATOM TOTAL ENERGY

SP	K+B	B	PNO
-54.43626	-54.43077	-54.39933	-54.39933

TABLE 10. COMPARISON OF SPECTROSCOPIC RESULTS FOR NH

SPECTROSCOPIC CONSTANTS	SP	PNO	EXPTL	SCF[a]
E_e(HARTREE)	-55.03365	-54.97293	-55.252[a]	-54.97838
R_e(BOHR)	1.9619	1.9449	1.9614[a]	1.923
B_e(1/CM)	16.625	16.917	16.668[a]	17.319
α_e(1/CM)	0.466	0.345	0.646[b]	0.5715
k_e(10^{-5}DYNES/CM)	13.359	13.935	5.410[b]	7.003
ω_e(1/CM)	4909.6	5014.3	3125.6[b]	3556
$\omega_e x_e$(1/CM)	78.3	98.2	78.5[c]	66.78

COEFFICIENTS IN THE POLYNOMIAL EXPANSION FOR THE ANALYSIS OF DUNHAM

	SP	PNO	EXPTL
a_0(1/CM)	362463.9	371564.2	146528.9
a_1	-2.053571	-2.008316	-2.211289
a_2	2.130814	1.173053	2.972499

[a] REFERENCE (1)
[b] REFERENCE (22)
[c] REFERENCE (39)

TABLE 11. DECOMPOSITION OF ONE-ELECTRON EXPECTATION VALUES

NH, R=1.9614

		K SHELL	LONE PAIR	BONDING	TRIPLET	TOTAL	%
$\langle r_N \rangle$	PNO	0.057305	0.337982	0.428235	0.361207	1.184730	
	CORR	0.000023	0.000363	0.000567	0.000091	0.001045	
	TOTAL	0.057329	0.338345	0.428803	0.361298	1.185775	0.088
$\langle r_H \rangle$	PNO	0.493539	0.656525	0.410371	0.601263	2.161698	
	CORR	0.000008	0.000238	-0.000099	0.000089	0.000236	
	TOTAL	0.493547	0.656763	0.410273	0.601352	2.161934	0.011
$\langle r_N{}^2 \rangle$	PNO	0.017871	0.559606	0.898016	0.667530	2.143024	
	CORR	0.000056	0.001780	0.003361	0.000550	0.005747	
	TOTAL	0.017928	0.561387	0.901377	0.668080	2.148771	0.267
$\langle r_H{}^2 \rangle$	PNO	0.980272	1.878250	0.921254	1.575166	5.354941	
	CORR	0.000055	0.001774	-0.000126	0.000600	0.002302	
	TOTAL	0.980326	1.880024	0.921128	1.575766	5.357244	0.043
$\langle r_N{}^{-1} \rangle$	PNO	1.659295	0.269655	0.193886	0.234338	2.357174	
	CORR	-0.000126	-0.000133	0.000147	0.000042	-0.000070	
	TOTAL	1.659169	0.269523	0.194033	0.234380	2.357104	-0.003

TABLE 11. (CONT.)

NH, R=1.9614

		K SHELL	LONE PAIR	BONDING	TRIPLET	TOTAL	%
$\langle r_H^{-1} \rangle$	PNO	0.127419	0.106784	0.227984	0.113546	0.575733	
	CORR	-0.000000	-0.000019	0.000356	-0.000009	0.000328	
	TOTAL	0.127418	0.106765	0.228341	0.113537	0.576061	0.057
$\langle \cos\ \theta_N \rangle$	PNO	-0.000224	-0.061968	0.125324	0.008026	0.071158	
	CORR	0.000000	0.000032	0.000180	-0.000003	0.000209	
	TOTAL	-0.000224	-0.061936	0.125504	0.008023	0.071367	0.293
$\langle \cos\ \theta_H \rangle$	PNO	0.248459	0.218614	0.123333	0.197963	0.788369	
	CORR	-0.000003	-0.000068	-0.000687	-0.000018	-0.000777	
	TOTAL	0.248455	0.218546	0.122646	0.197945	0.787592	-0.099
$\langle z_N \rangle$	PNO	-0.000160	-0.090974	0.239251	0.013801	0.161918	
	CORR	0.000000	0.000002	0.000889	-0.000013	0.000878	
	TOTAL	-0.000160	-0.090972	0.240140	0.013788	0.162796	0.539
$\langle z_H \rangle$	PNO	0.490510	0.581324	0.251099	0.476549	1.799482	
	CORR	-0.000000	-0.000002	-0.000889	0.000013	-0.000878	
	TOTAL	0.490510	0.581322	0.250210	0.476562	1.798604	-0.049

TABLE 11. (CONT.)

NH, R=1.9614

		K SHELL	LONE PAIR	BONDING	TRIPLET	TOTAL	%
$<z_N^2>$	PNO	0.005963	0.200792	0.633969	0.139241	0.979966	
	CORR	0.000022	0.000508	0.003021	0.000157	0.003707	
	TOTAL	0.005985	0.201300	0.636990	0.139397	0.983673	0.377
$<z_H^2>$	PNO	0.968363	1.519436	0.657207	1.046876	4.191883	
	CORR	0.000021	0.000501	-0.000467	0.000207	0.000262	
	TOTAL	0.968384	1.519937	0.656741	1.047084	4.192145	0.006
$<\xi>$	PNO	0.280842	0.507039	0.427555	0.490706	1.706143	
	CORR	0.000016	0.000306	0.000239	0.000092	0.000653	
	TOTAL	0.280858	0.507346	0.427794	0.490798	1.706796	0.038
$<\eta>$	PNO	-0.222409	-0.162406	0.009108	-0.122390	-0.498097	
	CORR	0.000008	0.000064	0.000340	0.000001	0.000413	
	TOTAL	-0.222401	-0.162342	0.009447	-0.122389	-0.497685	-0.083
$<\xi^2>$	PNO	0.318592	1.136214	0.850367	1.078235	3.383408	
	CORR	0.000066	0.001886	0.001314	0.000583	0.003848	
	TOTAL	0.318658	1.138100	0.851681	1.078817	3.387257	0.114

TABLE 11. (CONT.)

NH, R=1.9614

		K SHELL	LONE PAIR	BONDING	TRIPLET	TOTAL	%
$\langle\eta^2\rangle$	PNO	0.200316	0.131162	0.095423	0.087684	0.514585	
	CORR	-0.000009	-0.000038	0.000368	0.000015	0.000336	
	TOTAL	0.200308	0.131124	0.095791	0.087699	0.514922	0.065
$\langle r_N \cdot r_H\rangle$	PNO	0.113754	0.966631	0.726085	0.952685	2.759155	
	CORR	0.000072	0.001851	0.000910	0.000546	0.003378	
	TOTAL	0.113826	0.968482	0.726995	0.953231	2.762533	0.122
$\langle x^2+y^2\rangle$	PNO	0.011908	0.358814	0.264046	0.528290	1.163059	
	CORR	0.000034	0.001273	0.000341	0.000393	0.002040	
	TOTAL	0.011942	0.360087	0.264387	0.528682	1.165099	0.175
d	PNO	0.001280	0.727789	0.047390	-0.110405	0.666054	
	CORR	-0.000003	-0.000014	-0.007112	0.000103	-0.007025	
	TOTAL	0.001277	0.727775	0.040278	-0.110302	0.659029	-1.066
Q	PNO	-0.001184	-0.934718	-0.375544	2.088354	0.776908	
	CORR	-0.000083	0.000790	-0.039888	0.000746	-0.038435	
	TOTAL	-0.001267	-0.933928	-0.415432	2.089100	0.738473	-5.205

TABLE 12. ONE-ELECTRON PROPERTIES AS FUNCTIONS OF INTERNUCLEAR DISTANCE

		$\langle r_N \rangle$			$\langle r_H \rangle$	
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	1.157355	0.000849	1.158203	2.024953	0.000371	2.025324
1.9000	1.174861	0.000956	1.175817	2.109639	0.000290	2.109929
1.9230	1.178518	0.000989	1.179507	2.129153	0.000271	2.129424
1.9614	1.184730	0.001045	1.185775	2.161698	0.000236	2.161934
2.0000	1.190628	0.001106	1.191733	2.194327	0.000197	2.194525
2.0500	1.199457	0.001195	1.200653	2.237534	0.000150	2.237684
2.1000	1.206534	0.001305	1.207839	2.280071	0.000103	2.280174

		$\langle r_N^2 \rangle$			$\langle r_H^2 \rangle$	
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	2.028574	0.004519	2.033093	4.747971	0.002818	4.750788
1.9000	2.100594	0.005201	2.105795	5.120020	0.002521	5.122541
1.9230	2.116345	0.005398	2.121742	5.207259	0.002444	5.209703
1.9614	2.143024	0.005747	2.148771	5.354941	0.002302	5.357244
2.0000	2.168965	0.006124	2.175089	5.504861	0.002135	5.506995
2.0500	2.207668	0.006689	2.214356	5.708081	0.001929	5.710010
2.1000	2.240596	0.007361	2.247956	5.909912	0.001719	5.911631

TABLE 12. (CONT.)

	$\langle r_N^{-1} \rangle$			$\langle r_H^{-1} \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	2.368154	-0.000134	2.368020	0.621271	0.000183	0.621454
1.9000	2.360897	-0.000093	2.360805	0.592397	0.000273	0.592670
1.9230	2.359560	-0.000085	2.359475	0.585974	0.000293	0.586267
1.9614	2.357174	-0.000070	2.357104	0.575733	0.000328	0.576061
2.0000	2.354818	-0.000054	2.354765	0.565815	0.000364	0.566178
2.0500	2.351659	-0.000033	2.351626	0.553330	0.000408	0.553738
2.1000	2.349234	-0.000018	2.349217	0.541310	0.000450	0.541760

	$\langle \cos\ \theta_N \rangle$			$\langle \cos\ \theta_H \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	0.070001	0.000133	0.070134	0.773134	-0.000511	0.772623
1.9000	0.070776	0.000181	0.070957	0.782666	-0.000664	0.782002
1.9230	0.070867	0.000191	0.071058	0.784874	-0.000705	0.784168
1.9614	0.071158	0.000209	0.071367	0.788369	-0.000777	0.787592
2.0000	0.071360	0.000227	0.071587	0.791814	-0.000854	0.790960
2.0500	0.071651	0.000248	0.071899	0.795862	-0.000958	0.794904
2.1000	0.071910	0.000268	0.072178	0.800180	-0.001075	0.799105

TABLE 12. (CONT.)

	$\langle z_N \rangle$			$\langle z_H \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	0.144612	0.000473	0.145085	1.655388	-0.000473	1.654915
1.9000	0.155414	0.000705	0.156119	1.744586	-0.000705	1.743881
1.9230	0.157830	0.000768	0.158598	1.765170	-0.000768	1.764402
1.9614	0.161918	0.000878	0.162796	1.799482	-0.000878	1.798604
2.0000	0.166026	0.000997	0.167023	1.833974	-0.000997	1.832977
2.0500	0.171241	0.001161	0.172402	1.878759	-0.001161	1.877598
2.1000	0.176353	0.001343	0.177696	1.923647	-0.001343	1.922304

	$\langle z_N^2 \rangle$			$\langle z_H^2 \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	0.903821	0.002424	0.906245	3.623217	0.000723	3.623940
1.9000	0.951313	0.003127	0.954440	3.970740	0.000447	3.971187
1.9230	0.961871	0.003333	0.965204	4.052786	0.000379	4.053164
1.9614	0.979966	0.003707	0.983673	4.191883	0.000262	4.192145
2.0000	0.998140	0.004123	1.002263	4.334035	0.000134	4.334170
2.0500	1.023499	0.004737	1.028237	4.523912	-0.000022	4.523890
2.1000	1.046660	0.005466	1.052127	4.715977	-0.000176	4.715801

TABLE 12. (CONT.)

		$\langle\xi\rangle$			$\langle\eta\rangle$	
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	1.767948	0.000678	1.768626	-0.481999	0.000265	-0.481734
1.9000	1.728684	0.000656	1.729340	-0.491989	0.000351	-0.491638
1.9230	1.720058	0.000655	1.720713	-0.494350	0.000373	-0.493977
1.9614	1.706143	0.000653	1.706796	-0.498097	0.000413	-0.497685
2.0000	1.692477	0.000652	1.693129	-0.501850	0.000454	-0.501396
2.0500	1.676581	0.000656	1.677237	-0.506379	0.000510	-0.505869
2.1000	1.660288	0.000671	1.660959	-0.511208	0.000572	-0.510635

		$\langle\xi^2\rangle$			$\langle\eta^2\rangle$	
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	3.678629	0.004341	3.682970	0.504423	0.000188	0.504611
1.9000	3.489545	0.004005	3.493550	0.510796	0.000273	0.511068
1.9230	3.448700	0.003945	3.452645	0.512222	0.000295	0.512518
1.9614	3.383408	0.003848	3.387257	0.514585	0.000336	0.514922
2.0000	3.319886	0.003749	3.323635	0.517027	0.000380	0.517407
2.0500	3.247141	0.003660	3.250801	0.520021	0.000441	0.520462
2.1000	3.173351	0.003609	3.176960	0.523024	0.000509	0.523533

TABLE 12. (CONT.)

	$<r_N \cdot r_H>$			$<x^2+y^2>$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	2.571106	0.003364	2.574470	1.124753	0.002095	1.126848
1.9000	2.688321	0.003369	2.691690	1.149281	0.002074	1.151354
1.9230	2.714721	0.003374	2.718096	1.154474	0.002065	1.156538
1.9614	2.759155	0.003378	2.762533	1.163059	0.002040	1.165099
2.0000	2.802859	0.003369	2.806228	1.170825	0.002000	1.172826
2.0500	2.865181	0.003381	2.868562	1.184168	0.001951	1.186120
2.1000	2.921986	0.003418	2.925404	1.193935	0.001894	1.195830

	d			Q		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	0.643103	-0.003780	0.639322	0.541491	-0.019836	0.521655
1.9000	0.656687	-0.005641	0.651045	0.677186	-0.029924	0.647262
1.9230	0.660360	-0.006145	0.654215	0.715801	-0.032924	0.682877
1.9614	0.666054	-0.007025	0.659029	0.776908	-0.038435	0.738473
2.0000	0.671792	-0.007978	0.663813	0.837401	-0.044655	0.792746
2.0500	0.680075	-0.009287	0.670787	0.920910	-0.053807	0.867103
2.1000	0.689175	-0.010747	0.678428	1.020028	-0.064699	0.955329

TABLE 13. GEMINAL TWO-ELECTRON EXPECTATION VALUES

NH, R = 1.9614

$\langle r_{12}^{-1}\rangle$

PNO MATRIX

	K	L	B	T
K	0.147055			
L	0.133407	0.025065		
B	0.108549	0.072913	0.024528	
T	0.130473	0.084075	0.077617	0.020820

CORR MATRIX

	K	L	B	T
K	-0.001750			
L	-0.000062	-0.000369		
B	0.000046	-0.000023	-0.001853	
T	0.000018	-0.000023	-0.000033	-0.000294

$\langle r_{12}^{2}\rangle$

PNO MATRIX

	K	L	B	T
K	0.005106			
L	0.329995	0.150429		
B	0.523954	0.990157	0.191158	
T	0.392458	0.788042	0.882356	0.190505

CORR MATRIX

	K	L	B	T
K	0.000056			
L	0.001050	0.000650		
B	0.001955	0.002584	0.015991	
T	0.000346	0.001161	0.002214	0.000160

TABLE 13. (CONT.)

NH, R = 1.9614

$\langle \cos \theta_{N,12} \rangle$

PNO MATRIX

	K	L	B	T
K	0.000000			
L	-0.000076	0.002194		
B	-0.001009	-0.031377	0.008975	
T	-0.001662	-0.021193	0.001691	0.000037

CORR MATRIX

	K	L	B	T
K	-0.000409			
L	-0.000000	-0.000010		
B	-0.000005	0.000139	-0.001198	
T	-0.000001	0.000057	-0.000004	-0.000003

$\langle \cos \theta_{H,12} \rangle$

PNO MATRIX

	K	L	B	T
K	0.035275			
L	0.124151	0.027310		
B	0.070041	0.061049	0.008692	
T	0.112332	0.092213	0.054471	0.022394

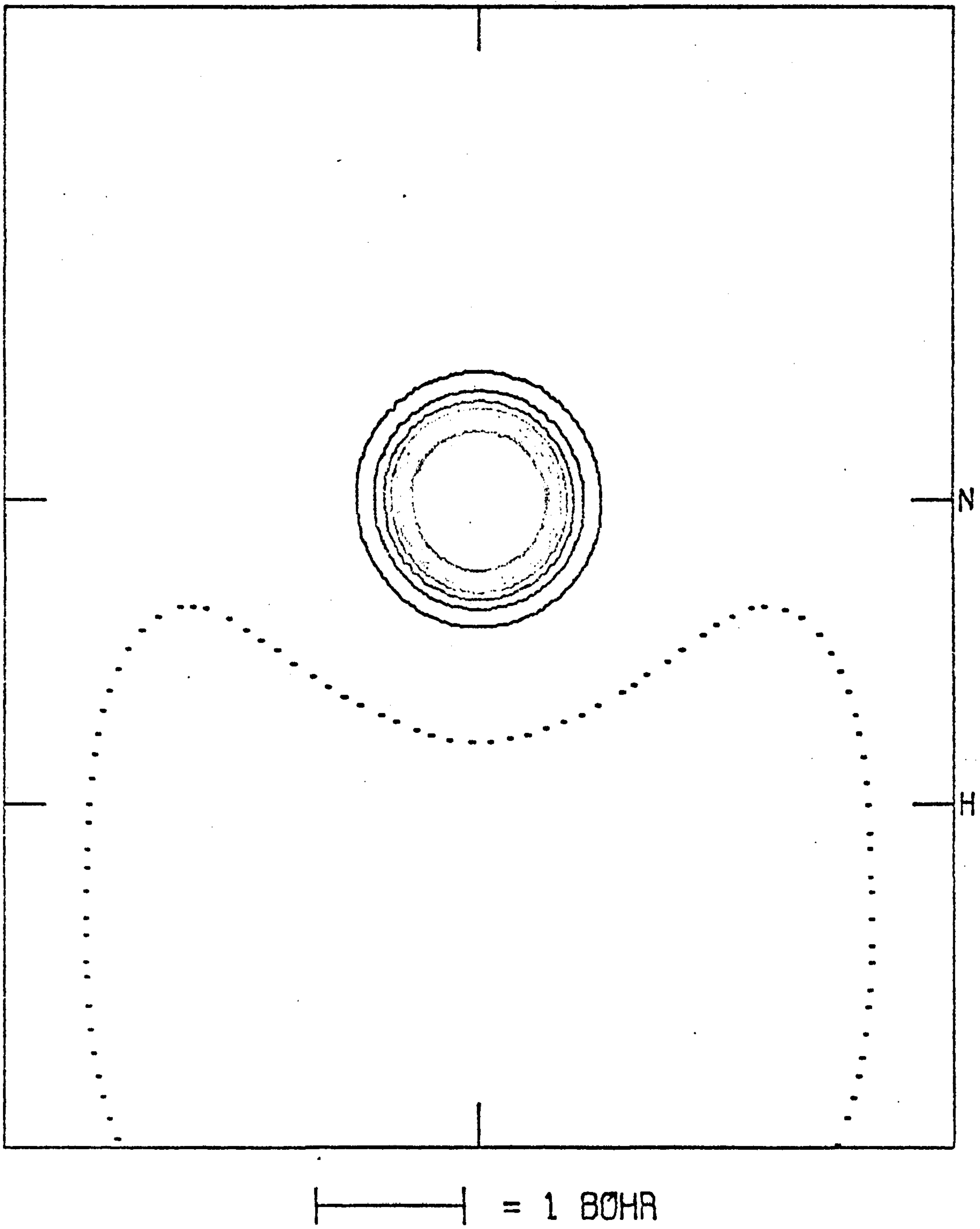
CORR MATRIX

	K	L	B	T
K	-0.000004			
L	-0.000041	-0.000025		
B	-0.000391	-0.000355	-0.002437	
T	-0.000012	-0.000023	-0.000300	-0.000063

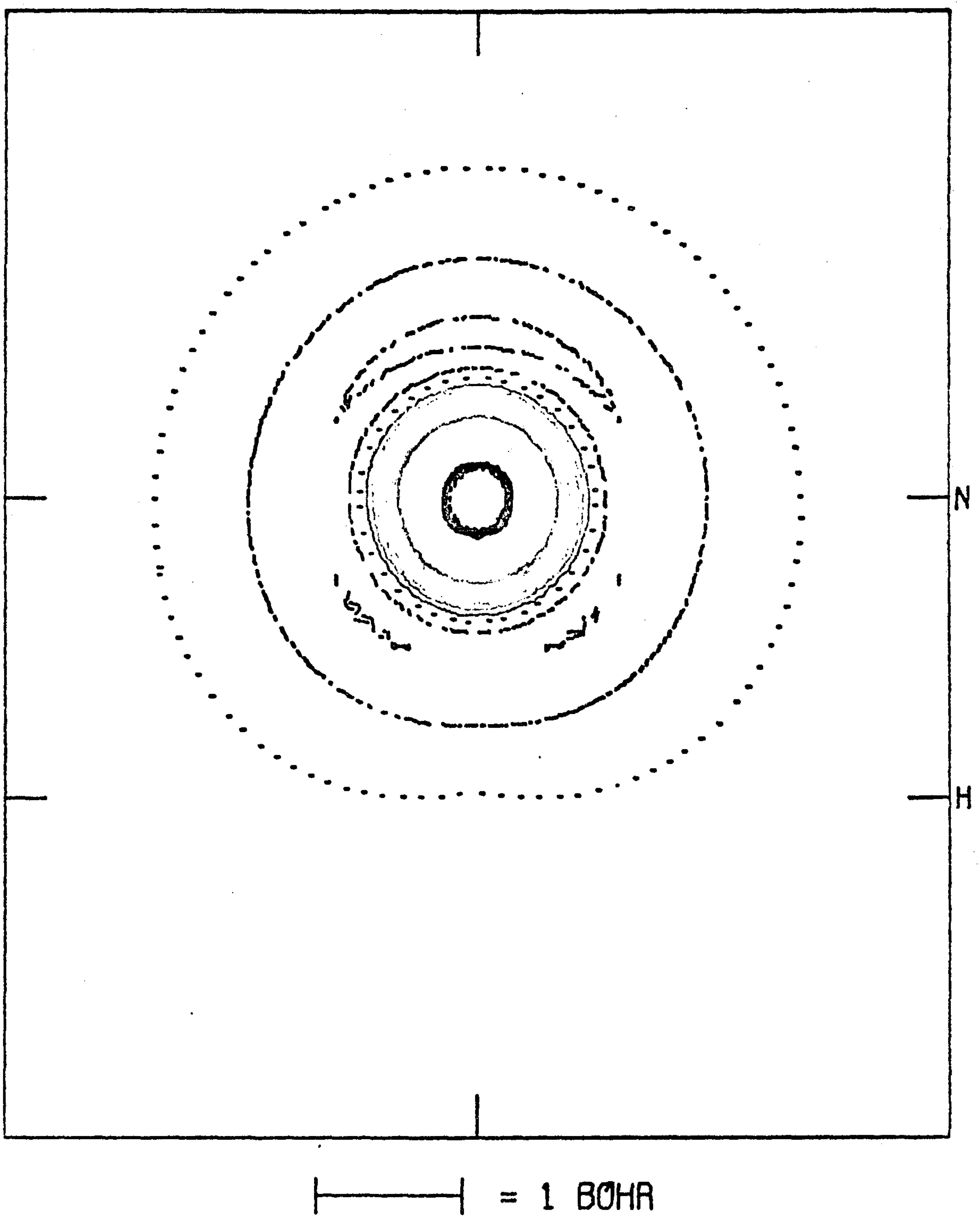
TABLE 14. TWO-ELECTRON PROPERTIES AS FUNCTIONS OF INTERNUCLEAR DISTANCE

	$\langle r_{12}^{-1} \rangle$			$\langle r_{12}^{2} \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	0.837289	-0.004192	0.833097	4.213272	0.020195	4.233466
1.9000	0.828914	-0.004288	0.824626	4.358732	0.023679	4.382411
1.9230	0.827267	-0.004311	0.822956	4.390426	0.024596	4.415023
1.9614	0.824503	-0.004348	0.820155	4.444160	0.026167	4.470326
2.0000	0.821939	-0.004381	0.817558	4.496178	0.027809	4.523987
2.0500	0.818085	-0.004426	0.813659	4.574153	0.030129	4.604282
2.1000	0.815285	-0.004473	0.810812	4.640013	0.032692	4.672705

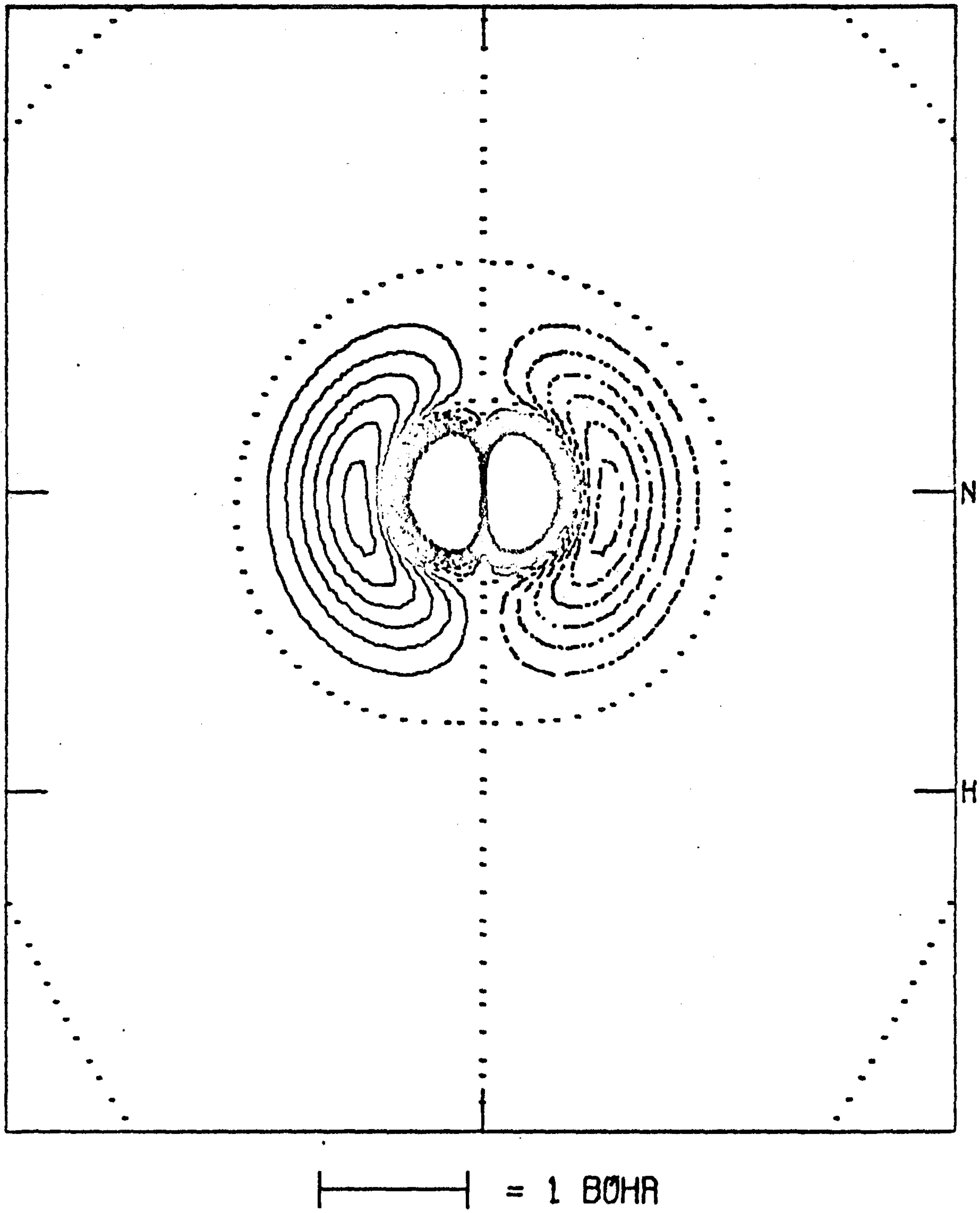
	$\langle \cos \theta_{N,12} \rangle$			$\langle \cos \theta_{H,12} \rangle$		
R	PNO	CORR	SP	PNO	CORR	SP
1.8000	-0.042490	-0.001357	-0.043847	0.582798	-0.002939	0.579859
1.9000	-0.042440	-0.001406	-0.043845	0.598470	-0.003364	0.595106
1.9230	-0.042437	-0.001417	-0.043854	0.602123	-0.003470	0.598653
1.9614	-0.042420	-0.001434	-0.043854	0.607927	-0.003652	0.604276
2.0000	-0.042411	-0.001452	-0.043863	0.613672	-0.003838	0.609834
2.0500	-0.042391	-0.001473	-0.043864	0.620454	-0.004087	0.616367
2.1000	-0.042373	-0.001494	-0.043868	0.627719	-0.004351	0.623369



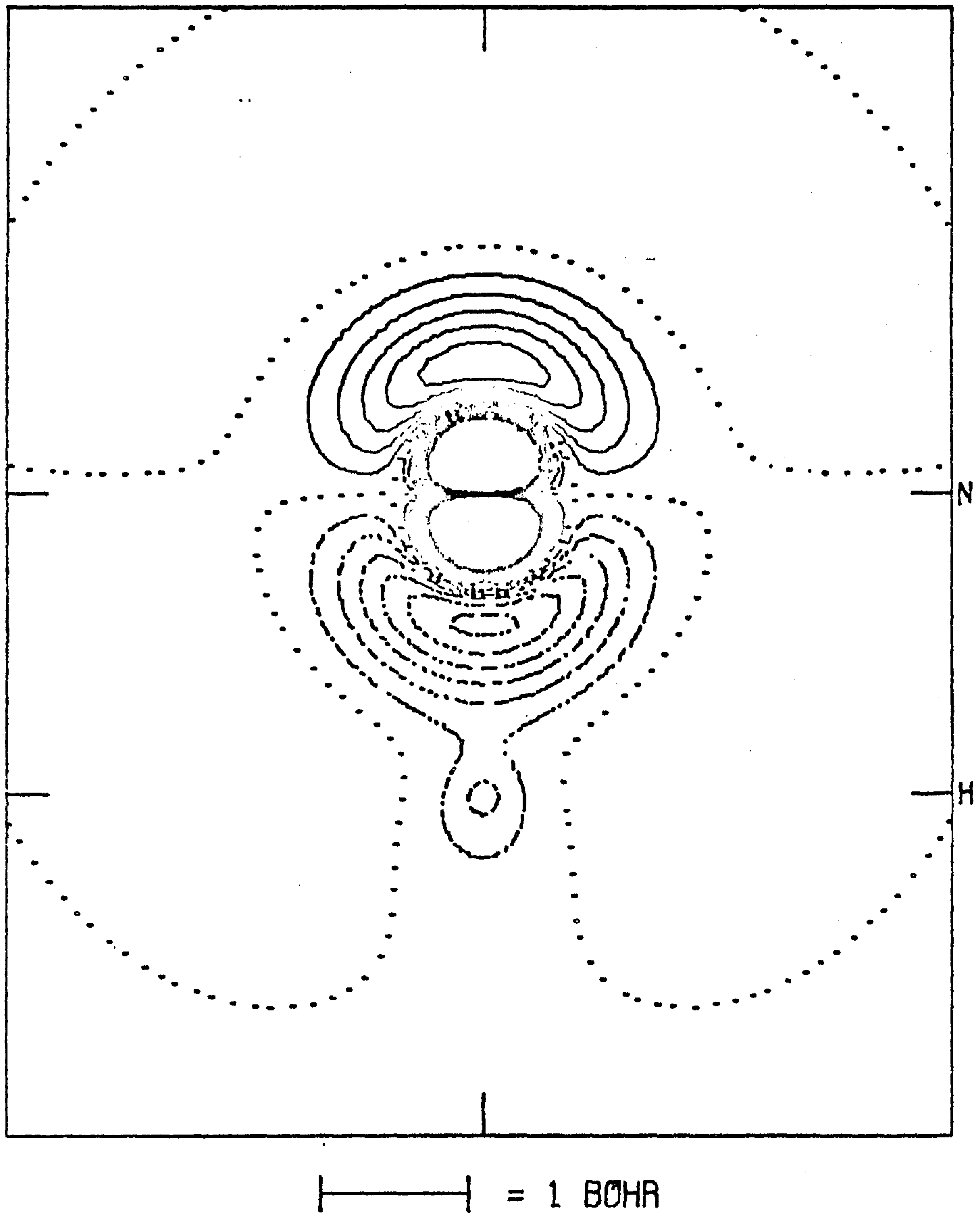
NATURAL ORBITAL CONTOUR MAP 1.
NH K SHELL 1 SIGMA 1 (OC=+0.99982)



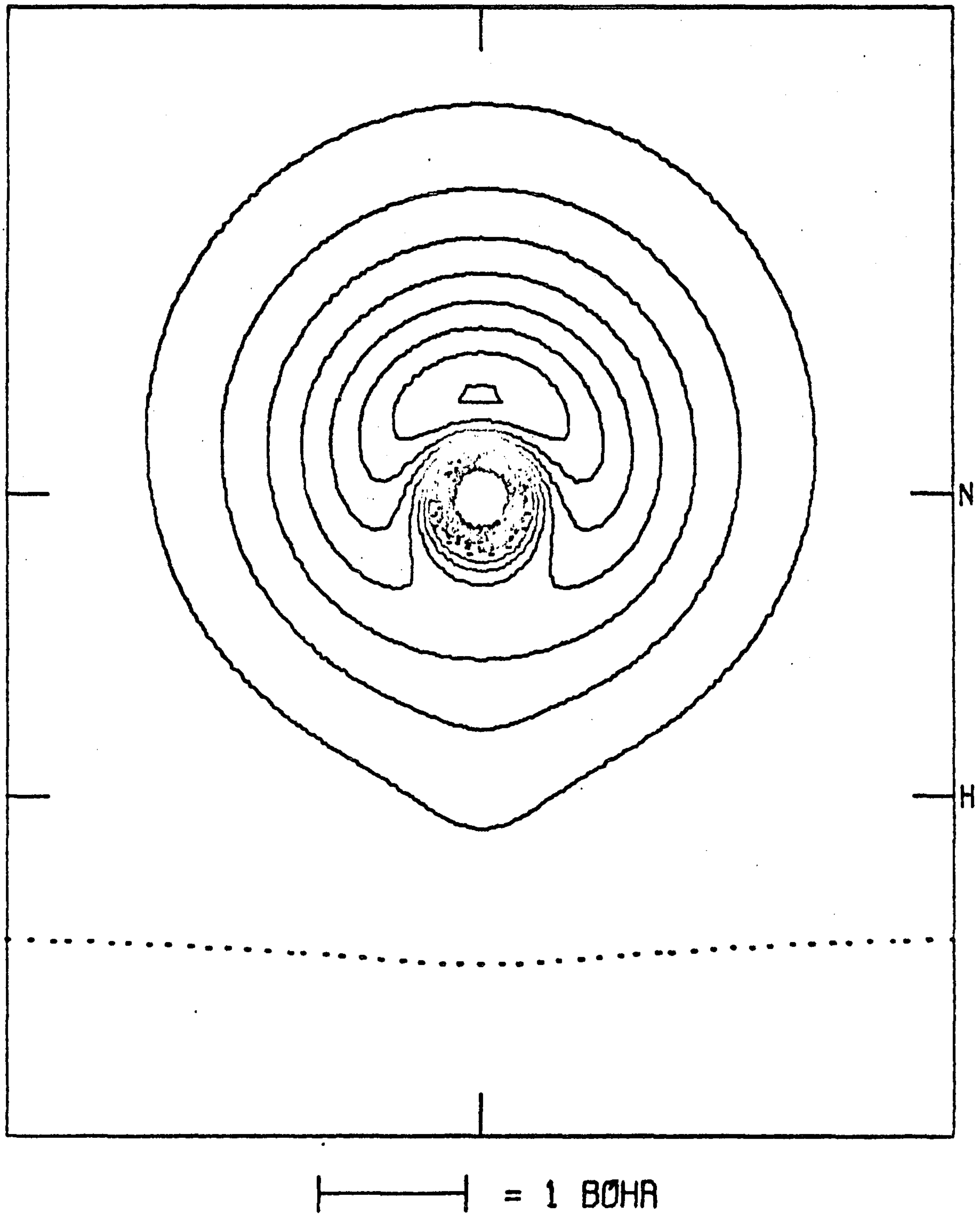
NATURAL ORBITAL CONTOUR MAP 2.
NH K SHELL 2 SIGMA 2 (OC=-0.01128)



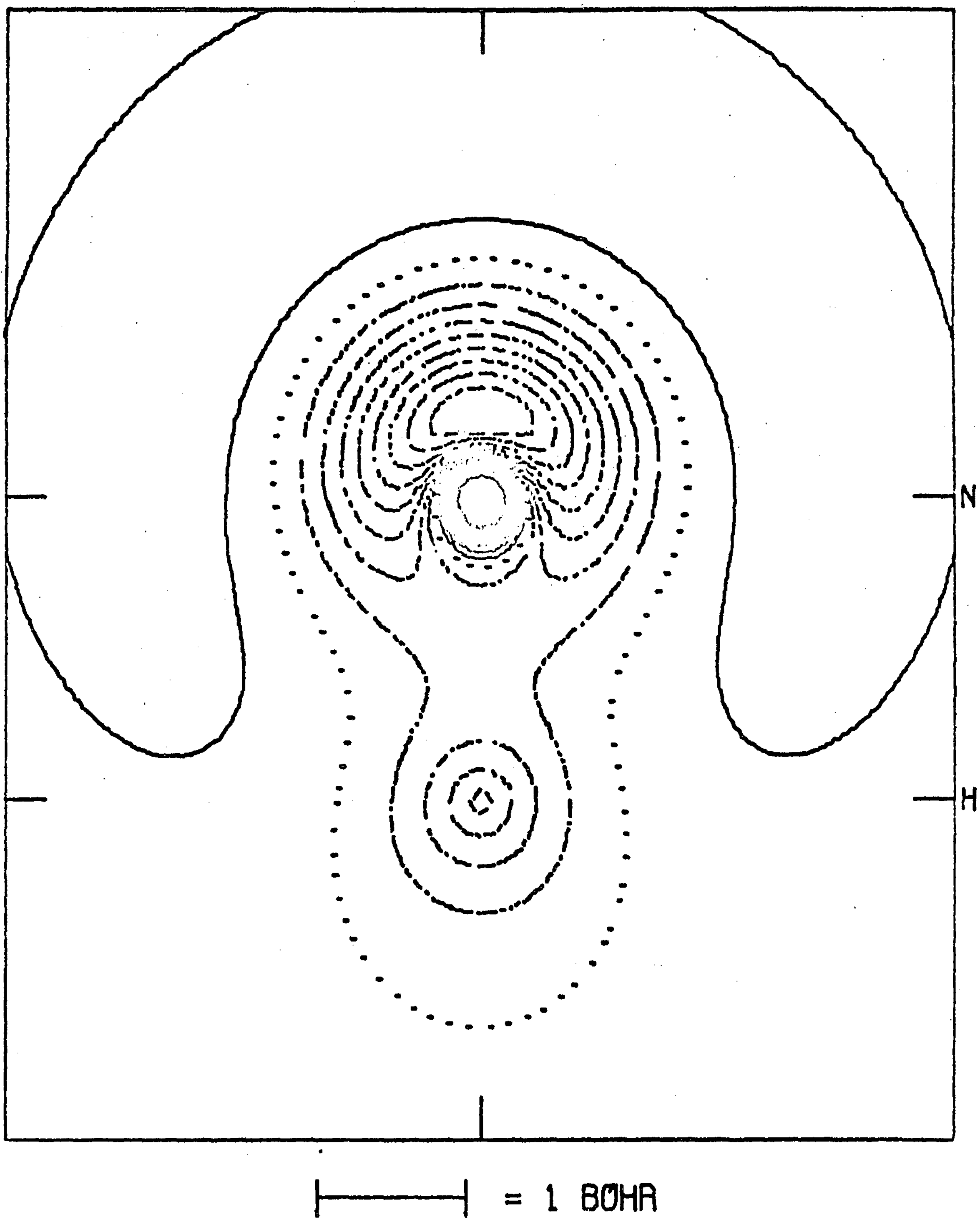
NATURAL ORBITAL CONTOUR MAP 3.
NH K SHELL 3 PI 1 (OC=-0.00873)



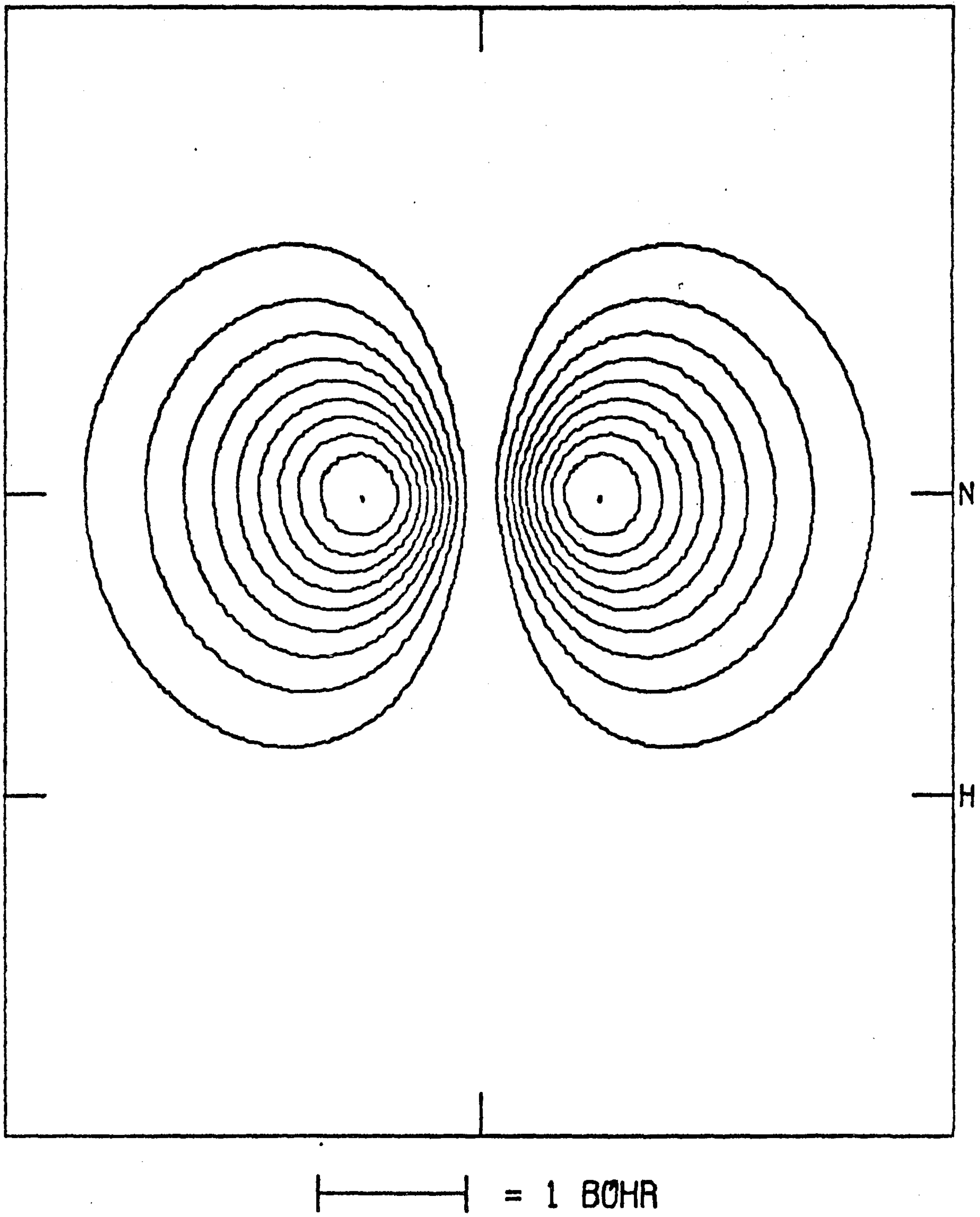
NATURAL ORBITAL CONTOUR MAP 4.
NH K SHELL 4 SIGMA 3 (OC=-0.00863)



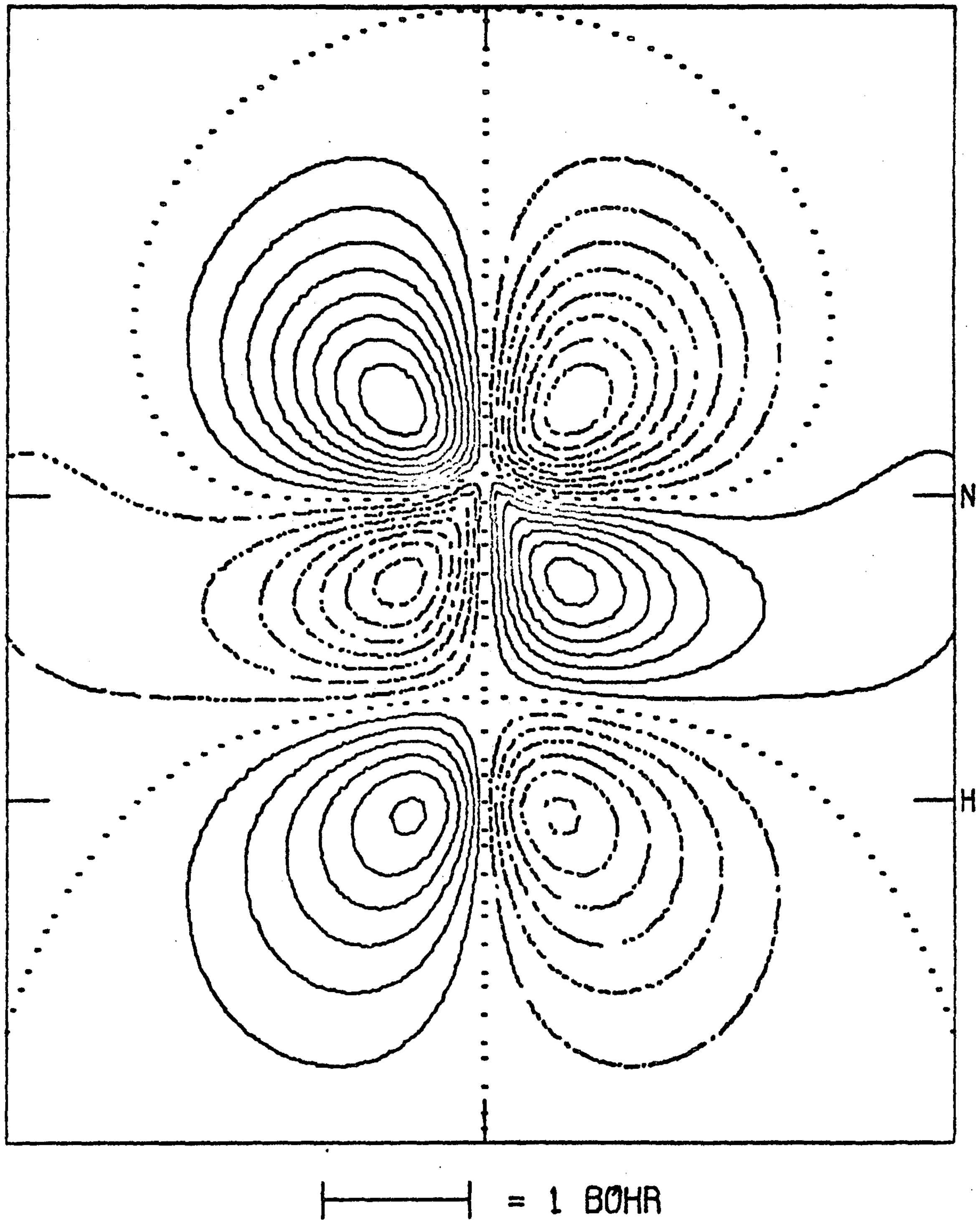
NATURAL ORBITAL CONTOUR MAP 5.
NH LONE PAIR 1 SIGMA 1 (OC=+0.99923)



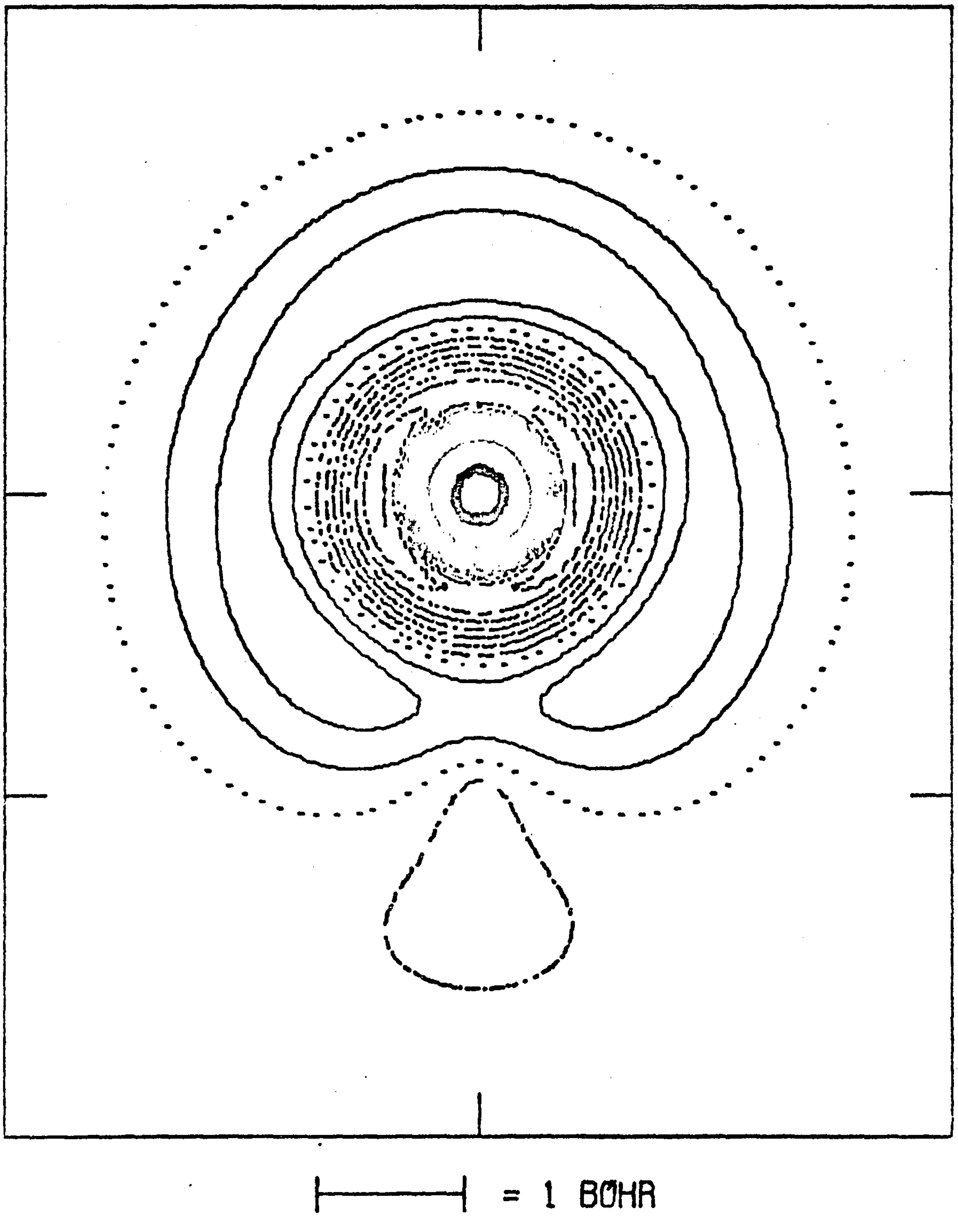
NATURAL ORBITAL CONTOUR MAP 6.
NH LONE PAIR 2 SIGMA 2 (OC=-0.03259)



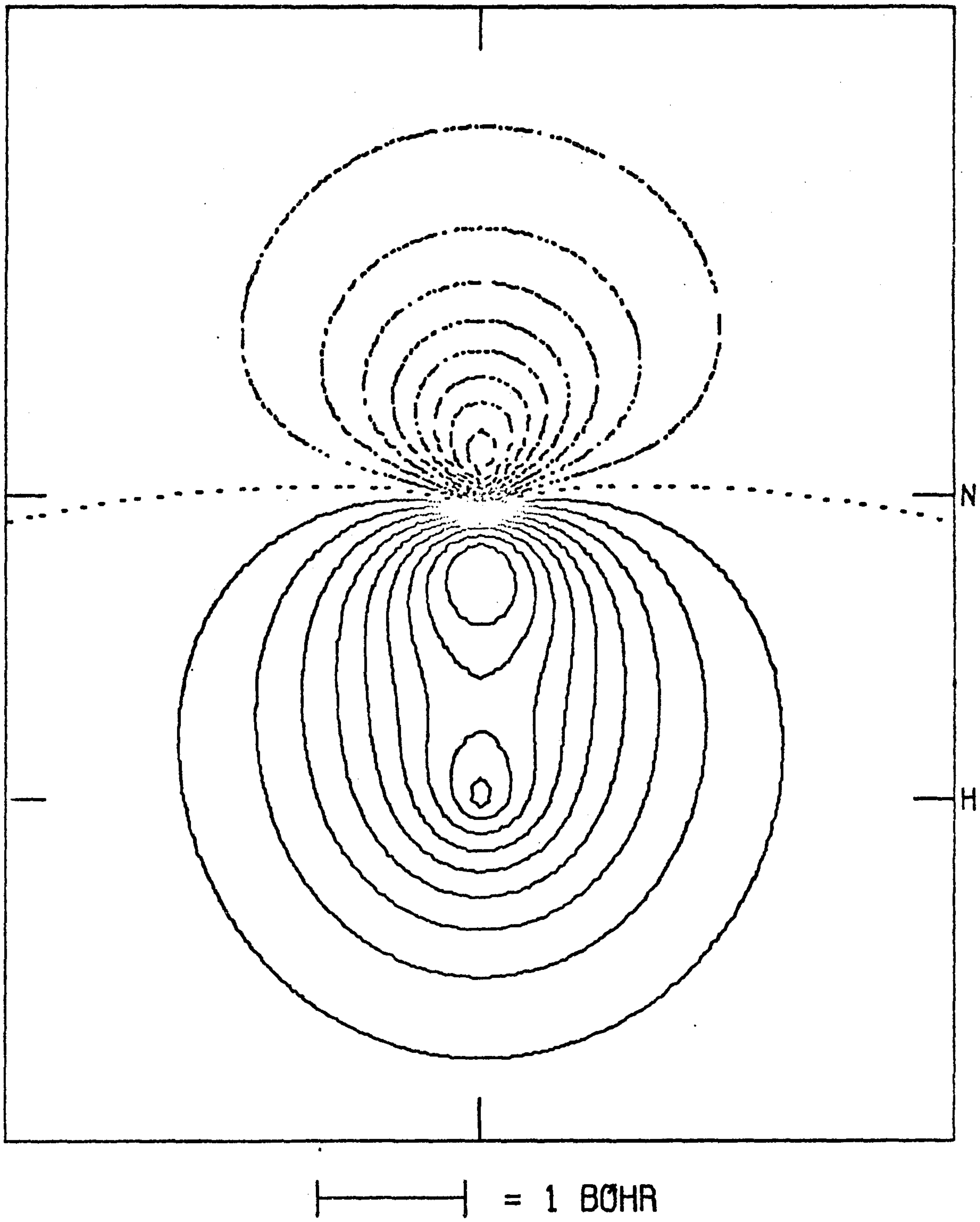
NATURAL ORBITAL CONTOUR MAP 7.
NH LONE PAIR 3 DELTA 1 (OC=-0.01254)



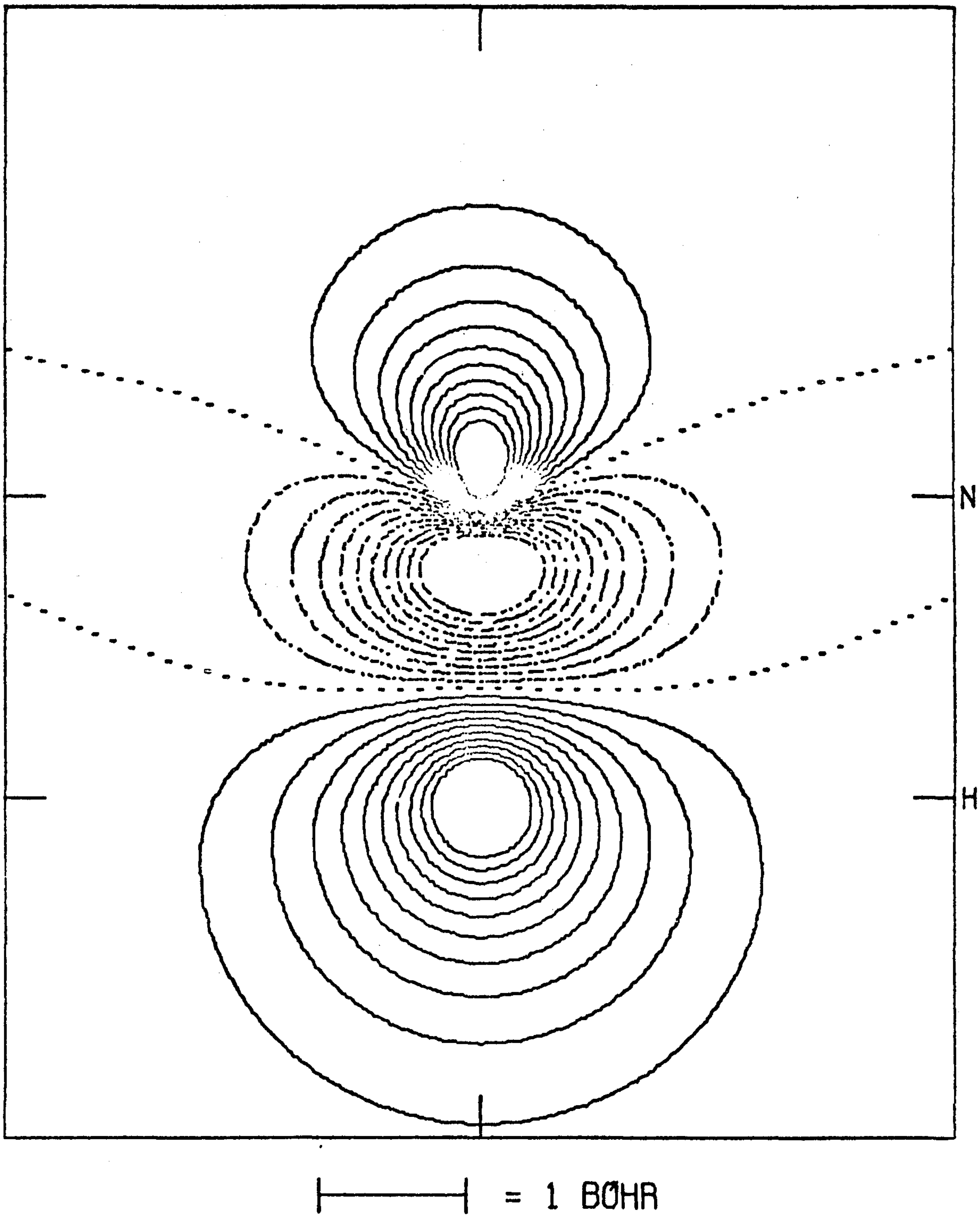
NATURAL ORBITAL CONTOUR MAP 8.
NH LONE PAIR 4 PI 1 (OC=-0.00907)



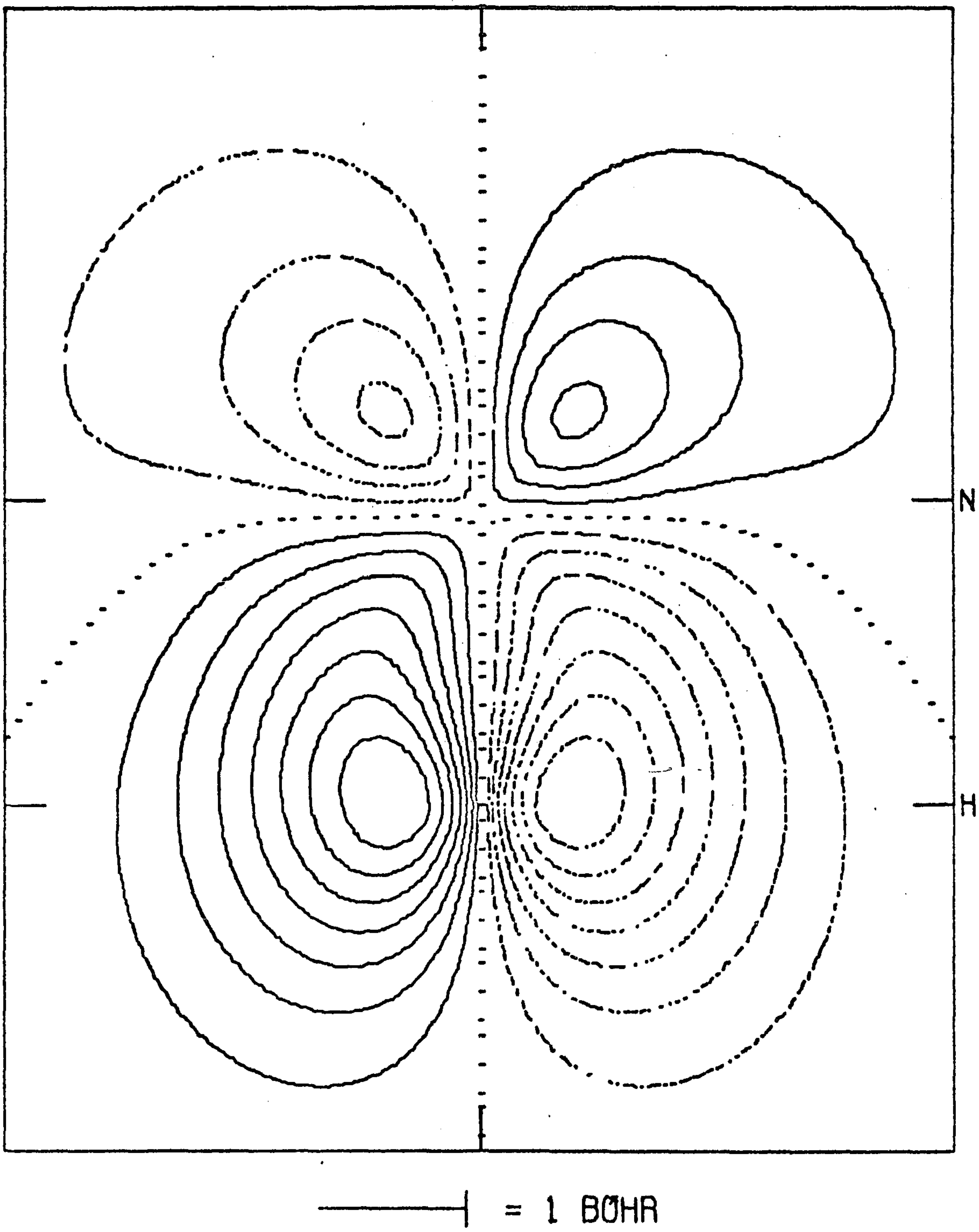
NATURAL ORBITAL CONTOUR MAP 9.
NH LONE PAIR 5 SIGMA 3 (OC=-0.00117)



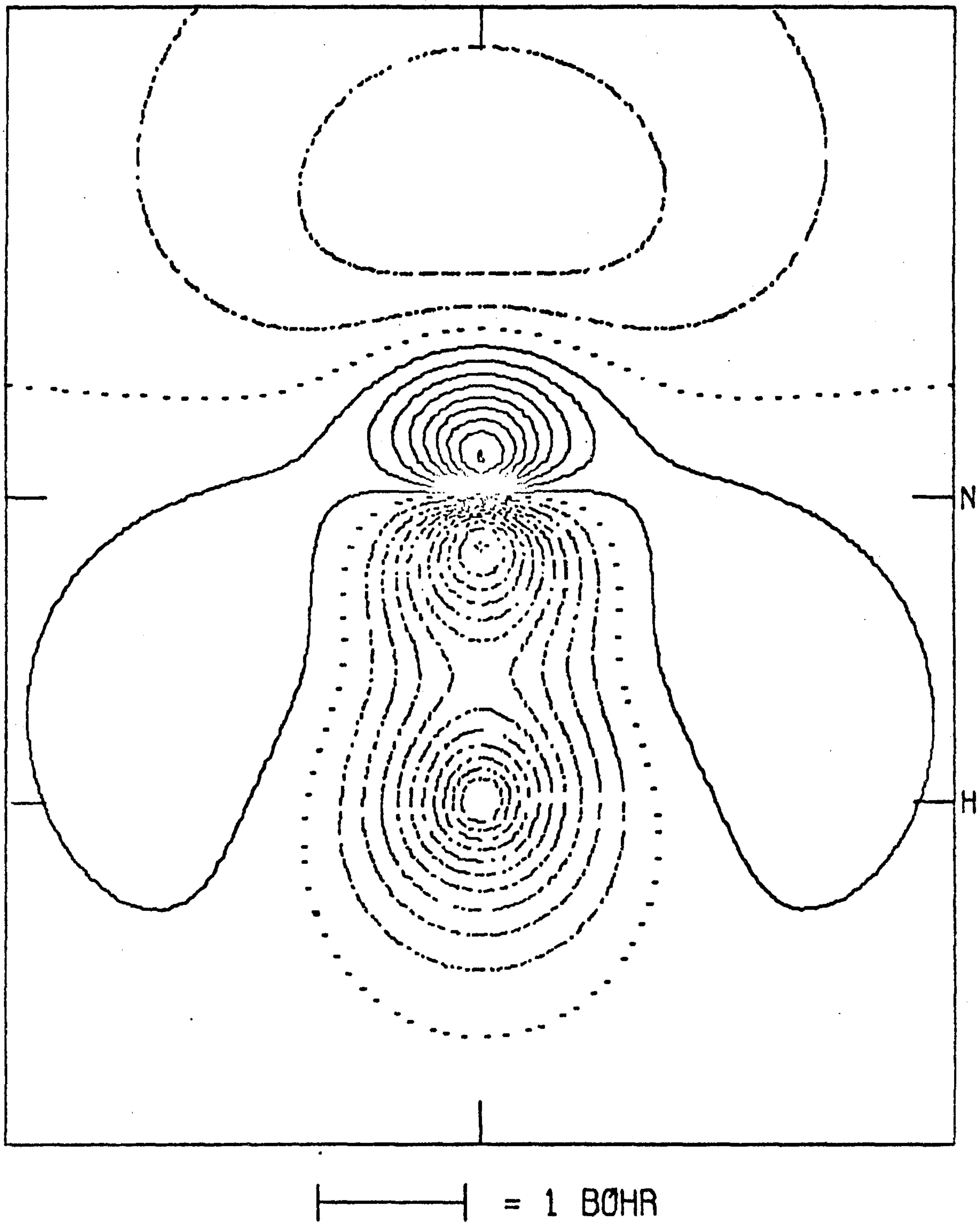
NATURAL ORBITAL CONTOUR MAP 10.
NH BONDING 1 SIGMA 1 (OC=+0.99377)



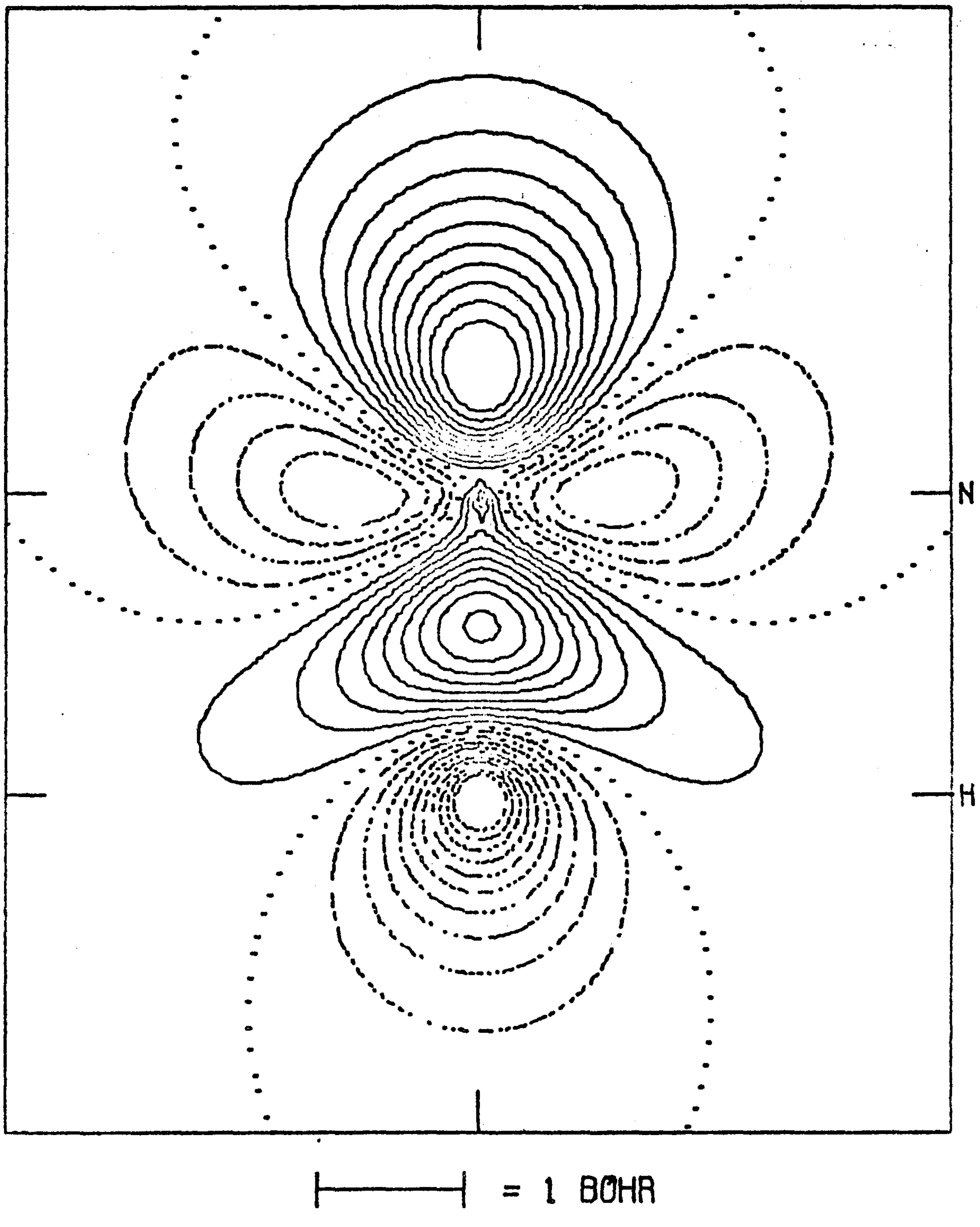
NATURAL ORBITAL CONTOUR MAP 11.
NH BONDING 2 SIGMA 2 (OC=-0.09961)



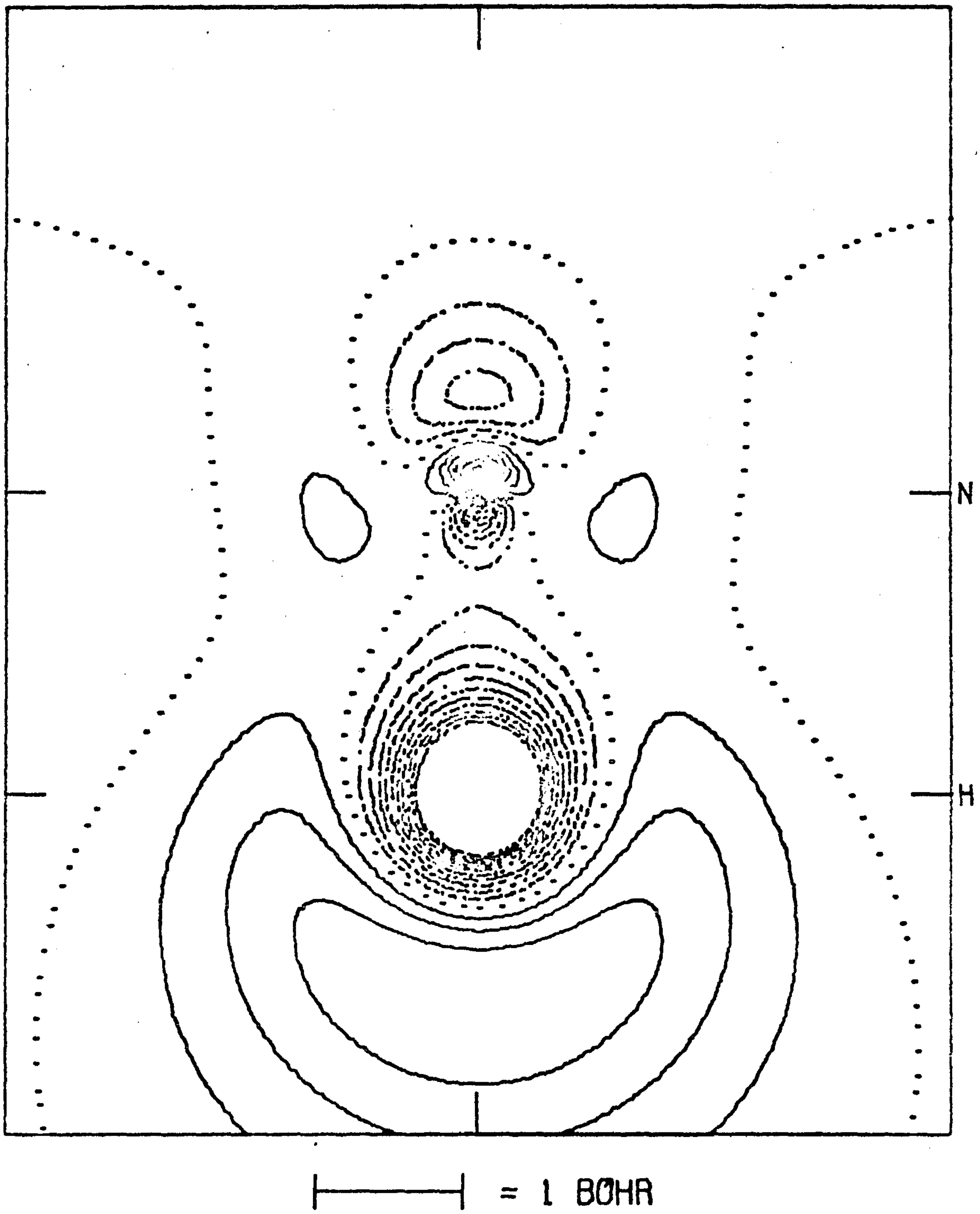
NATURAL ORBITAL CONTOUR MAP 12.
NH BONDING 3 PI 1 (OC=-0.02787)



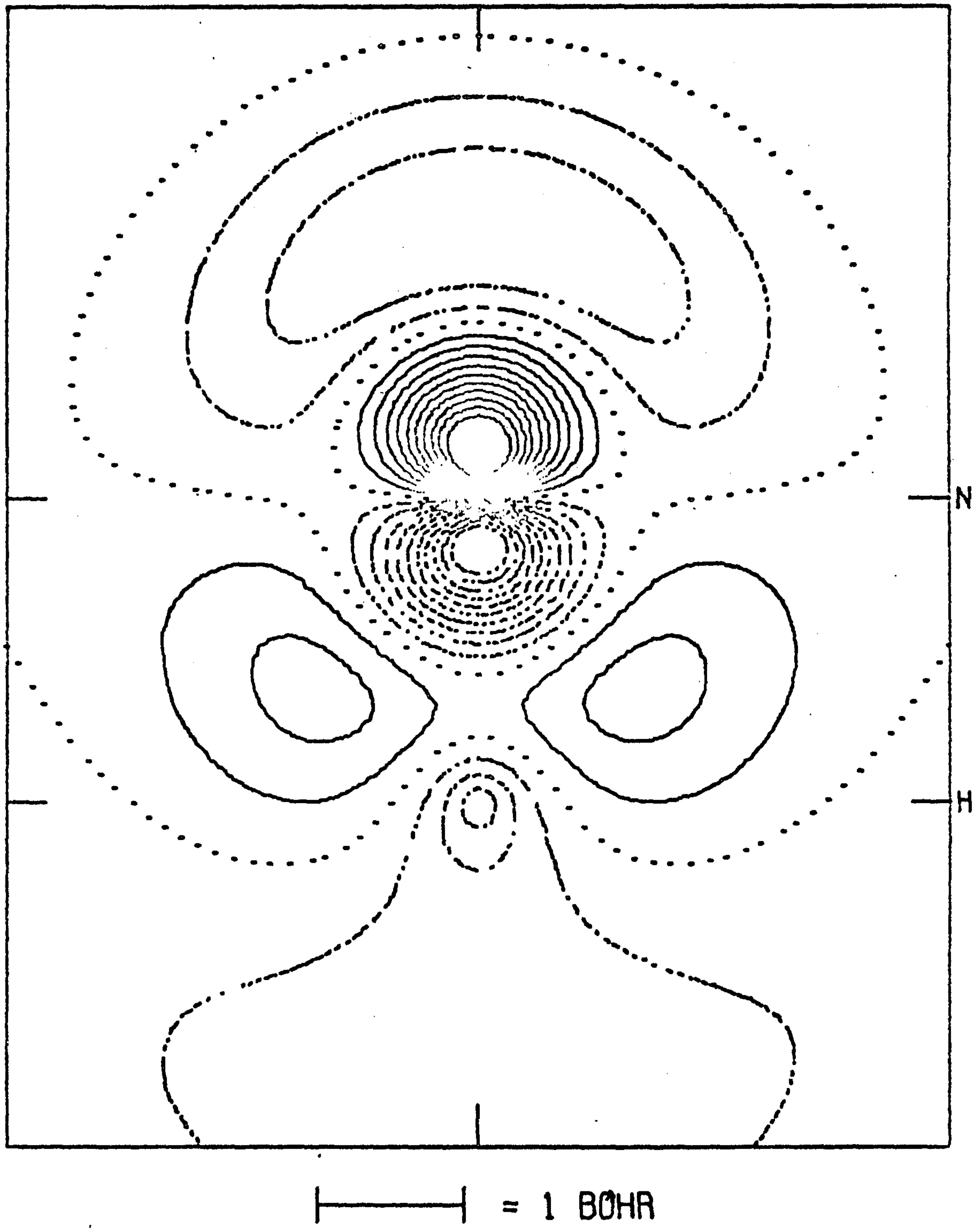
NATURAL ORBITAL CONTOUR MAP 13.
NH BONDING 4 SIGMA 3 (OC=-0.02652)



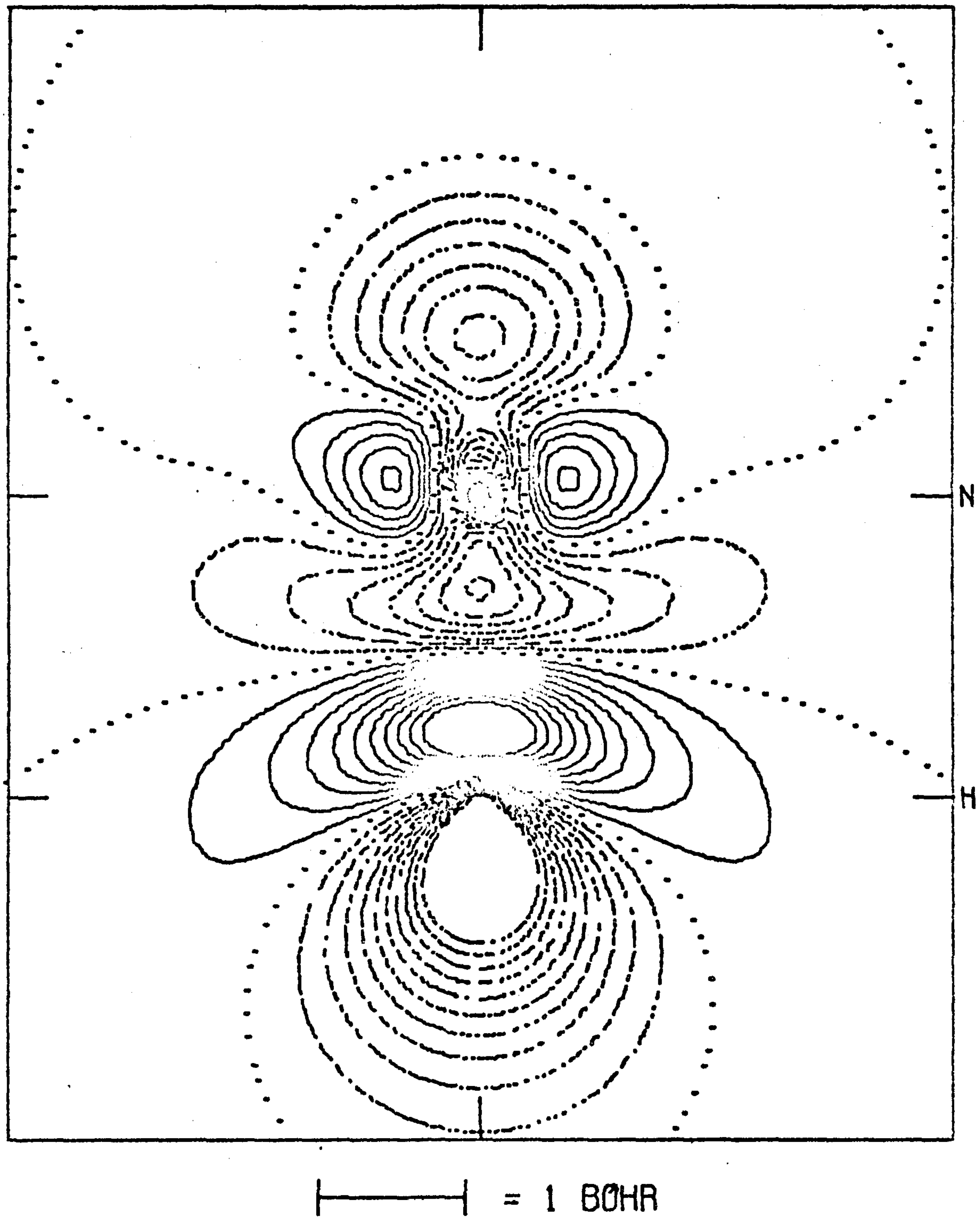
NATURAL ORBITAL CONTOUR MAP 14.
NH BONDING 5 SIGMA 4 (OC=-0.01091)



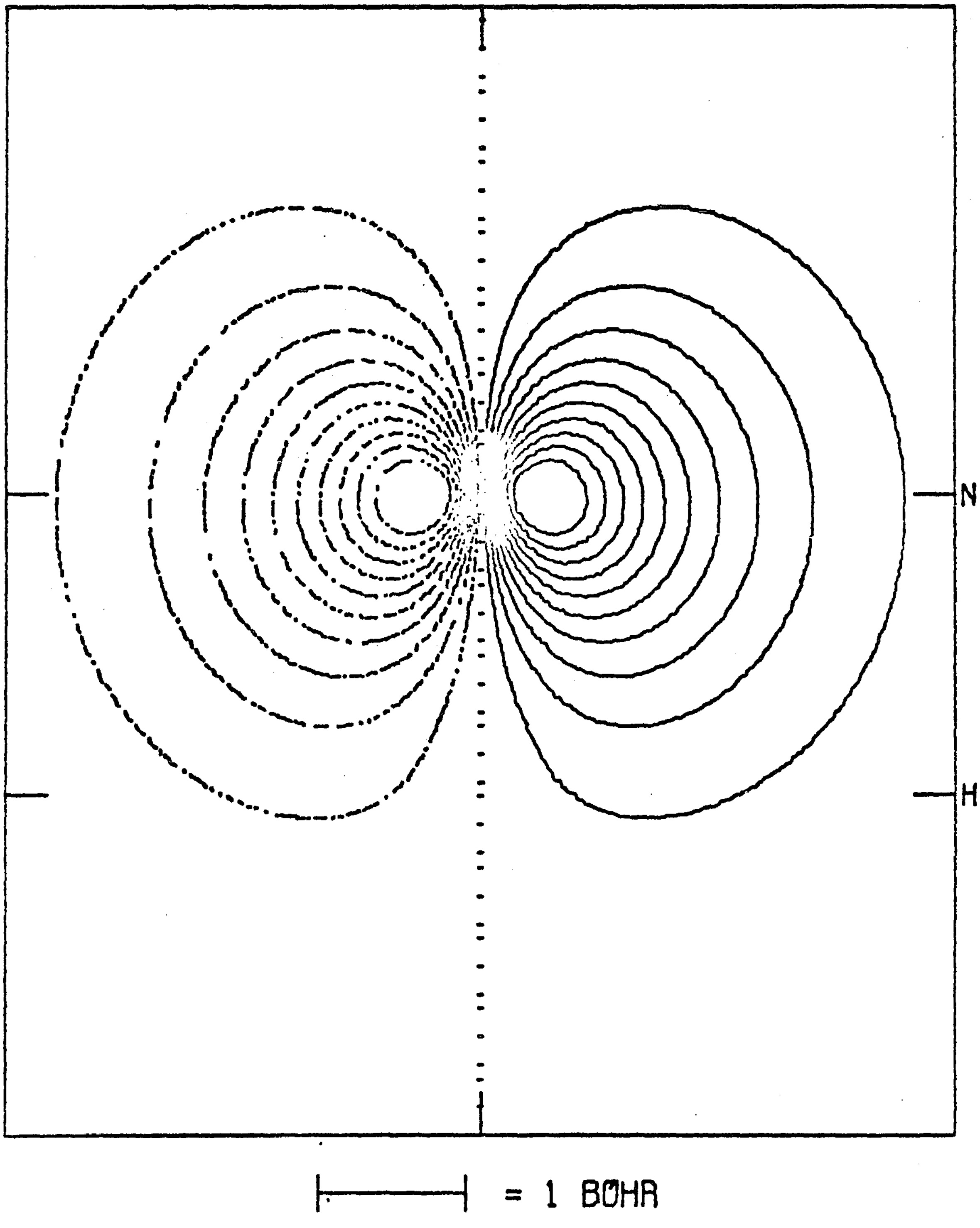
NATURAL ORBITAL CONTOUR MAP 15.
NH BONDING 6 SIGMA 5 (OC=-0.00797)



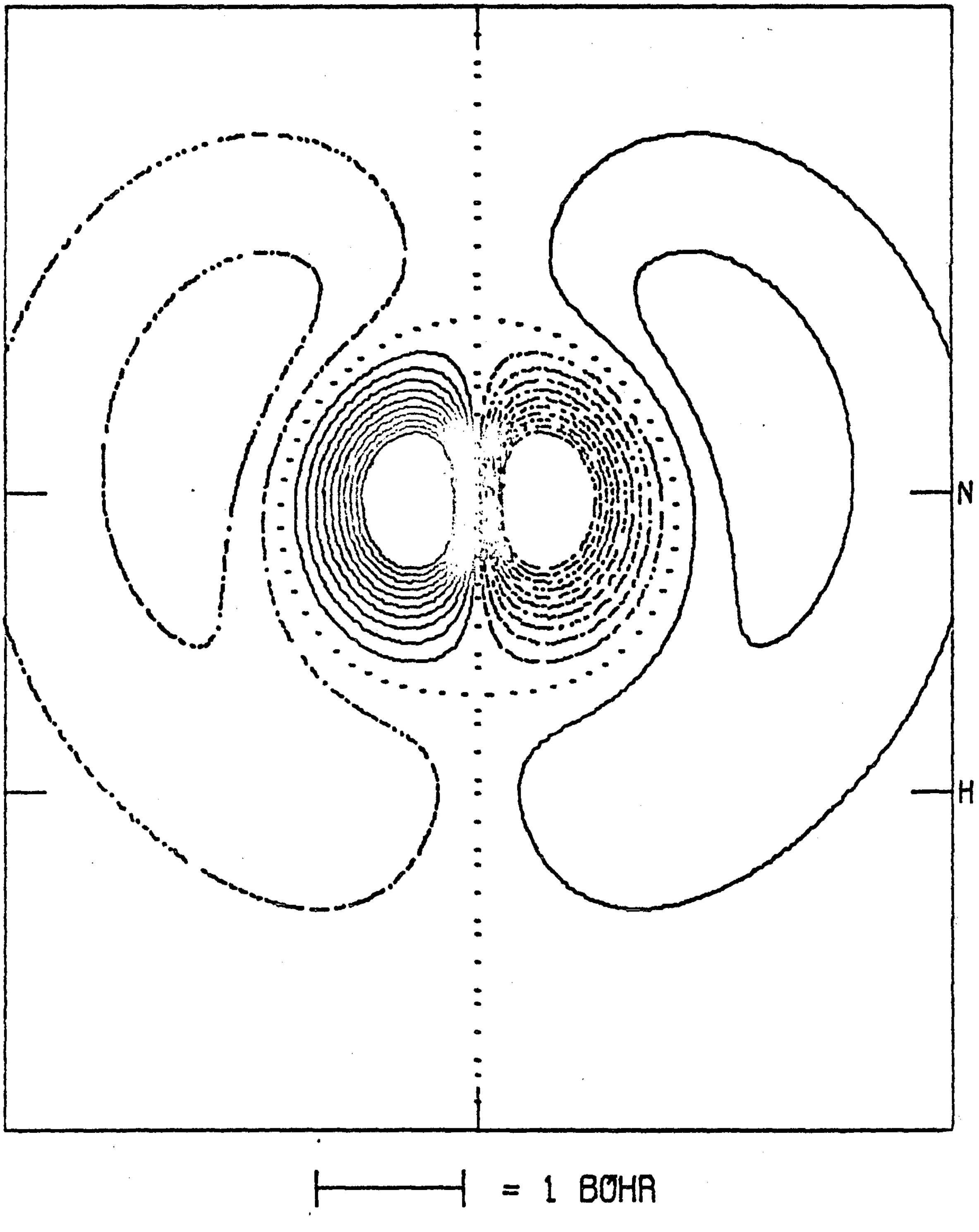
NATURAL ORBITAL CONTOUR MAP 16.
NH BONDING 7 SIGMA 6 (OC=-0.00617)



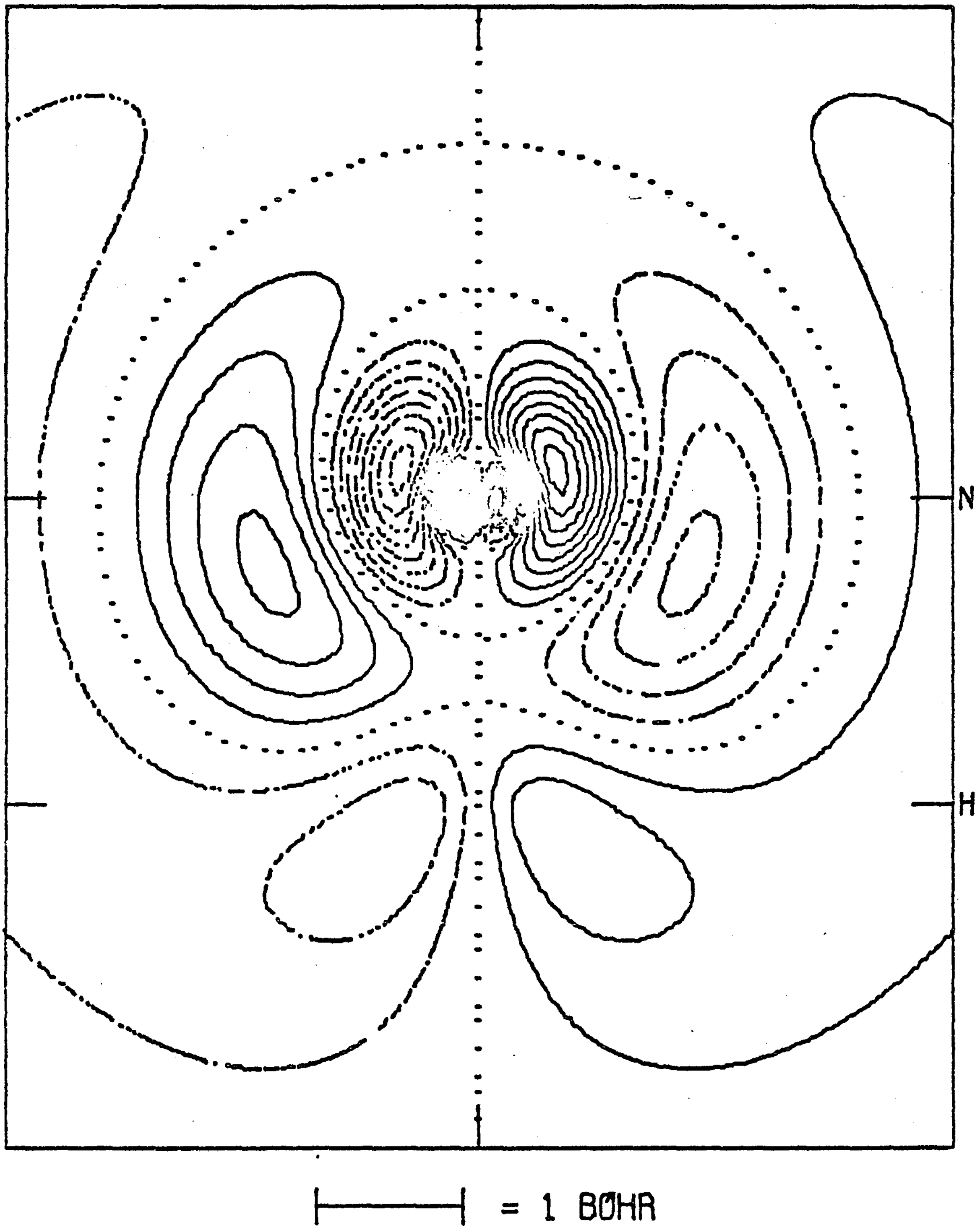
NATURAL ORBITAL CONTOUR MAP 17.
NH BONDING 8 SIGMA 7 (OC=-0.00369)



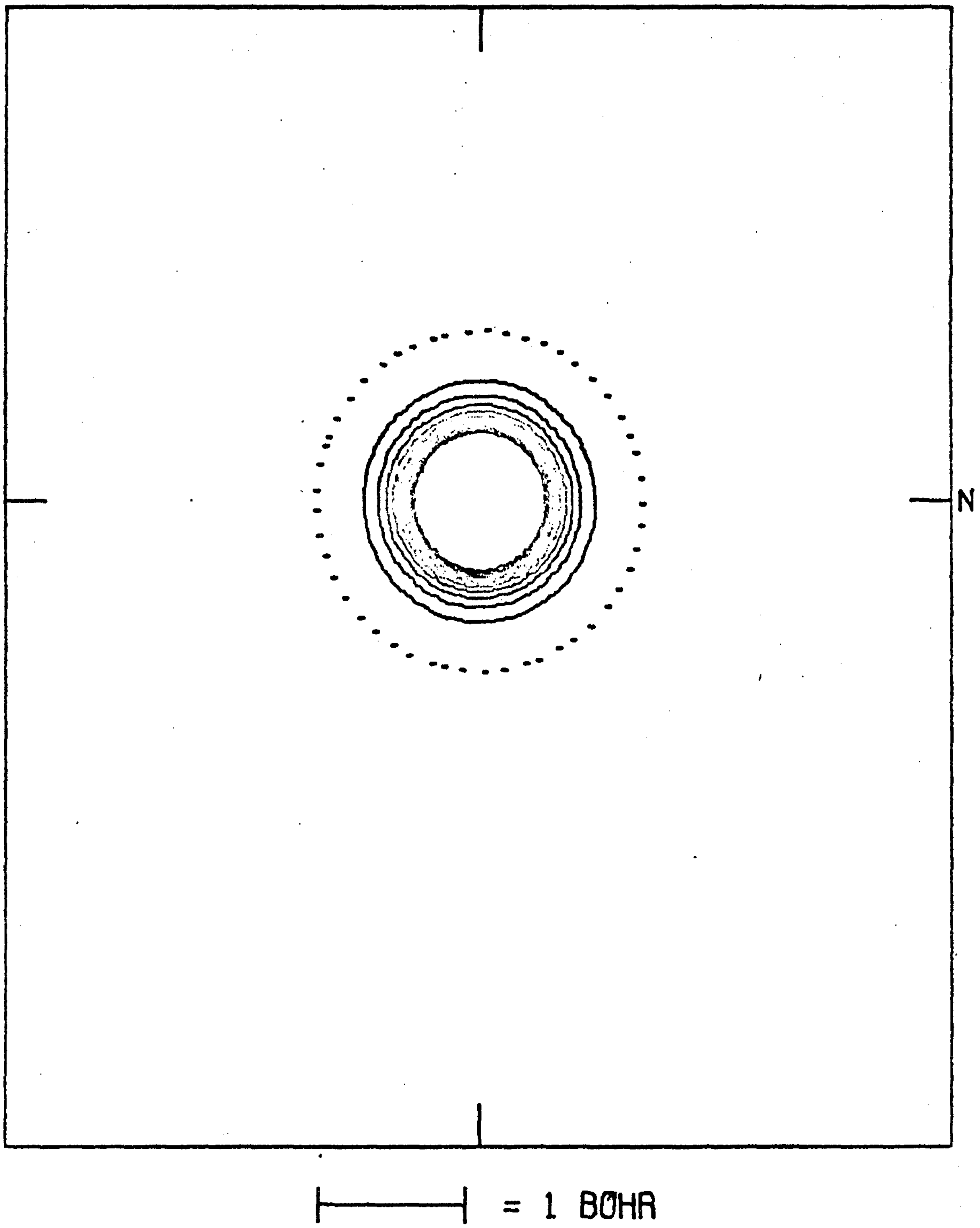
NATURAL ORBITAL CONTOUR MAP 18.
NH TRIPLET 1 PI 1 (OC=+0.99925)



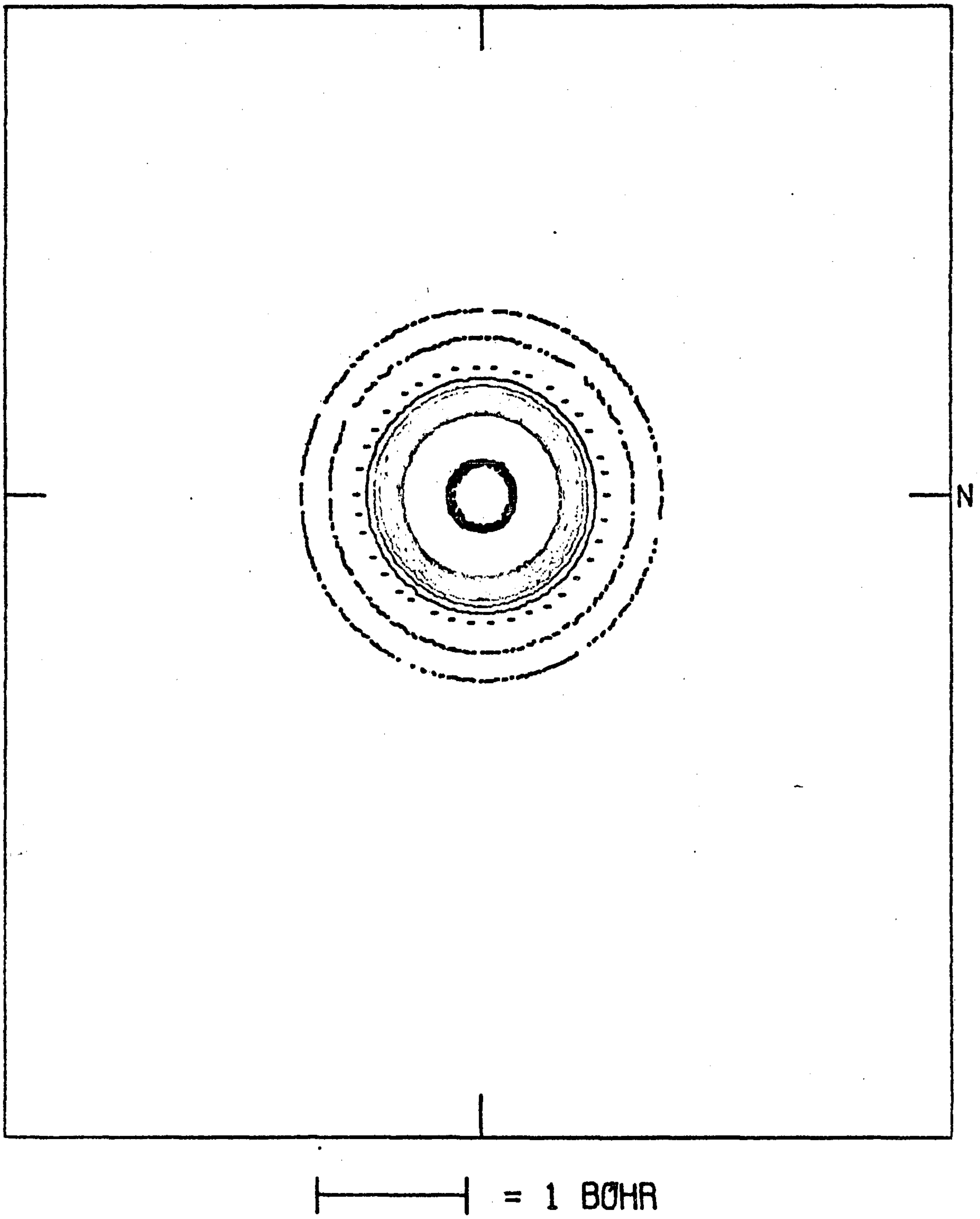
NATURAL ORBITAL CONTOUR MAP 19.
NH TRIPLET 2 PI 2 (OC=-0.03875)



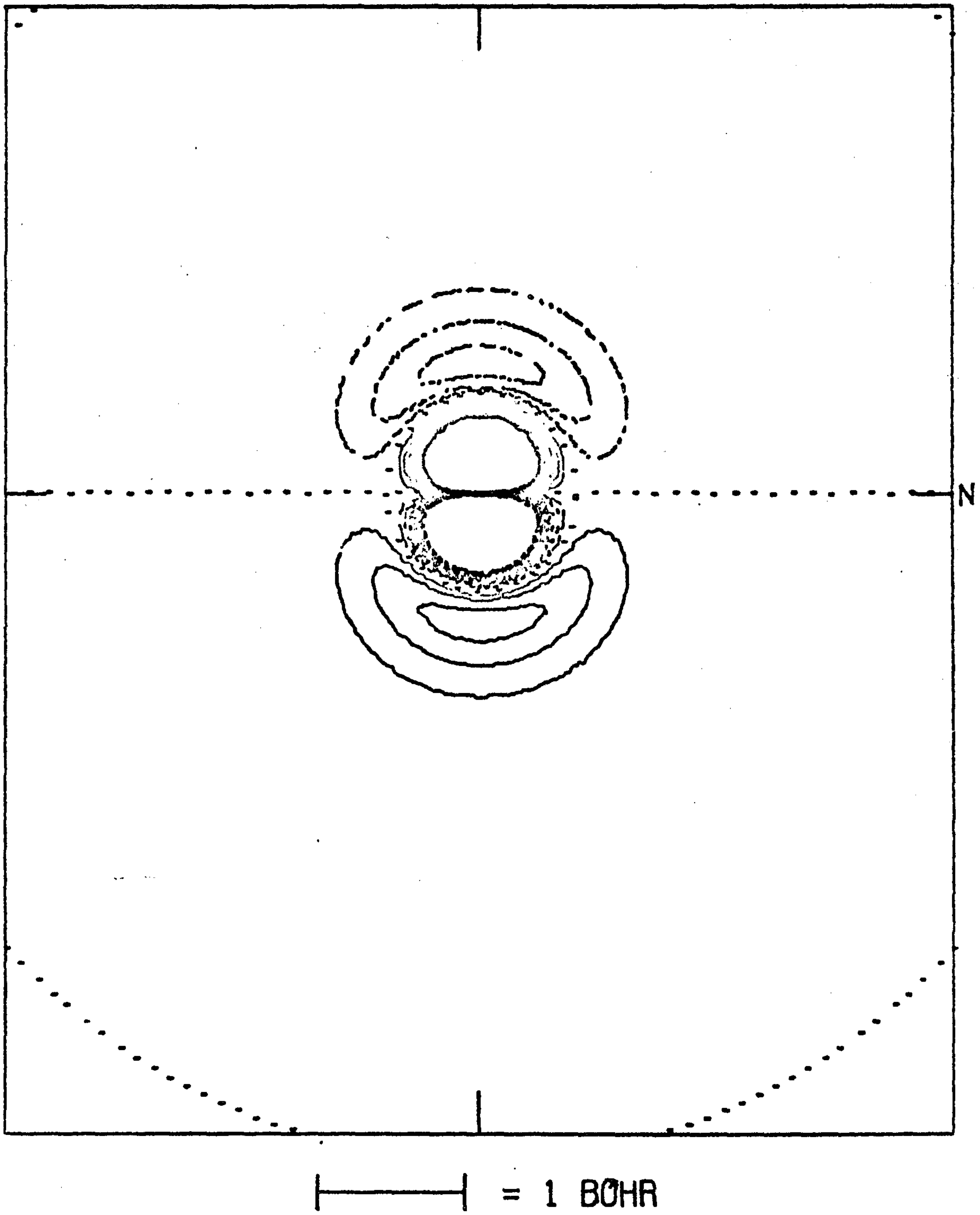
NATURAL ORBITAL CONTOUR MAP 20.
NH TRIPLET 3 PI 3 (OC=-0.00182)



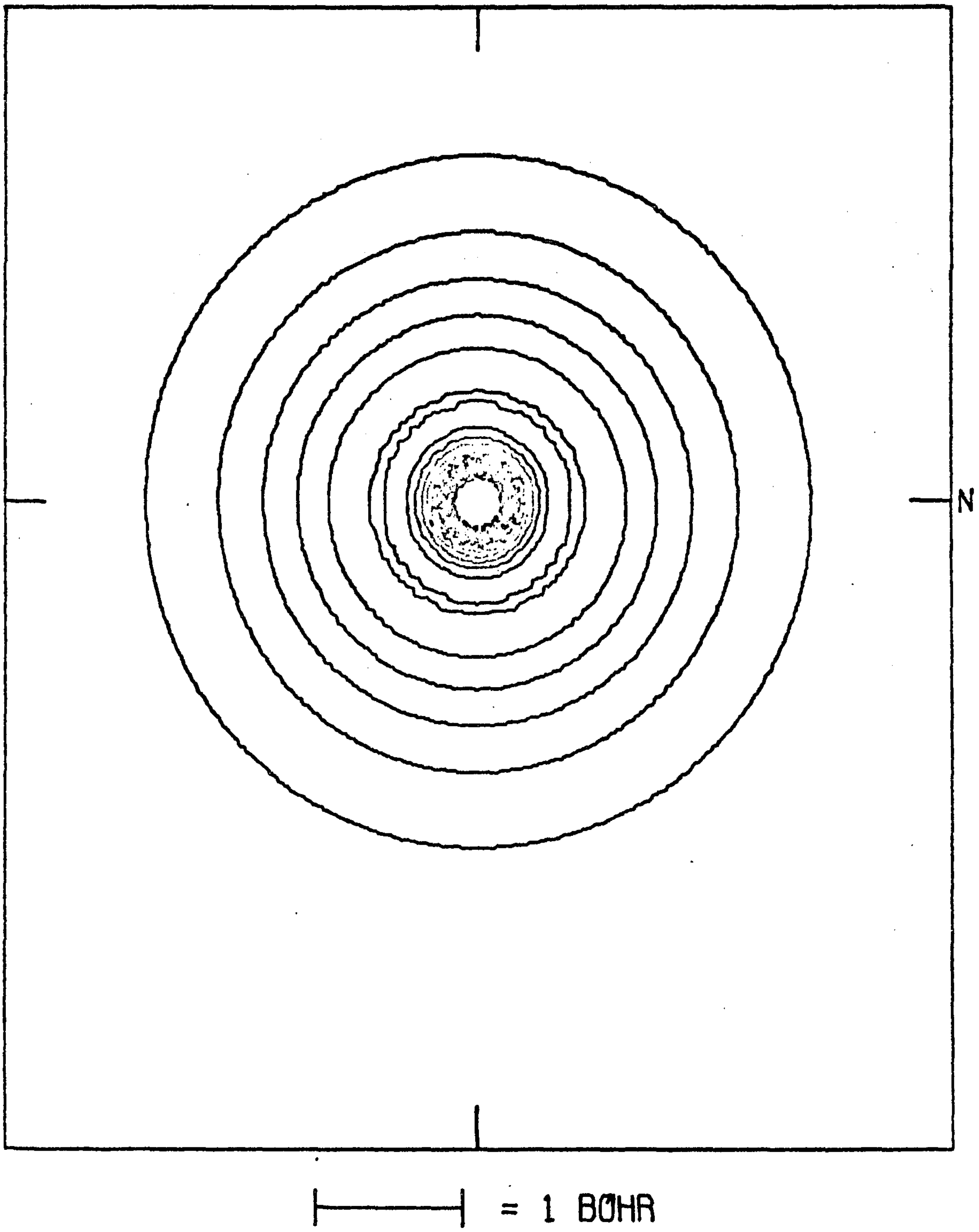
NATURAL ORBITAL CONTOUR MAP 21.
NITROGEN K 1 S 1 (OC=+0.99979)



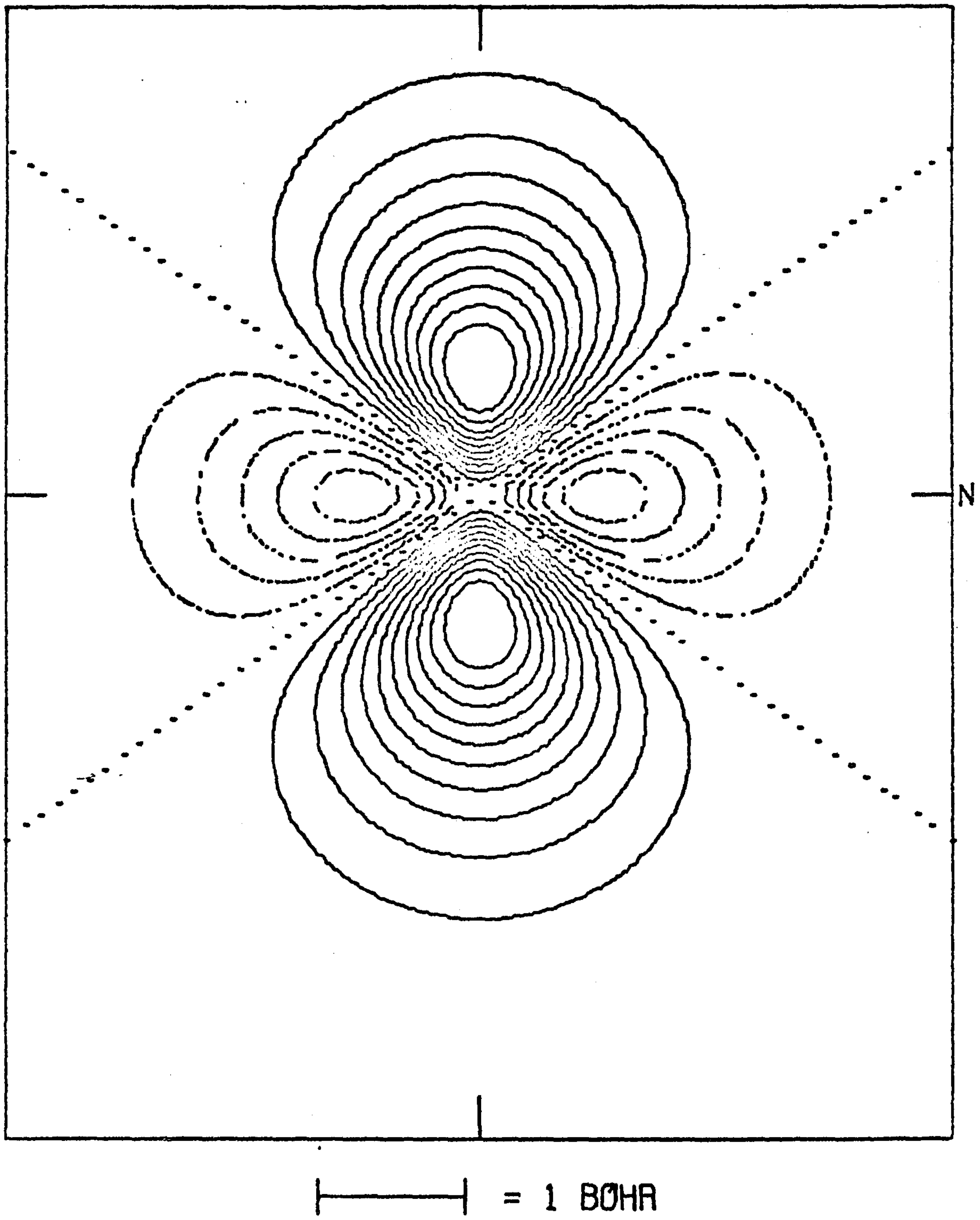
NATURAL ORBITAL CONTOUR MAP 22.
NITROGEN K 2 S 2 (OC=-0.01156)



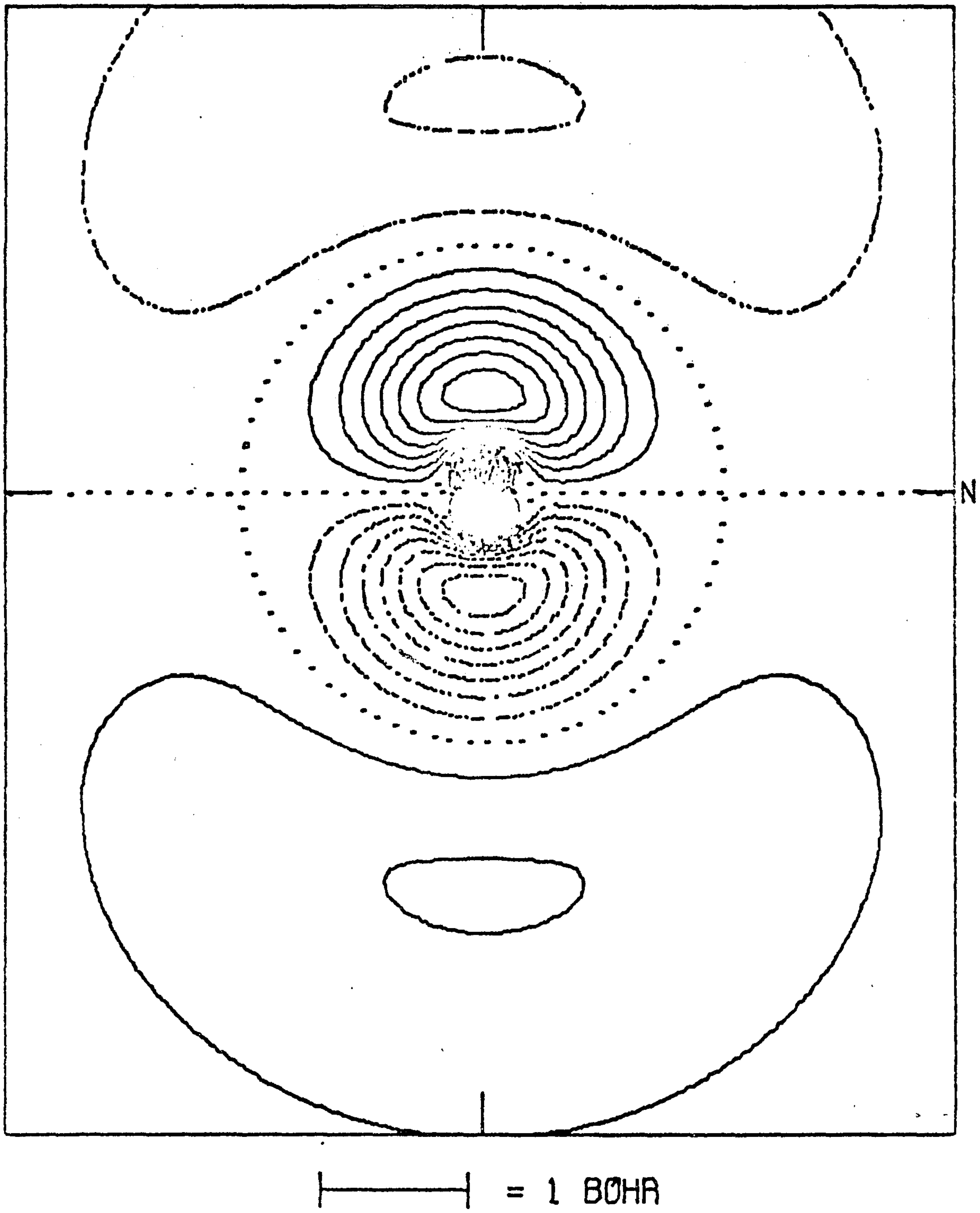
NATURAL ORBITAL CONTOUR MAP 23.
NITROGEN K 3 P 1 (OC=-0.00980)



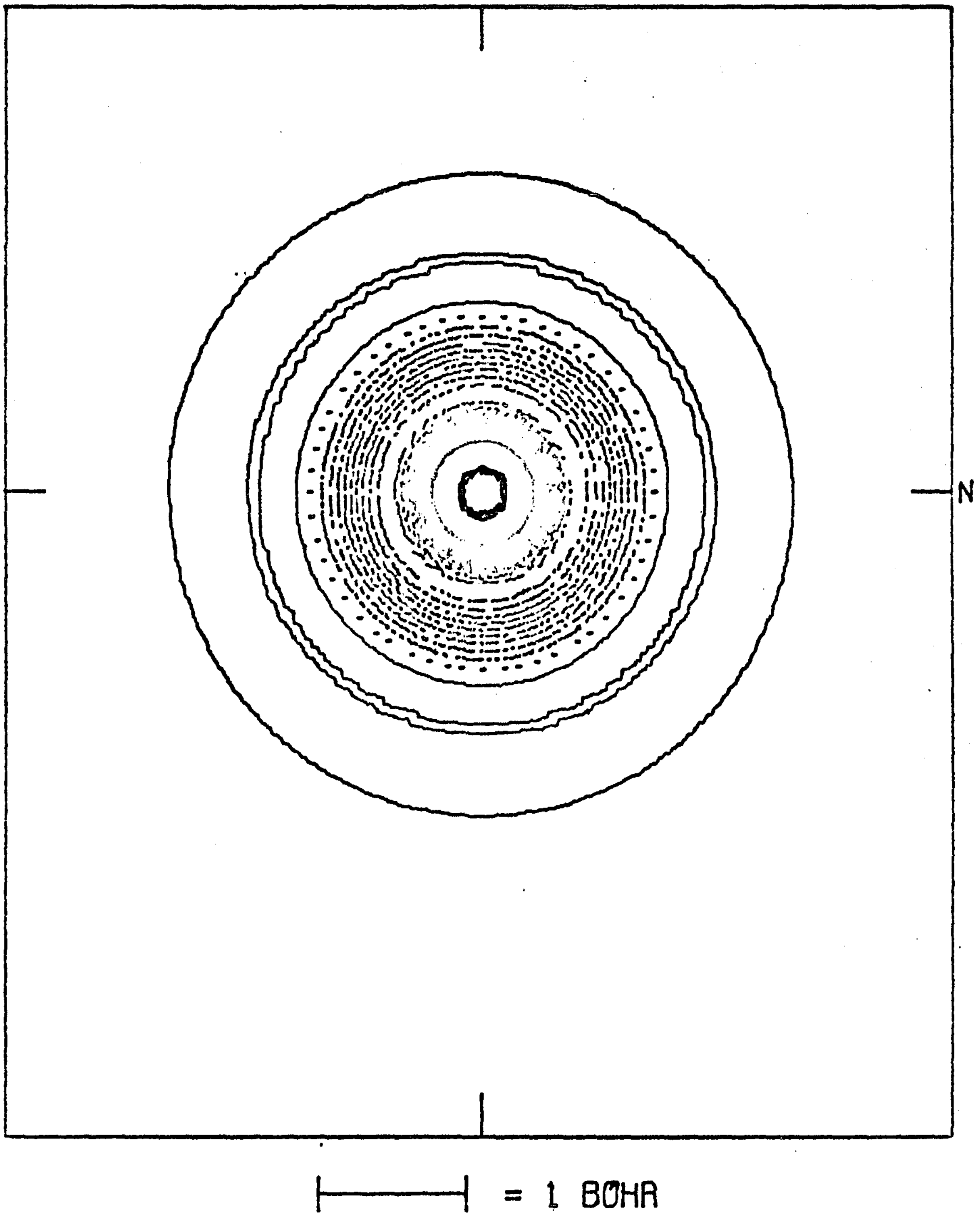
NATURAL ORBITAL CONTOUR MAP 24.
NITROGEN L 1 S 1 (OC=+0.99946)



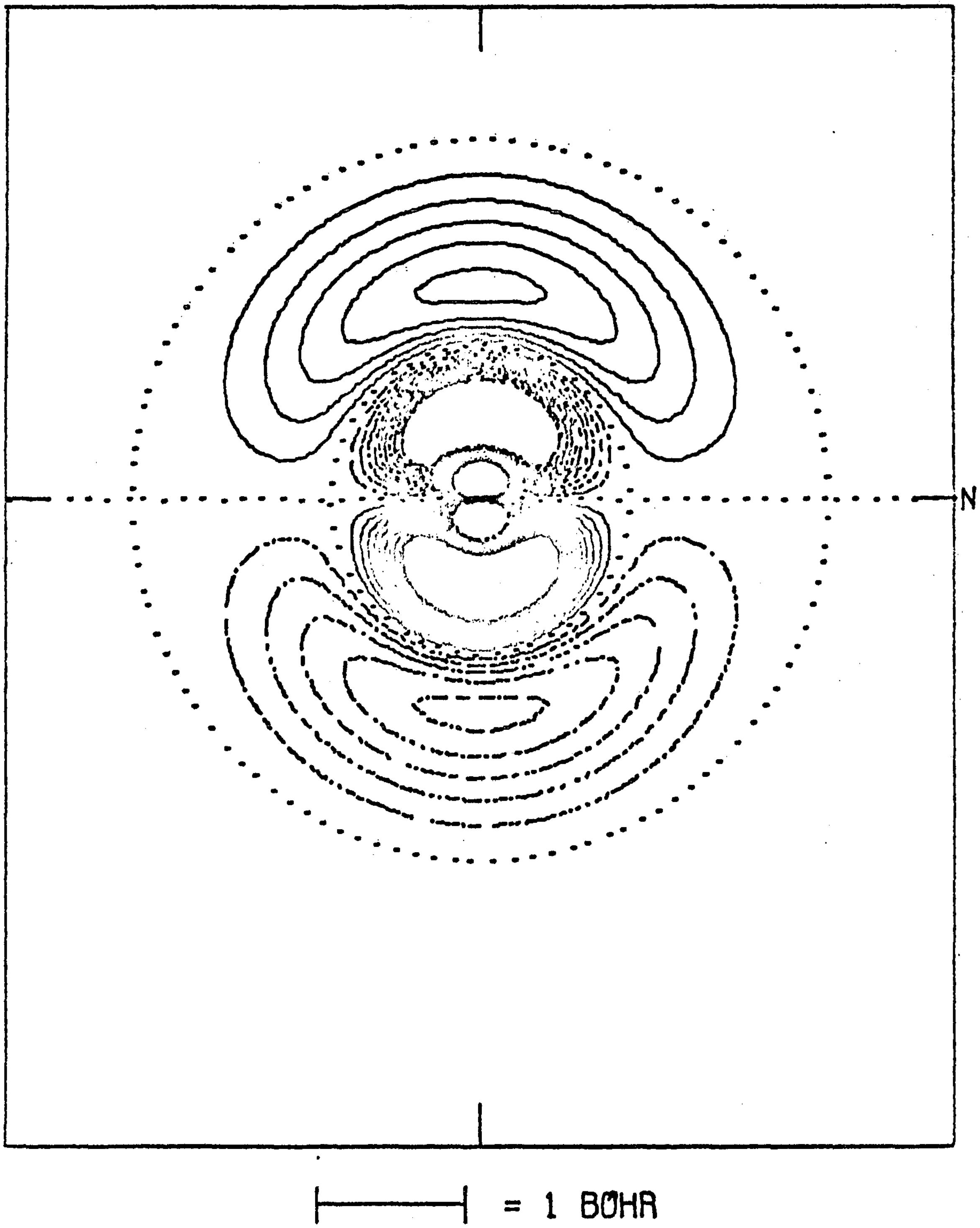
NATURAL ORBITAL CONTOUR MAP 25.
NITROGEN L 2 0 1 (OC=-0.01326)



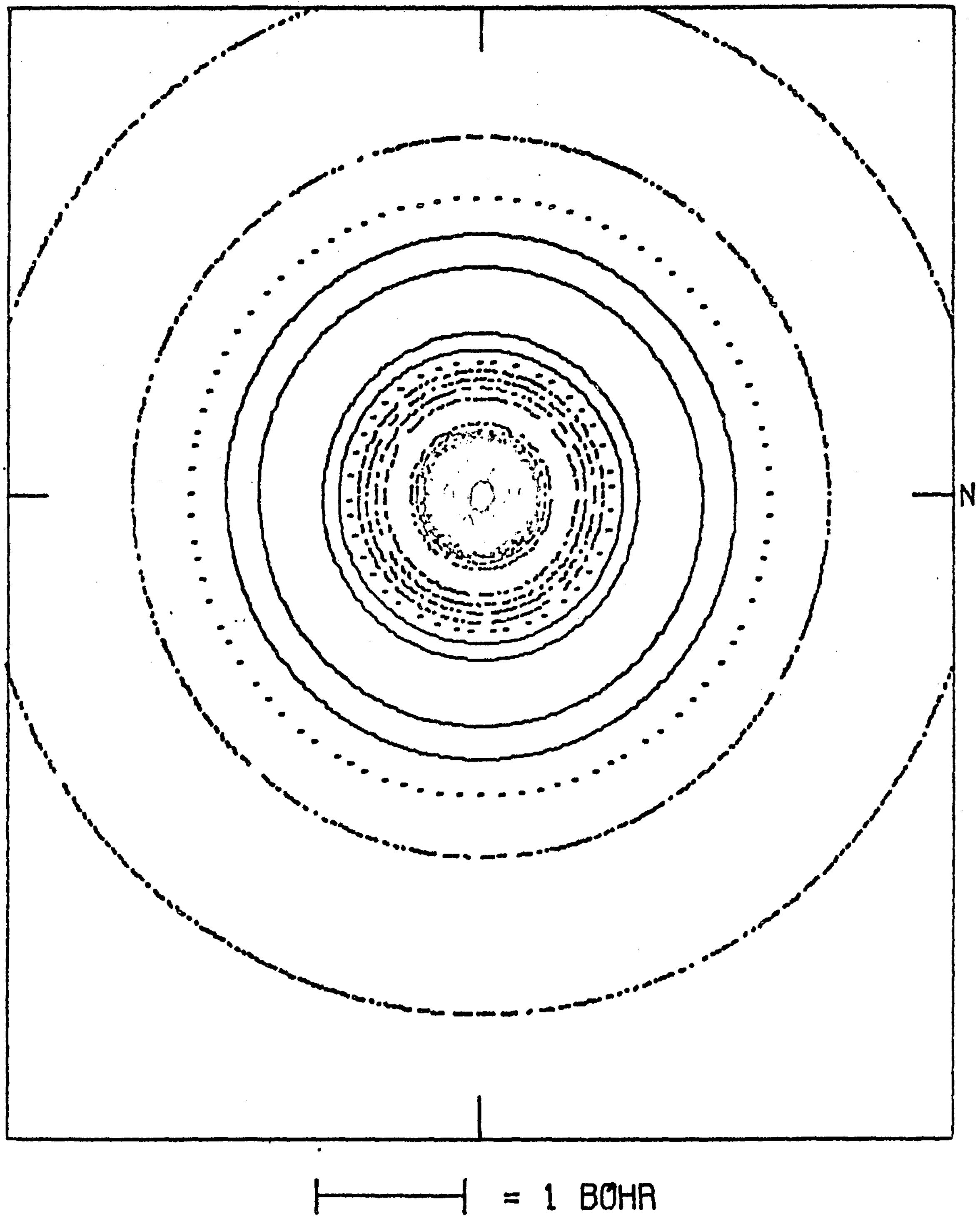
NATURAL ORBITAL CONTOUR MAP 26.
NITROGEN L 3 P 1 (OC=-0.00802)



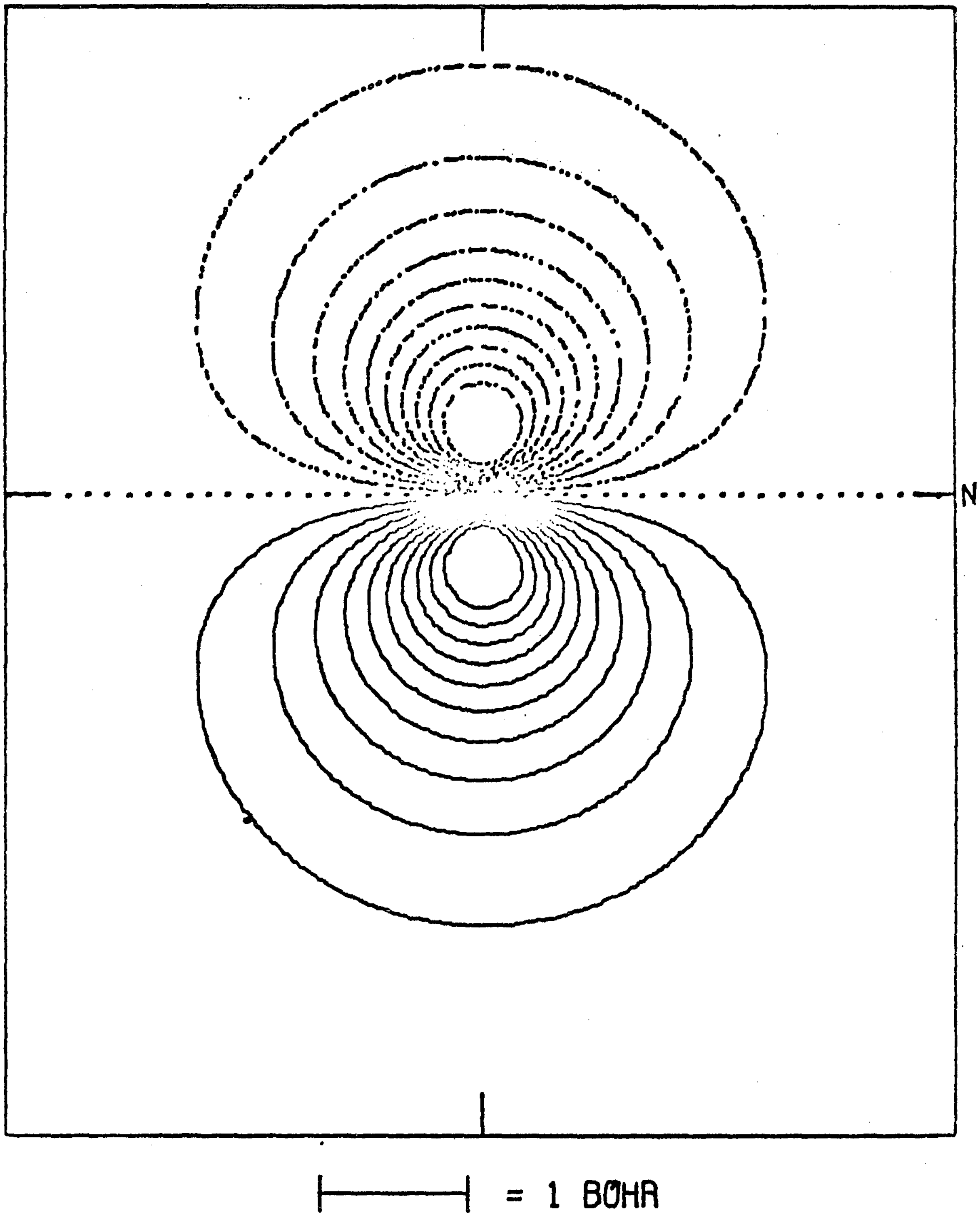
NATURAL ORBITAL CONTOUR MAP 27.
NITROGEN L 4 S 2 (OC=-0.00171)



NATURAL ORBITAL CONTOUR MAP 28.
NITROGEN L 5 P 2 (OC=-0.00169)



NATURAL ORBITAL CONTOUR MAP 29.
NITROGEN L 6 S 3 (OC=-0.00158)



NATURAL ORBITAL CONTOUR MAP 30.
NITROGEN Q 1 P 1 (OC=+1.00000)

CHAPTER II. ATOMIC ORBITAL OVERLAP INTEGRALS

INTRODUCTION

Overlap integrals play an important role in molecular quantum mechanics when atomic orbitals are used for expanding electronic wave functions. Since the expectation values of several one-electron operators can be expressed as linear combinations of overlap integrals, and since Coulomb integrals can be expressed as a quadrature over them (102), their usefulness transcends their function of determining the metric of the non-orthogonal basis set. In the context of *ab initio* calculations of molecular properties, an accurate and efficient method for numerically evaluating these integrals is essential.

Several schemes have recently been reported in the literature (103-105) for this purpose. Although the present investigation owes considerable stimulation to the work mentioned in Reference (103), it is based on a different analysis. The resulting expressions are different and considerably simpler than those obtained before. Compatibility with electronic digital computers has been influential in the arrangement of the resulting equations. The formulation given is particularly advantageous if ample storage capacity for large arrays of numbers is available.

OVERLAP INTEGRALS

Definition

If the normalized Slater-type atomic orbitals on centers A and B are given by

$$(An\ell m;\zeta) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2} r_A^{\,n-1} e^{-\zeta r_A} Y_{\ell m}(\Theta_A\phi_A),$$

$$(Bn'\ell'm';\zeta') = (2\zeta')^{n'+1/2}[(2n')!]^{-1/2} r_B^{\,n'-1} e^{-\zeta' r_B} Y_{\ell'm'}(\Theta_B\phi_B); \tag{105}$$

then the overlap integral between them is

$$S_{nn'}^{\ell\ell'mm'}(\rho_A,\rho_B) = \int dV(An\ell m;\zeta)^*(Bn'\ell'm';\zeta') \tag{106}$$

where

$$\rho_A = R\zeta \quad \text{and} \quad \rho_B = R\zeta' . \tag{107}$$

The coordinate systems on A and B are defined as follows: the z_A axis points toward the origin B, the Z_B axis points toward the origin A, X_A and X_B are parallel, Y_A and Y_B are parallel, and the distance between A and B is R. As a result of this choice, the integral values for R = 0 differ by the factor $(-1)^{\ell+m}$ from what they are when both atomic orbitals are referred to the same coordinate system, namely, $(X_AY_AZ_A)$.

The spherical harmonics can be chosen real or complex. In either case one finds

$$S_{nn'}^{\ell\ell'mm'}(\rho_A,\rho_B) = \delta_{mm'}S_{nn'}^{\ell\ell'm}(\rho_A,\rho_B) \tag{108}$$

where $S_{nn'}^{\ell\ell' m}$ depends only on $|m|$. We therefore consider the case $m \geq 0$. Then

$$Y_{\ell m}(\Theta\,\phi) = \mathcal{P}_{\ell}^{m}(\cos\Theta)\;\Phi_m(\phi) \tag{109}$$

where $\mathcal{P}_{\ell}^{m}$ are the normalized associated Legendre functions and the $\Phi_m(\phi)$ have the property $\int d\phi\; \Phi_m^{*}(\phi)\;\Phi_{m'}(\phi) = \delta_{mm'}$. By Rodrigue's formula, $\mathcal{P}_{\ell}^{m}$ can be expressed as

$$\mathcal{P}_{\ell}^{m}(\cos\Theta) = K_{\ell m}(1-\cos^2\Theta)^{m/2} \sum_{\alpha=m}^{\ell} C_{\alpha}^{\ell m}(\cos\Theta+1)^{\alpha-m}(\cos\Theta-1)^{\ell-\alpha} \tag{110}$$

with

$$K_{\ell m} = [(2\ell+1)\binom{\ell+m}{m}/2^{2\ell+1}\binom{\ell}{m}]^{1/2} \tag{111}$$

$$C_{\alpha}^{\ell m} = \binom{\ell}{\alpha}\binom{\ell}{\alpha+m}. \tag{112}$$

Integration

The integration is performed in elliptic coordinates defined by

$$\begin{aligned}
\xi &= (r_A + r_B)/R & 1 \leq \xi < \infty \\
\eta &= (r_A - r_B)/R & -1 \leq \eta \leq 1 \\
\phi &= \phi_A = \phi_B & 0 \leq \phi \leq 2\pi \\
dV &= (R/2)^3(\xi^2 - \eta^2)\, d\xi\, d\eta\, d\phi .
\end{aligned} \tag{113}$$

The integrand is transformed with the help of the relationships:

$$r_A = \tfrac{1}{2}R(\xi+\eta), \qquad r_B = \tfrac{1}{2}R(\xi-\eta), \tag{114}$$

$$(\cos\Theta_A \pm 1) = (1 \pm \xi)(1 \pm \eta)/(\xi+\eta), \tag{115}$$

$$(\cos \Theta_B \pm 1) = (1 \pm \xi)(1 \mp \eta)/(\xi - \eta), \tag{116}$$

$$(\xi \pm \eta)^j = \sum_{i=0}^{j} \binom{j}{i} (\xi-1)^{j-i} (1 \pm \eta)^i, \tag{117}$$

$$(\xi+1)^j = \sum_{i=0}^{j} \binom{j}{i} 2^i (\xi-1)^{j-i} . \tag{118}$$

Substitution of these identities into the integral and algebraic rearrangements yield

$$S = \rho_A^{n+1/2} \rho_B^{n'+1/2} e^{-\rho} \sum_{\alpha=m}^{\ell} \sum_{\alpha'=m}^{\ell'} \sum_{\beta=0}^{n-\ell} \sum_{\beta'=0}^{n'-\ell'} \sum_{\gamma=0}^{\alpha+\alpha'-m} T_{\alpha\alpha'\beta\beta'\gamma}$$

$$\int_1^{\infty} d\xi e^{-\rho(\xi-1)} (\xi-1)^{n+n'-\beta-\beta'-\gamma} \int_{-1}^{1} d\eta e^{-\sigma\eta} (1+\eta)^{\alpha-\alpha'+\beta+\ell'} (1-\eta)^{\alpha'-\alpha+\beta'+\ell} \tag{119}$$

where

$$T_{\alpha\alpha'\beta\beta'\gamma} = (-1)^{\ell+\ell'+\alpha+\alpha'} K_{\ell m} K_{\ell' m} [(2n)!\,(2n')!]^{-1/2} C_\alpha^{\ell m} C_\alpha^{\ell' m}$$

$$\binom{n-\ell}{\beta} \binom{n'-\ell'}{\beta} \binom{\alpha+\alpha'-m}{\gamma} 2^\gamma \tag{120}$$

and

$$\rho = \frac{1}{2}(\rho_A + \rho_B) , \quad \sigma = \frac{1}{2}(\rho_A - \rho_B). \tag{121}$$

The ξ integration is straight forward, and the η integration leads to the auxiliary functions $I_{\alpha\beta}(x)$, defined by (103, Eq. 19)

$$I = \int_{-1}^{1} d\eta e^{-x\eta} (1+\eta)^\alpha (1-\eta)^\beta = \frac{\alpha!\beta!2^{\alpha+\beta+1}}{(\alpha+\beta+1)!} I_{\alpha\beta}(x) . \tag{122}$$

In Appendix A, it is shown that

$$I = \sum_{\mu=0}^{\alpha+\beta} x^\mu I_\mu (x) W_\mu^{\alpha\beta} \tag{123}$$

where

$$I_\mu(x) = I_{\mu\mu}(x) = [(2\mu+1)/2^{2\mu+1}] \begin{pmatrix} 2\mu \\ \mu \end{pmatrix} \int_{-1}^{1} d\eta(1-\eta^2)^\mu e^{-x\eta} \tag{124}$$

and

$$W_\mu^{\alpha\beta} = 2^{\alpha+\beta+\mu+1} \sum_{\lambda=0}^{\mu} (-1)^\lambda \begin{pmatrix} \alpha+\lambda \\ \alpha \end{pmatrix} \begin{pmatrix} \beta+\mu-\lambda \\ \beta \end{pmatrix} \begin{pmatrix} \mu \\ \lambda \end{pmatrix} / (\mu+1)! \begin{pmatrix} 2\mu \\ \mu \end{pmatrix} \begin{pmatrix} \alpha+\beta \\ \alpha \end{pmatrix} \begin{pmatrix} \alpha+\beta+\mu+1 \\ \alpha+\beta \end{pmatrix}. \tag{125}$$

Thus Eq. 119 becomes:

$$S=(\rho_A{}^{n+1/2}\rho_B{}^{n'+1/2}/\rho^{n+n'+1})\ e^{-\rho} \sum_{\alpha=m}^{\ell} \sum_{\alpha'=m}^{\ell'} \sum_{\beta=0}^{n-\ell} \sum_{\beta'=0}^{n'-\ell'} \sum_{\gamma=0}^{\alpha+\alpha'-m}$$

$$\sum_{\mu=0}^{\ell+\ell'+\beta+\beta'} (n+n'-\beta-\beta'-\gamma)!\ T_{\alpha\alpha'\beta\beta'\gamma}$$

$$W_\mu^{\alpha-\alpha'+\beta+\ell',\alpha'-\alpha+\beta'+\ell}\ \rho^{\beta+\beta'+\gamma}\ \sigma^\mu\ I_\mu(\sigma). \tag{126}$$

The expression, Eq. 126, is now rearranged in two steps. First the summation over γ is replaced by a summation over the new index υ defined by

$$\upsilon = \beta + \beta' + \gamma \tag{127}$$

then the summations are rearranged as follows

$$\sum_{\alpha} \sum_{\alpha'} \sum_{\beta} \sum_{\beta'} \sum_{\mu} \sum_{\upsilon} \longrightarrow \sum_{\mu} \sum_{\upsilon} \sum_{\beta} \sum_{\beta'} \sum_{\alpha} \sum_{\alpha'} \tag{128}$$

and the corresponding changes in the summation limits are made. Thereby one arrives at the final formula

$$S_{nn'}^{\ell\ell'm}(\rho_A,\rho_B) = (2\rho_A/\rho_A+\rho_B)^{n+1/2}(2\rho_B/\rho_A+\rho_B)^{n'+1/2}$$

$$\sum_{\mu=0}^{n+n'} (\rho_A-\rho_B)^\mu\ f_\mu\ g_\mu \tag{129}$$

where

$$f_\mu = I_\mu[(\rho_A-\rho_B)/2] \exp[(\rho_A+\rho_B)/2] \tag{130}$$

$$g_\mu = \sum_{\upsilon=\upsilon_1}^{\upsilon_2} (\rho_A+\rho_B)^{\upsilon} A_{\mu\upsilon}(nn'\ell\ell'm) \tag{131}$$

with the limits

$$\upsilon_1 = \mathrm{Max}\,\{0,\ |\ell-\ell'|-\mu,\ \mu-(\ell+\ell')\} \tag{132}$$

$$\upsilon_2 = n + n' - m. \tag{133}$$

The constants A are defined by

$$A_{\mu\upsilon}(nn'\ell\ell'm)=(-1)^{\ell+\ell'}\left[\frac{(2\ell+1)(2\ell'+1)\binom{\ell+m}{m}\binom{\ell'+m}{m}}{\binom{\ell}{m}\binom{\ell'}{m}\binom{2n}{n}\binom{2n'}{n'}}\right]^{1/2}$$

$$\cdot\frac{(n+n'-\upsilon)!}{n!n'!\binom{2\mu}{\mu}\Delta!}\ B_{\mu\upsilon}(nn'\ell\ell'm) \tag{134}$$

where

$$B_{\mu\upsilon}(nn'\ell\ell'm) = \sum_{\beta=\beta_1}^{\beta_2}\binom{n-\ell}{\beta}\sum_{\beta'=\beta'_1}^{\beta'_2}\binom{n'-\ell'}{\beta'}\frac{\Delta!}{(\mu+\beta+\beta'+\ell+\ell'+1)!}$$

$$\cdot\sum_{\alpha=\alpha_1}^{\ell}(-1)^{\alpha}\binom{\ell}{\alpha}\binom{\ell}{\alpha-m}\sum_{\alpha'=\alpha'_1}^{\ell'}(-1)^{\alpha'}\binom{\ell'}{\alpha'}\binom{\ell'}{\alpha'-m}$$

$$\cdot\binom{\alpha+\alpha'-m}{\upsilon-\beta-\beta'}(\alpha-\alpha'+\beta+\ell')!\ (\alpha'-\alpha+\beta'+\ell)!$$

$$\cdot\sum_{\lambda=0}^{\mu}(-1)^{\lambda}\binom{\alpha-\alpha'+\beta+\ell'+\lambda}{\lambda}\binom{\alpha'-\alpha+\beta'+\ell+\mu-\lambda}{\mu-\lambda}\binom{\mu}{\lambda}. \tag{135}$$

In Eqs. 134 and 135, the following definitions have been used:

$$\Delta = \mathrm{Min}\{\mu+\upsilon+\ell+\ell',\ \mu+n+n'\}+1$$

$$\beta_1 = \mathrm{Max}\{0,\ \mu-n'-\ell,\ \upsilon-n'-\ell+m\}$$

$$\beta_2 = \mathrm{Min}\{n-\ell,\ \upsilon\}$$

$$\beta_1' = \mathrm{Max}\{0,\ \mu-\beta-\ell-\ell',\ \upsilon-\beta-\ell-\ell'+m\}$$
$$\beta_2' = \mathrm{Min}\{n'-\ell',\ \upsilon-\beta\}$$
$$\alpha_1 = \mathrm{Max}\{m, \upsilon-\beta-\beta'-\ell'+m\}$$
$$\alpha_1' = \mathrm{Max}\{m,\ \upsilon-\beta-\beta'-\alpha+m\}.$$

Discussion

The constants B have the symmetry

$$B_{\mu\upsilon}(nn'\ell\ell'm) = (-1)^{\mu}B_{\mu\upsilon}(n'n\ell'\ell m) \qquad (136)$$

corresponding to the identity

$$S_{nn'}^{\ell\ell'm}\ (\rho_A,\rho_B) = S_{n'n}^{\ell'\ell m}\ (\rho_B,\rho_A). \qquad (137)$$

Guided by the observation (103) that the overlap integral should be proportional to $R^{|\ell-\ell'|}$, the constants $B_{\mu\upsilon}$ were investigated and shown to be identically zero whenever $\mu + \upsilon < |\ell-\ell'|$ for all possible combinations of quantum numbers. Thus $R^{|\ell-\ell'|}$ is the lowest power of R occurring in the overlap integral. It was further found that for n=n' and $\ell=\ell'$, $B_{\mu\upsilon}$ is identically zero if μ is odd.

The constants B involve only the multiplication, addition and subtraction of exact integers (the factor Δ used in Eq. 135, is chosen such as to be always greater than $(\mu+\beta+\beta'+\ell+\ell'+1)$ so that the quotient of the corresponding factorials is an exact integer). Therefore, in spite of negative terms, no loss of figures is incurred if integer arithmetic is used to evaluate the B's.

The final constants, $A_{\mu\upsilon}$, Eq. 134, can be computed once for all combinations of quantum numbers desired, stored on tape or disc in a continuous one-dimensional array and read into the computer as a block when a calculation of these integrals is to be made. They are best stored sequentially in the order in which they are used when evaluating the expression in Eq. 131. From a given set of quantum numbers, the starting index which corresponds to the first constant can be generated.

The functions f_μ are discussed in Appendix B.

The special case of $\zeta=\zeta'$ yields

$$S_{nn'}^{\ell\ell'm}(\rho_A,\rho_A) = e^{-\rho_A} \sum_{\upsilon=|\ell-\ell'|}^{n+n'-m} (2\rho_A)^{\upsilon} A_{0\,\upsilon}^{nn'\ell\ell'm} . \qquad (138)$$

NUCLEAR ATTRACTION AND KINETIC ENERGY INTEGRALS

An energy minimization calculation implies the continued recalculation of certain one-electron two-center integrals for each variation of the atomic orbitals. Considerable savings of computational time can be achieved by calculating certain two-center nuclear attraction, kinetic energy and overlap integrals at the same time. The former types of integrals are given by the following standard formulas (106):

$$<(An\ell m;\zeta)\ \left|\frac{-Z_A}{r_A}\right|\ (Bn'\ell'm';\zeta')> = -Z_A\ \delta_{mm'}a_n\zeta S^{\ell\ell'm}_{n-1,n'}\ (\rho_A,\rho_B) \quad (139)$$

$$<(An\ell m;\zeta)\left|\ \frac{-Z_B}{r_B}\ \right|(Bn'\ell'm';\zeta')> = -Z_B\ \delta_{mm'}a_{n'}\zeta' S^{\ell\ell'm}_{nn'-1}\ (\rho_A,\rho_B) \quad (140)$$

$$<(An\ell m;\zeta)\ \left|-\tfrac{1}{2}\nabla^2\right|\ (Bn'\ell'\ m';\zeta')> = -\ \tfrac{1}{2}\zeta^2\ \delta_{mm'}\{S^{\ell\ell'm}_{nn'}\ (\rho_A,\rho_B)$$

$$+\ b_n S^{\ell\ell'm}_{n-1,n'}\ (\rho_A,\rho_B)\ +\ \delta_{0,n-\ell-1}c_{n\ell}\ S^{\ell\ell'm}_{n-2,n'}(\rho_A,\rho_B)\} \quad (141)$$

where

$$a_n = \left[\frac{2}{n(2n-1)}\right]^{1/2}$$

$$b_n = -\left[\frac{8n}{2n-1}\right]^{1/2} \quad (142)$$

$$c_n = \frac{2(n+\ell)(n-\ell-1)}{[n(n-1)(2n-1)(2n-3)]}^{1/2}\ .$$

Thus it can be seen that for a particular pair of orbitals, only one array of the functions $f_\mu(\rho_A,\rho_B)$, needs to be calculated for $0\leq\mu\leq n+n'$. From this <u>one</u> set of f values, the overlap function S with subscript pairs (n,n'), (n-1,n'), (n, n'-1) and if necessary (n-2, n') can be computed by summing the double series in Eq. 129. Since the calculation of the f functions represents the largest expenditure of time, this grouping is economical.

COMPUTATION TIMES

For each of the 83 distinct combinations of the quantum numbers, $(n\ell m)$ and $(n'\ell'm)$ which give rise to non-zero integrals for n and $n' \leq 4$, the two-center overlap, kinetic energy and nuclear attraction integrals, as described above, were computed and timed for the most time consuming case of $\zeta_a \neq \zeta_b$. By taking all integrals with a given value of $n_{av} = (n + n')/2$ and averaging the observed times per integral, the following formula was found to give the computation time dependence of these integrals on the average principal quantum number n_{av}:

time per integral = $1.1 + 0.5\, n_{av}^2$ (milliseconds/integral).

Calculations of all two-center integrals of the above types occurring over basis sets of orbitals (again with different orbital exponents) were performed and timed as a function of N, the number of orbitals on each center: N = 1 correspondng to a 1s orbital on each center, N = 2 corresponding to a 1s and 2s orbital on each center, . . . , N = 14 corresponding to 1s, 2s, $2p\sigma$, $2p\pi$, $2p\bar{\pi}$, 3s, $3p\sigma$, $3p\pi$, $3p\bar{\pi}$, $3d\sigma$, $3d\pi$, $3d\bar{\pi}$, $3d\delta$, $3d\bar{\delta}$ on each center. By taking the value of the total time spent in each case and dividing by the number of non-zero integrals actually computed, the following formula was found:

$$\left(\begin{array}{l}\text{Average time per}\\ \text{non-zero integral}\end{array}\right) = 1.4 + 0.4\ N - 0.01\ N^2 \ \text{(milliseconds/integral).}$$

However, dividing the total computation time in each case by the *total* number of integrals, N^2, which includes those integrals that are identically zero, gives an average time of 1.9 ± 0.3 milliseconds per integral, independent of N.

The times quoted here were obtained on an IBM 360/50 computer using all FORTRAN programs with double precision arithmetic and making use of the criteria discussed in Appendix B for computing the functions f_μ to ten figures. Multiplication by 0.3 would give times comparable with IBM 7094-type equipment.

APPENDIX A: DERIVATION OF EQUATION 123

It can be shown that the functions in Eq. 124,

$$I_k(x) = I_{kk}(x) = \frac{2k+1}{2^{2k+1}} \binom{2k}{k} \int_{-1}^{1} d\eta e^{-x\eta}(1-\eta^2)^k, \qquad \text{(A1)}$$

can be expressed as

$$I_k(x) = \frac{(-1)^k k!\ (2k+1)}{x^k\ 2^{k+1}} \binom{2k}{k} \int_{-1}^{1} d\eta e^{-x\eta}\ P_k(\eta). \qquad \text{(A2)}$$

The expression of Eq. 123 is therefore obtained by substituting in Eq. 122 the expansion,

$$(1+\eta)^{\alpha}(1-\eta)^{\beta} = \sum_{k=0}^{\alpha+\beta} D_k^{\alpha\beta} P_k(\eta) \qquad \text{(A3)}$$

where

$$D_k^{\alpha\beta} = \frac{1}{2}(2k+1) \int_{-1}^{1} P_k(\eta)(1+\eta)^{\alpha}(1-\eta)^{\beta} d\eta. \qquad \text{(A4)}$$

Using, in Eq. A4, the representation,

$$P_k(\eta) = 2^{-k} \sum_{\lambda=0}^{k} \binom{k}{\lambda}^2 (\eta+1)^{\lambda}(\eta-1)^{k-\lambda}, \qquad \text{(A5)}$$

one finds

$$D_k^{\alpha\beta} = (2k+1)2^{\alpha+\beta}(-1)^k \sum_{\lambda=0}^{k} (-1)^{\lambda} \binom{k}{\lambda}^2 \frac{(\alpha+\lambda)!(\beta+k-\lambda)!}{(\alpha+\beta+k+1)!} \qquad \text{(A6)}$$

whence Eq. 123 follows directly. A different expansion of these functions has been discussed by Roothaan (107). It may also be mentioned that

$$I_k(x) = [(2k+1)!/k](2ix)^{-k} j_k(ix) \qquad \text{(A7)}$$

where $j_k(z)$ is the spherical Bessel function (108, p. 437, 443).

APPENDIX B: DISCUSSION OF AUXILIARY FUNCTIONS $f_\mu(\rho_A,\rho_B)$

The functions $f_\mu(\rho_A,\rho_B)$ are proportional to the confluent hypergeometric functions:

$$f_\mu(\rho_A,\rho_B) = e^{-\rho_A}\,{}_1F_1\,(\mu+1,\ 2\mu+2;\ \rho_A-\rho_B)$$

$$= e^{-\rho_B}\,{}_1F_1\,(\mu+1,\ 2\mu+2;\rho_B-\rho_A). \qquad \text{(B1)}$$

and can also be represented by the generalized hypergeometric series:

$$f_\mu(\rho_A,\rho_B) = e^{-(\rho_A+\rho_B)/2}\ {}_0F_1[\mu+3/2;\ (\rho_A-\rho_B/2)^2]. \qquad \text{(B2)}$$

From this representation follows the property:

$$f_\mu(\rho_A,\rho_B) = f_\mu(\rho_B,\rho_A) \qquad \text{(B3)}$$

which was used in Eq. 137. It is also easily shown that the following relation is satisfied:

$$\exp[\mathrm{Min}(\rho_A,\rho_B)] \leq f_\mu(\rho_A,\rho_B) \leq \exp[\mathrm{Max}(\rho_A,\rho_B)]. \qquad \text{(B4)}$$

These functions can be calculated by means of the recurrence relation

$$f_\mu(\rho_A,\rho_B) = [4(2\mu+1)(2\mu-1)/(\rho_A-\rho_B)^2][f_{\mu-2}(\rho_A,\rho_B)$$

$$- f_{\mu-1}(\rho_A,\rho_B)], \qquad \text{(B5)}$$

where the starting functions are given by:

$$f_{-1}(\rho_A,\rho_B) = \tfrac{1}{2}(e^{-\rho_B} + e^{-\rho_A}) \qquad \text{(B6)}$$

$$f_0(\rho_A,\rho_B) = (e^{-\rho_B} - e^{-\rho_A})/(\rho_A - \rho_B) \qquad \text{(B6')}$$

$$f_\mu(\rho_A,\rho_A) = e^{-\rho_A} . \tag{B7}$$

Using an IBM 360/50 with double precision arithmetic, the relation (B5), gives ten or more significant figure results whenever

$$|\rho_A-\rho_B| \geq (-0.13 + 0.15\ \mu_{max})\ \mu_{max} \tag{B8}$$

is satisfied. Here μ_{max} represents the highest index value μ needed for a particular integral, namely $\mu_{max}=n+n'$. When $(\rho_A-\rho_B)$ is smaller than given by Eq. B8, then f_μ is calculated by means of a continued fraction (109):

$$f_\mu(\rho_A,\rho_B) = r_\mu(\rho_A,\rho_B)\ f_{\mu-1}(\rho_A,\rho_B) \tag{B9}$$

where

$$r_\mu(\rho_A,\rho_B) = \{1+[(\rho_A-\rho_B)^2/4(2\mu+1)(2\mu-1)]r_{\mu+1}(\rho_A,\rho_B)\}^{-1}. \tag{B10}$$

The number of terms t, needed in the continued fraction in order to guarantee convergence to ten significant places was found to be approximately:

$$t = \text{largest integer in } \{2.5 + 3.75|\rho_A-\rho_B|/\mu_{max}\}. \tag{B11}$$

The values of the cut-off points for the two schemes in Eq. B8 and B11 can be stored as an array indexed by μ_{max} so that only a negligible amount of time is used to determine which method to use.

The accuracy with which the functions f_μ are calculated determines the accuracy of the final result since the remaining factors in Eq. 129 can all be calculated without any loss of figures. For a particular problem, the criteria in Eqs. B8 and B11 can be adjusted to yield optimal balance between speed and accuracy.

CHAPTER III. ATOMIC ORBITAL COULOMB INTEGRALS

INTRODUCTION

The accurate and efficient numerical evaluation of electron repulsion integrals is a necessary and essential step in molecular calculations. Among them, the one-center integrals, and the two-center Coulomb integrals are the largest in magnitude. The latter moreover, have long-range character and cannot be neglected even for large internuclear distances.

Recently, O-Ohata and Ruedenberg (102) observed that a Coulomb integral, C, is related to a corresponding overlap integral, S, by Poisson's equation $\Delta C = -4\pi S$, and that methods for evaluating Coulomb integrals can therefore be obtained from appropriate overlap integral representations with the help of the potential integral $C = \int dV\, S/r$. Using their own results for overlap integrals (103), they furthermore derived certain expressions for Coulomb integrals (102). It has been found that these expressions, although useful in various respects, still contain some cumbersome parts and numerical instabilities, but that these shortcomings can be eliminated if, instead, one inserts in the potential integral the new overlap formulation given in the preceding chapter. The results, which are given below, furnish an efficient procedure involving a finite triple sum over powers, two special functions and constants.

In this scheme, no advantage is being taken of those economies which result from an explicit use of the charge distribution concept (110,111,104) but as a compensation, all manipulations involving the four quantum-number doubles, ℓm, can be embedded in the constants which can be calculated once and for all. Thereafter they can be stored permanently for use in the evaluation of specific Coulomb integrals. In contrast to other procedures advanced for these integrals (105,112), the expressions given here gain in accuracy or can be computed to the same accuracy in less time when the orbital exponents of the atomic orbitals on one center approach those on the other center.

DEFINITIONS

Let a real, normalized, Slater-type atomic orbital on nucleus A, as a function of particle i, be denoted by

$$(An\ell m\zeta,\ i) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2} r_{Ai}^{n-1}\ e^{-r_{Ai}}\ \mathcal{Y}_{\ell m}(\theta_{Ai}\phi_{Ai}). \quad (143)$$

Then the Coulomb integral is defined as

$$\begin{aligned} C &= [An_1\ell_1m_1\zeta_1An_2\ell_2m_2\zeta_2 \mid Bn_3\ell_3m_3\zeta_3Bn_4\ell_4m_4\zeta_4] \\ &= \int dV_1 \int dV_2 (An_1\ell_1m_1\zeta_1,1)(An_2\ell_2m_2\zeta_2,1) \\ &\cdot (r_{12}^{-1})(Bn_3\ell_3m_3\zeta_3,2)(Bn_4\ell_4m_4\zeta_4,2). \end{aligned} \quad (144)$$

The real spherical harmonics, $\mathcal{Y}_{\ell m}$, are defined by

$$\begin{aligned} \mathcal{Y}_{\ell m}(\theta\phi) &= \mathcal{P}_\ell^{|m|}(\cos\theta)[(1+\delta_{m,0})\pi]^{-1/2} \cos m\phi, \quad m \geq 0 \\ &= \mathcal{P}_\ell^{|m|}(\cos\theta)\pi^{-1/2} \sin|m|\phi, \quad m < 0 \end{aligned} \quad (145)$$

where $\mathcal{P}_\ell^{|m|}$ are the normalized associated Legendre functions. The coordinate system used here is the same as in the preceding chapter and R is the internuclear distance.

The Coulomb integral, Eq. 144, will be evaluated with the help of the Poisson equation (102),

$$\nabla^2 C = -4\pi S \quad (146)$$

where

$$S = \int dV_1 (An_1\ell_1m_1\zeta_1,\ 1)(An_2\ell_2m_2\zeta_2,1)(Bn_3\ell_3m_3\zeta_3,1)(Bn_4\ell_4m_4\zeta_4,1) \quad (147)$$

and the differentiations in ∇^2 refer to the components of the interatomic distance.

By virtue of the discussion in (102, section 5), the overlap integral, S, just introduced can be related to the overlap integrals defined in Eq. 106 in the preceding chapter by the identity

$$S = \sum_{\ell_A \ell_B} \sum_{m_A m_B} P \, S_{n_A n_B}^{\ell_A \ell_B m_A m_B} (\zeta_A R, \zeta_B R) \tag{148}$$

where the symbol P is used to abbreviate the expression:

$$P = (2\ell_A+1)^{1/2} \, p(n_1\ell_1\zeta_1, n_2\ell_2\zeta_2) \, q_{\ell_A m_A}(\ell_1 m_1 \ell_2 m_2)$$

$$\cdot \, (2\ell_B+1)^{1/2} \, p(n_3\ell_3\zeta_3, n_4\ell_4\zeta_4) \, q_{\ell_B m_B}(\ell_3 m_3 \ell_4 m_4). \tag{149}$$

In Eqs. 148 and 149, the following definitions are used:

$$n_A = n_1 + n_2 - 1 \qquad n_B = n_3 + n_4 - 1 \tag{150}$$

$$\zeta_A = \zeta_1 + \zeta_2 \qquad \zeta_B = \zeta_3 + \zeta_4 \tag{151}$$

$$p(n_1\ell_1\zeta_1, n_2\ell_2\zeta_2) = [2(\ell_1+1)(\ell_2+1)(2n_1+2n_2-2)!/\pi(2n_1)!(2n_2)!]^{1/2}$$

$$\cdot \, \zeta_1^{\,n_1+1/2} \, \zeta_2^{\,n_2+1/2} / (\zeta_1+\zeta_2)^{n_1+n_2-1/2} . \tag{152}$$

The summation over ℓ_A is limited by

$$|\ell_1 - \ell_2| \le \ell_A \le \ell_1 + \ell_2, \quad \ell_1 + \ell_2 + \ell_A = \text{even} \tag{153}$$

and the summation over m_A is restricted to the two values, m_{A+} and m_{A-}, given by

$$m_{A\pm} = \text{sign } (m_1) \text{ sign } (m_2) \; | \, (|m_1| \pm |m_2|) \, | \tag{154}$$

where

$$\mathrm{sign}\ (x) = x/|x| \text{ and } \mathrm{sign}\ (0) = +1. \tag{155}$$

The remaining quantities are:

$$q_{\ell_A m_{A+}}(\ell_1 m_1 \ell_2 m_2) = \varepsilon_+(m_1,m_2)(-1)^{m_1+m_2}[1+\delta_{0,m_1 m_2}]^{1/2}/\sqrt{2} \cdot \begin{pmatrix} \ell_1 & \ell_2 & \ell_A \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_A \\ |m_1| & |m_2| & -(|m_1|+|m_2|) \end{pmatrix} \tag{156}$$

$$q_{\ell_A m_{A-}}(\ell_1 m_1 \ell_2 m_2) = \varepsilon_-(m_1,m_2)(-1)^{\mathrm{Max}\{|m_1|,\ |m_2|\}}[1+\delta_{m_1,m_2}]^{1/2}/\sqrt{2} \cdot \begin{pmatrix} \ell_1 & \ell_2 & \ell_A \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_A \\ -|m_1| & |m_2| & (|m_1|-|m_2|) \end{pmatrix} \tag{157}$$

where the symbol, $\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is the Wigner 3j coefficient (113 and 103, Eqs. 3.19 to 3.22) and ε_+ and ε_- depend upon the signs of the product, $(m_1 m_2)$, and the sum, (m_1+m_2), according to Figure 1. The parameters ℓ_B and m_B are similarly related to $\ell_3 m_3 \ell_4$ and m_4.

$(m_1 m_2)$	(m_1+m_2)	ε_+	ε_-
+	+	1	1
+	-	-1	1
-	+	1	-1
-	-	1	1
-	0	1	0
0	+,0,-	1	0

Figure 1. Values for Epsilons

DERIVATION

Integration of Poisson Equation

The integration of Eq. 146 is discussed in (102, section 1.4) and its application to the present case leads to:

$$C = 4\pi \sum_{\ell_A \ell_B} \sum_{m_A m_B} P \sum_{LM} \begin{pmatrix} \ell_A & \ell_B & L \\ m_A & -m_B & 0 \end{pmatrix} \begin{pmatrix} \ell_A & \ell_B & L \\ M & -M & 0 \end{pmatrix}$$

$$\cdot \left\{ R^{-L-1} \int_0^R dR'(R')^{L+2} S_{n_A n_B}^{\ell_A \ell_B M} (R\zeta_A, R'\zeta_B) \right.$$

$$\left. + R^L \int_R^\infty dR'(R')^{-L+1} S_{n_A n_B}^{\ell_A \ell_B M} (R'\zeta_A, R'\zeta_B) \right\}, \qquad (158)$$

where $S_{n_A n_B}^{\ell_A \ell_B M}$ is the overlap integral defined in Eq. 129 of the preceding chapter. The summation over L is limited by

$$|\ell_A - \ell_B| \leq L \leq \ell_A + \ell_B, \quad \ell_A + \ell_B + L = \text{even} \qquad (159)$$

and the summation over M is restricted to

$$-\min \{\ell_A, \ell_B\} \leq M \leq + \min \{\ell_A, \ell_B\}. \qquad (160)$$

Introduction of Auxiliary Functions

The expression enclosed in braces in Eq. 158 can be transformed as follows:

$$K = \{\ldots\} = R^2 \left[\int_0^1 dt\ t^{L+2} S_{n_A n_B}^{\ell_A \ell_B M} (t\rho_A, t\rho_B) \right.$$

$$\left. + \int_1^\infty dt\ t^{-L+1} S_{n_A n_B}^{\ell_A \ell_B M} (t\rho_A, t\rho_B) \right], \qquad (161)$$

with

$$\rho_i = R\zeta_i . \tag{162}$$

Substitution of Eq. 129 from the preceding chapter into Eq. 161 yields

$$K = R^2 P' \sum_{\mu=0}^{n_A+n_B} (\rho_A - \rho_B)^{\mu} \left[\int_0^1 dt\ t^{\mu+L+2} f_{\mu}(t\rho_A, t\rho_B) g_{\mu}(t\rho_A, t\rho_B) \right.$$

$$\left. + \int_1^{\infty} dt\ t^{\mu-L+1}\ f_{\mu}(t\rho_A, t\rho_B) g_{\mu}(t\rho_A, t\rho_B) \right] \tag{163}$$

where P' is an abbreviation for

$$P' = (2\rho_A/\rho_A + \rho_B)^{n_A+1/2} (2\rho_B/\rho_A + \rho_B)^{n_B+1/2} . \tag{164}$$

The functions g_{μ} and f_{μ} were defined in Eqs. 130 and 131 of the preceding chapter, respectively. The function f_{μ} was discussed further in Appendix B of that chapter.

We substitute the definition of g_{μ} into Eq. 163 and define the auxiliary functions:

$$G_{n,\mu}(x,y) = \int_0^1 dt\ t^n\ f_{\mu}(tx,\ ty) \tag{165}$$

$$H_{n,\mu}(x,y) = \int_1^{\infty} dt\ t^n\ f_{\mu}(tx,\ ty). \tag{166}$$

Thus we obtain for K the expression

$$K = R^2 P' \sum_{\mu=0}^{n_a+n_b} (\rho_A - \rho_B)^{\mu} \sum_{\nu=\nu_1}^{\nu_2} (\rho_A + \rho_B)^{\nu} A_{\mu\nu}(n_A n_B \ell_A \ell_B M)$$

$$\cdot \left[G_{\mu+\nu+L+2,\mu}(\rho_A, \rho_B) + H_{\mu+\nu-L+1,\mu}(\rho_A, \rho_B) \right] \tag{167}$$

where the limits, ν_1 and ν_2, and the constants $A_{\mu\nu}$ are defined by Eqs. 132, 133 and 134, respectively in the preceding chapter.

Substition of this expression into Eq. 158 yields

$$C = 4\pi R^2 P' \sum_{\ell_A \ell_B} \sum_{m_A m_B} \tilde{P} \sum_{LM} \begin{pmatrix} \ell_A & \ell_B & L \\ m_A & -m_B & 0 \end{pmatrix}$$

$$\cdot \begin{pmatrix} \ell_A & \ell_B & L \\ M & -M & 0 \end{pmatrix} \sum_{\mu} (\rho_A - \rho_B)^{\mu} \sum_{\nu} (\rho_A + \rho_B)^{\nu} A_{\mu\nu}(n_A n_B \ell_A \ell_B M),$$

$$\cdot [G_{\mu+\nu+L+2,\mu}(\rho_A, \rho_B) + H_{\mu+\nu-L+1,\mu}(\rho_A, \rho_B)]. \tag{168}$$

Rearrangement of Summations

Finally we rearrange Eq. 168 by interchanging summations as follows:

$$\sum_{\ell_A} \sum_{\ell_B} \sum_{m_A} \sum_{m_B} \sum_{L} \sum_{M} \sum_{\mu} \sum_{\nu} \longrightarrow \sum_{\mu} \sum_{\nu} \sum_{L} \sum_{m_A} \sum_{m_B} \sum_{\ell_A} \sum_{\ell_B} \sum_{M} \tag{169}$$

and by making the corresponding changes in summation limits. Thereby we arrive at the end result

$$C = Z \sum_{\mu=0}^{n_A+n_B} (\rho_A - \rho_B)^{\mu} \sum_{\nu=\nu_{min}}^{n_A+n_B} (\rho_A + \rho_B)^{\nu} \sum_{L=L_{min}}^{L_{max}} D_{\mu\nu L}$$

$$\cdot [G_{\mu+\nu+L+2,\mu}(\rho_A, \rho_B) + H_{\mu+\nu-L+1,\mu}(\rho_A, \rho_B)] \tag{170}$$

with the limits and restrictions

$\nu_{min} = \mathrm{Max}\ [\nu^*,\ \mu-(\ell_1+\ell_2+\ell_3+\ell_4),\ |\ell_1-\ell_2|-(\ell_3+\ell_4+\mu),$

$$|\ell_3-\ell_4|-(\ell_1+\ell_2+\mu)]$$

$$\nu^* = \begin{bmatrix}0\\1\end{bmatrix} \text{ if } \ell_1+\ell_2+\ell_3+\ell_4+\mu \text{ is } \begin{bmatrix}\text{even}\\\text{odd}\end{bmatrix}$$

$$L_{min} = \text{Max}\{0,\ \mu-\nu,\ |\ell_1-\ell_2|-(\ell_3+\ell_4),\ |\ell_3-\ell_4|-(\ell_1+\ell_2)\}$$

$$L_{max} = \text{Min}\ \{\ell_1+\ell_2+\ell_3+\ell_4,\ \mu+\nu\}$$

$$L + \ell_1+\ell_2+\ell_3+\ell_4 = \text{even}.$$

The coefficient Z is given by

$$\begin{aligned} Z &= Z(R\zeta_1\zeta_2\zeta_3\zeta_4 n_1 n_2 n_3 n_4) \\ &= R^{-1} \prod_{i=1}^{4} \{(2\rho_i)^{n_i+1/2}\ [(2n_i)!]^{-1/2}\}/(\sum_{i=1}^{4} \rho_i)^{n_A+n_B+1}. \end{aligned} \tag{171}$$

The constants $D_{\mu\nu L}$ are given by

$$\begin{aligned} D_{\mu\nu L}(n_A\ell_1 m_1\ell_2 m_2,\ n_B\ell_3 m_3\ell_4 m_4) &= Q(n_A+n_B-\nu)!/\binom{2\mu}{\mu} \\ &\cdot \sum_{m_A m_B} \delta_{m_A,m_B} \sum_{\ell_A=\ell_{A,min}}^{\ell_{A,max}} q_{\ell_A,m_A}(\ell_1 m_1\ell_2 m_2) \\ &\cdot (2\ell_A+1)[(\ell_A+m)!\ (\ell_A-m)!]^{1/2}/\ell_A! \sum_{\ell_B=\ell_{B,min}}^{\ell_{B,\ max}} q_{\ell_B,m_B}(\ell_3 m_3\ell_4 m_4) \\ &\cdot (2\ell_B+1)[(\ell_B+m)!\ (\ell_B-m)!]^{1/2}/\ell_B! \begin{pmatrix}\ell_A & \ell_B & L\\ m & -m & 0\end{pmatrix} \\ &\cdot \sum_{M=0}^{M_{max}} [(2-\delta_{M,0})/\Delta!][(\ell_a+M)!(\ell_a-M)!(\ell_B+M)!(\ell_B-M)!]^{1/2} \\ &\cdot \begin{pmatrix}\ell_A & \ell_B & L\\ M & -M & 0\end{pmatrix} B_{\mu\nu}(n_A n_B \ell_A \ell_B M) \end{aligned} \tag{172}$$

where the constants $B_{\mu\upsilon}$ are defined in Eq. 135 of the preceding chapter and the following further definitions have been introduced:

$$Q = \prod_{i=1}^{4} [(-1)^{\ell_i} (2\ell_i+1)^{1/2}]$$

$$m = |m_A|$$

$$\ell_{A,min} = \mathrm{Max}\{m, |\ell_1-\ell_2|, |\ell_3-\ell_4|-L, L-(\ell_3+\ell_4)\}$$

$$\ell_{A,max} = \mathrm{Min}\{\ell_1+\ell_2, L+\ell_3+\ell_4\}$$

$$\ell_{B,min} = \mathrm{Max}\{m, |\ell_3-\ell_4|, |L-\ell|\}$$

$$\ell_{B,max} = \mathrm{Min}\{\ell_3+\ell_4, L+\ell\}$$

$$M_{max} = \mathrm{Min}\ \{\ell_A, \ell_B, n_a+n_b-\nu\}$$

$$\Delta = \mathrm{Min}\{\mu+\nu+\ell_A+\ell_B, \mu+n_A+n_B\}+1.$$

The indices ℓ_A and ℓ_B are subject to the restrictions:

$$\ell_1+\ell_2+\ell_A = \text{even and } \ell_3+\ell_4+\ell_B = \text{even.}$$

Case of Equal Orbital Exponents

For the special case of $\rho_A = \rho_B$, one finds that in Eq. 170 the only surviving term of the summation over μ is $\mu = 0$ and therefore,

$$C = Z \sum_{\upsilon=\upsilon_{min}}^{n_A+n_B} (2\rho_A)^{\nu} \sum_{L=L_{min}}^{L_{max}} [E_{\nu+L+2}(\rho_A) + A_{\nu-L+1}(\rho_A)]D_{0\nu L} \quad (173)$$

where (104, Eqs. III.35 and III.34)

$$E_n(x) = \int_0^1 dt\ t^n\ e^{-xt} = G_{n,\mu}(x,x) \quad (174)$$

$$A_n(x) = \int_1^{\infty} dt\ t^n\ e^{-xt} = H_{n,\mu}(x,x). \quad (175)$$

DISCUSSION

The Constants $D_{\mu\nu L}$

The constants $D_{\mu\nu L}$ are invariant when $(\ell_1 m_1)$ is permuted with $(\ell_2 m_2)$ and/or when $(\ell_3 m_3)$ is permuted with $(\ell_4 m_4)$. Moreover, from Eq. 136 of the preceding chapter, it follows that

$$D_{\mu\nu L}(n_A \ell_1 m_1 \ell_2 m_2,\ n_B \ell_3 m_3 \ell_4 m_4) = (-1)^{\mu}\ D_{\mu\nu L}(n_B \ell_3 m_3 \ell_4 m_4,\ n_A \ell_1 m_1 \ell_2 m_2), \tag{176}$$

whence

$$D_{\mu\nu L}(n\ell_1 m_1 \ell_2 m_2,\ n\ell_1 m_1 \ell_2 m_2) = 0, \text{ for } \mu = \text{odd}. \tag{177}$$

The summation over μ in Eq. 170 can therefore be restricted to even values if the quantum numbers, $n_B \ell_3 m_3 \ell_4 m_4$, are equal to the quantum numbers, $n_A \ell_1 m_1 \ell_2 m_2$, respectively.

Index Limits

In order to evaluate a particular integral, one requires a table of $G_{n\mu}$ functions and a table of $H_{n\mu}$ functions. In both, the index μ is limited by the inequality

$$0 \leq \mu \leq n_A + n_B, \tag{178}$$

while the limits on the index n differ for the two tables and are functions of μ. For $G_{g\mu}$, the index g ranges from g_{min} to g_{max} where

$$g_{min} = \begin{cases} 2\alpha+2 & \text{when } 0 \leq \mu \leq \alpha \\ 2\mu+2 & \text{when } \alpha \leq \mu \leq n_A+n_B \end{cases} \tag{179}$$

$$\alpha = \text{Max}\,\{0,\ |\ell_1-\ell_2|-(\ell_3+\ell_4),\ |\ell_3-\ell_4|-(\ell_1+\ell_2)\}$$

$$g_{max} = \mu+n_A+n_B+\ell_1+\ell_2+\ell_3+\ell_4+2. \tag{180}$$

For $H_{h\mu}$, the index h ranges from h_{min} to h_{max} where

$$h_{min} = \begin{cases} 1 & \text{when} \quad 0 \leq \mu \leq \ell_1+\ell_2+\ell_3+\ell_4 \\ 2\mu-2(\ell_1+\ell_2+\ell_3+\ell_4)+1 & \text{when} \quad \ell_1+\ell_2+\ell_3+\ell_4 \leq \mu \leq n_A+n_B \end{cases} \tag{181}$$

$$h_{max} = \mu+n_A+n_B+1-\alpha. \tag{182}$$

Properties of Auxiliary Functions

The auxiliary functions $G_{n\mu}$ and $H_{n\mu}$ were defined in Eqs. 165 and 166. They are related to the functions, previously defined by O-Ohata and Ruedenberg (102, Eqs. 2.13 and 2.12), $G^{\gamma}_{\alpha\beta}$ and $H^{\gamma}_{\alpha\beta}$:

$$G_{n,\mu}(x,y) = (2/x+y)\ G^{n-2\mu-1}_{\mu\mu}\ [\tfrac{1}{2}(x+y),\ (x-y)/(x+y)] \tag{183}$$

$$H_{n,\mu}(x,y) = n!\ (2/x+y)^{n+1}\ H^{n}_{\mu\mu}[\tfrac{1}{2}(x+y),\ (x-y)/(x+y)]. \tag{184}$$

The functions $G_{n,\mu}$ and $H_{n,\mu}$ satisfy very similar identities and, in the following equations the generic symbol, $F_{n\mu}$, is used to denote either one. By substituting into Eqs. 165 and 166 the hypergeometric series for f_μ given in Eqs. B1 and B2 of the preceding chapter, one finds the series representations,

$$F_{n,\mu}(x,y) = \sum_{k=0}^{\infty}\ [a(\mu,k)/(2\mu+k+1)!]\,(x-y)^k\ U_{n+k}(x) \tag{185}$$

$$F_{n,\mu}(x,y) = \sum_{k=0}^{\infty}\ [a(\mu,k)/(2\mu+k+1)!]\,(y-x)^k\ U_{n+k}(y) \tag{186}$$

$$F_{n,\mu}(x,y) = \sum_{k=0}^{\infty}\ [a(\mu,k)/(2\mu+2k+1)!]\,(x-y/2)^{2k}\ U_{n+2k}(x-y/2). \tag{187}$$

Here,

$$a(\mu,k) = (2\mu+1)!\ (\mu+k)!/(\mu!k!),$$

and the symbol, U_n, denotes the function E_n if $f_{n\mu} \equiv G_{n\mu}$, and the function A_n if $F_{n\mu} \equiv H_{n\mu}$. These were defined in Eqs. 174 and 175.

By substituting into Eqs. 165 and 166 the integral representation of f_μ, obtained by combining Eqs. 124 and 130 of the preceding chapter, one finds the integral representation

$$F_{n,\mu}(x,y) = [(2\mu+1)/2^{2\mu+1}] \binom{2\mu}{\mu} \cdot \int_{-1}^{1} d\eta\,(1-\eta^2)^\mu U_n[\tfrac{1}{2}(x+y) + \tfrac{1}{2}(x-y)\eta] \tag{188}$$

where the U_n are the same as before.

The most useful recursion relation for these functions is obtained by inserting in Eqs. 165 and 166 for f_μ the relation in Eq. B5 of the preceding chapter. This yields

$$F_{n,\mu}(x,y) = F_{n,\mu+1}(x,y) + [(x-y)^2/4(2\mu+3)(2\mu+5)]F_{n+2,\mu+2}(x,y). \tag{189}$$

This recurence relation involves only positive terms since both $G_{n\mu}$ and $H_{n\mu}$ are always positive.

Evaluation of the Functions $G_{n\mu}$ and $H_{n\mu}$

The functions needed are obtained by use of the recursion relation in Eq. 189 which involves only the addition of positive terms so that no subtractive losses of accuracy occur. Only certain rows of each table are needed as starting functions for this recursive procedure.

As an example, diagrams of the required G and H function tables are given in Figure 2 for the evaluation of the integral [A2p, A1s | B2p, B2s]. The starting functions are denoted by the symbol s and the elements obtained by recursion are denoted by r.

The starting functions are obtained from the integral representation of Eq. 188 by a Gaussian numerical integration (108, p. 887, Eq. 25.4.29). Thus, one obtains the formula

$$F_{n,\mu}(x,y) = \sum_{i=1}^{N} \omega_{\mu,i} \, U_n[\tfrac{1}{2}(x+y) + \tfrac{1}{2}(x-y)\eta_i] \quad (190)$$

where η_i is the i-th zero of the Legendre functions, $P_N(\eta)$, and

$$\omega_{\mu,i}=[(2\mu+1)/2^{2\mu+1}] \binom{2\mu}{\mu} (1-\eta_i^{\,2})^{\mu} w_i \quad (191)$$

with w_i being the weights given by

$$w_i = 2/(1-\eta_i)^2 \, [P'_N(\eta_i)]^2. \quad (192)$$

To obtain an accuray of 10^{-6} atomic units, the order, N, of the numerical integration was found to be dependent on the arguments ρ_A and ρ_B by the approximate relationship

$$N=2 \times \text{the largest integer in } \{5 + 7.5\,[(\rho_A-\rho_B)/(\rho_A+\rho_B)]\} \quad (193)$$

Evaluation of the Functions A_n and E_n

The functions, A_n, are obtained in all cases using the recursion relation:

$$A_n(x) = (n\,A_{n-1}(x) + e^{-x})/x \quad (194)$$

— g →

μ ↓	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0			s	s	r	r	r	r	r	r					
1					s	s	r	r	r	r	r				
2							s	s	r	r	r	r			
3									s	s	r	r	r		
4											s	s	s	s	
5													s	s	s

— h →

μ ↓	0	1	2	3	4	5	6	7	8	9	10	11
0		r	r	r	r	r	r					
1		r	r	r	r	r	r	r				
2		s	s	r	r	r	r	r	r			
3				s	s	r	r	r	r	r		
4						s	s	s	s	s	s	
5								s	s	s	s	s

Figure 2. Auxiliary functions needed to evaluate the integral [A2p A1s | B2p B2s]: G functions in upper diagram, H functions in lower diagram

from the starting function

$$A_0(x) = e^{-x}/x. \tag{195}$$

The functions E_n can be obtained with an accuracy of ten significant figures, using the recursion relation

$$E_n(x) = (n\ E_{n-1}(x) - e^{-x})/x \tag{196}$$

with the starting function

$$E_0(x) = (1-e^{-x})/x, \tag{197}$$

whenever the following relation is satisfied:

$$x \geq (+0.072 + 0.012\ n_{max})\ n_{max}. \tag{198}$$

Here n_{max} is the maximum index value required. When this relation is not satisfied, Eq. 196 loses too many significant figures and one must use the recursion relation in the reverse direction in which no subtractions occur. In this case, one needs $E_{n_{max}}$ as a starting function. The most rapid scheme for obtaining it was found to be the Taylor Series expansion,

$$E_n(x) = \sum_{k=0}^{\infty} [(\gamma-x)^k/k!]\ E_{n+k}(\gamma), \tag{199}$$

if function values $E_n(\gamma)$ were stored at sufficiently close intervals of γ. This table of fixed values was computed by the infinite series,

$$E_n(\gamma) = n!\ e^{-\gamma} \sum_{k=0}^{\infty} \gamma^k/(n+k+1)!. \tag{200}$$

The number of terms needed in the series, Eq. 199, depends on the size of the interval of grid points γ stored. With an interval of 0.33 units, no more than six terms are needed in the Taylor Series in order to converge to ten significant places.

COMPUTATION TIMES

The computer times quoted here are for FORTRAN programs written with double precision arithmetic for use on an IBM 360/50 computer. The times include the calculation of all auxiliary functions required, retrieval and use of the $D_{\mu\nu L}$ constants from permanent disc storage, summation of the series in Eq. 170, as well as writing out the matrix of integrals onto disc storage.

The actual time per single integral is a function of the quantum numbers, since the latter determine the size of the G and H tables required as well as the number of terms in the series in Eq. 170. A significant fraction of the time is spent on the numerical integrations of Eq. 190 for the starting functions and the number of points required depends on the values of the orbital exponents according to Eq. 193. Quoted here is the time needed for the relatively unfavorable case requiring a 16 point numerical integration. Letting n represent the average of the four principal quantum numbers, n_i, and letting ℓ represent the average of the four angular quantum numbers, ℓ_i, the time for a single non-zero integral was found to be $n(30 + 12\ell)$ milliseconds.

After an initial calculation of all integrals occurring over a basis set of functions on each center, subsequent changes in the orbital exponents require recalculation of only part of the Coulomb matrix. Provision for this is incorporated into the computer program and results in a substantial savings of time. For the initial calculation of the matrix of 11,025 Coulomb integrals arising from the basis set consisting of the functions 1s, 2s, $2p\sigma$, $2p\pi$, $2p\bar{\pi}$, 3s, $3p\sigma$, $3p\pi$, $3p\bar{\pi}$, $3d\sigma$, $3d\pi$, $3d\bar{\pi}$, $3d\delta$, $3d\bar{\delta}$, on each center, each function having a different ζ value, five minutes are needed. Changing one of the basis functions and recalculating the new matrix of integrals, requires 45 seconds.

Whereas in some methods, serious difficulties arise when the orbital exponents on the two centers approach each other, the present procedure becomes more accurate as well as faster in this case. For example, when all ζ's are equal, the aforementioned time of five minutes is reduced to 46 seconds while the aforementioned time of 45 seconds is reduced to 26 seconds.

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ACKNOWLEDGMENTS

The author wishes to thank Professor Klaus Ruedenberg for the guidance and understanding received during the course of this work and for suggesting this problem. The author thanks Ernest Mehler for the rewarding relationship which has grown from working together on molecular calculations and for providing the author with exchange integral programs. Thanks are also extended to Ralph Christoffersen for providing the author with hybrid integral programs. The author is especially appreciative of the service and help received from all members of the Iowa State University Computation Center. The author is also indebted to the remainder of his colleagues at Iowa State University, who are too numerous to name individually, for their contributions to this work.