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ELECTRON CORRELATION IN DIATOMIC MOLECULES: EXCHANGE INTEGRALS AND SEPARATED PAIR CALCULATIONS ON LITHIUM HYDRIDE AND BORON HYDRIDE

by

Ernest Louis Mehler

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PART I. SEPARATED PAIR APPROXIMATION FOR LITHIUM HYDRIDE AND BORON HYDRIDE

INTRODUCTION

Well before the formulation of quantum mechanics and its application to problems of atomic and molecular structure, the importance of the electron pair had already been recognized. The ideas which were developed after the discovery of the electron culminated in the work of G. N. Lewis who pointed out not only the central role of the shared electron pair in bonding but also that of unshared pairs (1). Langmuir and others continued the development of these ideas and showed that they could be used to explain a large variety of chemical facts (2,3). With the development of quantum mechanics it became possible to go considerably further and to elucidate the detailed structure of electron pairs. The combination of these ideas with the insights provided by quantum mechanics resulted in rapid strides in gaining a qualitative understanding of atomic and molecular structure.

In contrast, the attempts to obtain quantitative results along with qualitative explanations encountered insuperable mathematical and computational difficulties which did not become amenable to solution until the development of the high-speed digital computer. The recent advances in computer technology have led to a corresponding increase in the number of quantitative molecular calculations.

The main thrust of quantitative ab-initio investigations has been in the development and refinement of the self-consistent independent particle model as formulated by Hartree and Fock (4-6). By use of Roothaan's expansion procedure (7), nearly exact Hartree-Fock wave functions are becoming available, especially for atoms and diatomic molecules (8-11).

These investigations make it clear that, while the Hartree-Fock wave functions are quite capable of yielding satisfactory predictions of one-electron properties, their failure to account for the individual electron correlations makes their use for chemical purposes dependent on developing schemes which yield reliable predictions of the correlation effects. For this reason ab-initio determinations of wave functions beyond the Hartree-Fock level have become essential.

The most common avenue of attack for constructing correlated wave functions has been the configuration interaction (CI) technique, where the wave function is built up from a linear combination of configurations (Slater determinants, antisymmetrized products), Ψ_i, namely

$$\Phi = \sum_i C_i \Psi_i$$

where the C_i are determined variationaly. This formulation is a restatement of the general existence theorem for infinite expansions of antisymmetric functions in Hilbert Space. In order to fill such a framework with physical content, it is necessary to find a-priori ways to anticipate which of the many configurations that can be constructed will yield substantial contributions to the total energy. The first of these antisymmetrized products, Ψ_0, is usually taken to be the Hartree-Fock wave function. It is therefore essential to look for formulations of the higher terms which will yield physically significant information.

As a possible step in this direction it seems appealing to incorporate into the rigorous framework qualitative and intuitive chemical concepts, which would thus be preserved throughout the quantum mechanical formulation, and, at the same time, be critically tested. The concept of electron pairs is of considerable importance in chemistry and also simple enough to maintain in the quantum mechanical treatment.

The formulation of pair theory goes back to the work of Hurley (12), Lennard-Jones and Pople (13) who proposed the use of functions of the form

$$\Psi_\mu = \sum_{k\ell} a^\mu_{k\ell} \, \psi_{\mu k}(1) \, \psi^*_{\mu\ell}(2) \quad .$$

In addition, they introduced the "strong orthogonality" condition

$$\int dV_1 \, \Psi_\mu(1,2) \, \Psi^*_\nu(1,3) = 0 \qquad \mu \neq \nu$$

so that the resulting formulas would be tractable. With this additional constraint, the functions, Ψ_μ, are called separated pair functions. These authors further simplified the separated pair functions by expanding them in terms of their natural orbitals (14), viz.,

$$\Psi_\mu(1,2) = \sum_i C_{\mu i} \, \phi_{\mu i}(1) \, \phi^*_{\mu i}(2) \quad .$$

Since its original introduction several investigations have been carried out using the separated pair approximation. Parks and Parr (15) suggested several alternative schemes for minimizing the energy to obtain the optimal wave function. The separated pair approximation was applied to LiH by Csizmadia, Sutcliffe and Barnett (16), and by Ebbing and Henderson (17) who also transformed the expansions to the natural form and compared their wave function to the CI wave function calculated earlier by Ebbing (18). McWeeny and Ohno (19) applied the approximation to the water molecule, and McWeeny and Sutcliffe to Be (20). In addition, Kutzelnigg (21) has compared the separated pair approximation to a different pair approximation suggested by Coleman (22), namely an antisymmetrized product of identical pair functions. Kutzelnigg concluded that the first and second order density matrices of the separated pair wave function of Be conformed to the predicted properties of the density matrices, while the antisymmetrized product of identical pair functions did not. In all these cases, various simplifications and truncated basis expansions limited the effectiveness of the separated pair approximation rather drastically and made it impossible to determine its intrinsic efficacy.

The first rigorous application, without simplifying assumptions and using extended basis sets, was done by Miller (23) and Ruedenberg (24) (hereafter referred to as MR) on Be and the isoelectronic first row ions. They uniformly recovered about 90% of the correlation energy with their best wave functions. The considerable success enjoyed by the separated pair approximation in that investigation suggests its application to more complicated systems. It is of particular interest whether the separated pair approximation will be equally successful in atomic and diatomic systems with more than four electrons.

To this end the separated pair approximation has been applied to LiH, BH, NH and their respective separated atoms. The determination of the separated pair wave functions for the first two hydrides, LiH and BH, and their separated atoms is the subject of the present investigation. The separated pair wave functions for N and NH have been obtained by D. Silver (25).

Lithium hydride is well known. Its properties have been accurately determined and provide an excellent basis of comparison for theoretically calculated properties. The spectra of LiH have been thoroughly investigated by Crawford and Jorgensen (26,27).

Boron hydride, on the other hand, is considerably less well known, and many of its properties have not been obtained experimentally. Its spectra were first investigated by Lochte-Holtgreven and Vleagel (28) who produced it from reacting boron trichloride with hydrogen. More recently, Bauer, Herzberg and Johns (29) have investigated the spectra of BH. They proposed the reactions

$$H_3BCO + h\nu \rightarrow BH + H_2^* + CO$$

$$H_3BCO + h\nu \rightarrow BH + H_2 + CO^*$$

for its formation from borine carbonyl, where * indicates vibrational excitation. Boron hydride has also been detected in sun spot spectra by Babcock (30) but not in solar disk spectra.

The present investigation and that conducted on NH indicate that the separated pair approximation has only limited applicability in systems with more than four electrons. In boron, the lack of _inter_-pair correlations and the strong orthogonality constraint proved to be especially severe. On the other hand, the form of the wave function is particularly amenable to analysis, and it is readily possible to isolate particular aspects of electronic structure out of the total wave function. It may be that the relaxation of the strong orthogonality constraint could, in certain cases, enlarge the applicability of the general pair approximation.

GLOSSARY OF ABBREVIATIONS

APSG	Antisymmetrized Product of Separated Geminals
CI	Configuration Interaction
CI-NO	Configuration Interaction-Natural Orbital
HF-SCF	Hartree-Fock-Self-Consistent-Field
LP	Lone Pair
NO	Natural Orbital
PNO	Principal Natural Orbital
SCF	Self-Consistent-Field
SNO	Secondary Natural Orbital
SPA	Separated Pair Approximation
STAO	Slater Type Atomic Orbital
VB-CI	Valence Bond-Configuration Interaction

VARIATIONAL APPROACH TO THE SEPARATED PAIR APPROXIMATION

Wave Function, Density Matrices, Natural Orbitals

In the pair approximation the wave function for an $N = 2n$ electron system may be written as an antisymmetrized product of pair functions called geminals (31)

$$\Phi(1,2,\ldots,N) = \mathcal{A}\prod_{\mu=1}^{n} \Psi_{\mu}(2\mu-1,\ 2\mu) \quad . \tag{1}$$

This formulation can also be adopted for a $(2n-1)=N$ electron system if $\Psi_N=\phi_N$ is interpreted as a spin orbital. The spin geminals are assumed to be antisymmetric in their two coordinates and $\mathcal{A}$ is a partial antisymmetrizer which acts on the electron coordinates between different space-spin products.

Since the geminals are two electron functions, they may be factored into the product of a space part, Λ, and a spin part, θ,

$$\Psi_{\mu}(1,2) = \Lambda_{\mu}(1,2)\ \theta_{\mu}(1,2) \quad . \tag{2}$$

The space geminals, Λ_{μ}, can be expanded in terms of their natural orbitals

$$\left.\begin{aligned} \Lambda_{\mu}(1,2) &= \sum_{i} C_{\mu i}\ \phi_{\mu i}(1)\ \phi^{*}_{\mu i}(2) \\ \Lambda_{N}(1) &= \phi_{N}(1) \quad \text{if} \quad N=(2n-1) \end{aligned}\right\} \tag{3}$$

where the $\phi_{\mu i}$ are mutually orthogonal and the $C_{\mu i}$ are the occupation coefficients; which are real (32,33) if θ_{μ} is a singlet. As a consequence of Eq. 2 the spin factors can be integrated out in the formulas for the energy and density matrices.

It is possible to derive expressions for the energy and the first and second order density matrices without any further assumptions. However, the equations become very complex (20,34-36) if one assumes only the weak orthogonality condition

$$\int dV_1 \int dV_2\, \Lambda_\mu(1,2)\, \Lambda_\nu^*(1,2) = \int dV_1 \rho_{\mu\nu}(1,1) = \delta_{\mu\nu} \quad . \tag{4}$$

A significant simplification is achieved by introducing the strong orthogonality condition of Hurley, Lennard-Jones and Pople (13), to wit

$$\int dV_2\, \Lambda_\mu(1,2)\, \Lambda_\nu^*(1',2) = \rho_{\mu\nu}(1,1') = 0 \quad \mu \neq \nu \quad . \tag{5}$$

Such wave functions are called Antisymmetrized Products of Separated Geminals (APSG), and form the basis of the present investigation. Arai (37) and more generally Löwdin (38) have shown that the strong orthogonality conditions are equivalent to the assumption that the natural orbitals of different geminals are mutually orthogonal, i.e.,

$$\int dV\, \phi_{\mu i}^*\, \phi_{\nu j} = \delta_{\mu\nu}\, \delta_{ij} \quad . \tag{6}$$

In order to formulate expressions for the density matrices, use is made of McWeeny's (39,40) relations between the first and second order density matrices of group wave functions and the first and second order density matrices associated with the individual groups. Let

$$\left.\begin{aligned} \rho_\mu(1,1') &= \varkappa_\mu \int dV_2\, \Lambda_\mu(1,2)\, \Lambda_\mu^*(1',2) \\ &= \varkappa_\mu \sum_i C_{\mu i}^2\, \phi_{\mu i}(1)\, \phi_{\mu i}^*(1') \end{aligned}\right\} \tag{7a}$$

$$\pi_\mu(1,2;\ 1',2') = 2(\varkappa_\mu - 1)\, \Lambda_\mu(1,2)\, \Lambda_\mu^*(1',2') \tag{7b}$$

be the first and second order density matrices for the μ'th geminal or orbital, where

$$\varkappa_\mu = \begin{cases} 2 \text{ if } \mu \text{ is a geminal} \\ 1 \text{ if } \mu \text{ is an orbital.} \end{cases}$$

Then the first order density matrix of the total wave function, Φ, of Eq. 1 is

$$\rho(1,1') = \sum_\mu \rho_\mu(1,1') \tag{8}$$

and the second order density matrix of Φ becomes

$$\pi(1,2;\ 1',2') = \sum_\mu \pi_\mu(1,2;\ 1',2') + \sum_{\substack{\mu,\nu \\ (\mu\neq\nu)}} \{\rho_\mu(1,1')\ \rho_\nu(2,2') - \tfrac{1}{2}\rho_\mu(1,2')\ \rho_\nu(2,1')\}\ . \tag{9}$$

Eq. 8 shows that the natural orbitals of the geminals are the natural orbitals of the total wave function.

Eq. 6 suggests (38) that the natural orbitals are conveniently constructed by an isometric transformation, $\underline{\underline{T}}$,

$$\vec{\phi} = \vec{\chi}^{\,or}\ \underline{\underline{T}} \tag{10}$$

from a suitable orthonormal basis set,

$$\vec{\chi}^{\,or} = (\chi_1^{or}, \chi_2^{or}, \ldots) \quad , \tag{11}$$

and this procedure is adopted here.

Total Energy and Geminal Energy

The non-relativistic Hamiltonian for an N-electron system in atomic units (1.0 hartree = 27.2097 e.v.; 1.0 bohr = 0.529172 A), assuming the Born-Oppenheimer approximation (41), is

$$\mathcal{H} = \sum_{i} h(i) + \sum_{i<j} r_{ij}^{-1} + \sum_{\alpha<\beta} Z_{\alpha} Z_{\beta} R_{\alpha\beta}^{-1} \tag{12}$$

with

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} Z_{\alpha} r_{\alpha i}^{-1} \tag{13}$$

where the labels i, j, . . . indicate electron coordinates, the labels α, β, . . . indicate nuclear coordinates, and Z_α is the charge on nucleus α.

The electronic energy for singlet and doublet states in the APSG approximation can be obtained from Eqs. 8 and 9, and becomes

$$E = \sum_{\mu} E(\mu) + \sum_{\mu<\nu} I(\mu,\nu) \tag{14}$$

with

$$E(\mu) = \sum_{i,j} C_{\mu i} C_{\mu j} E(\mu i,\mu j) \tag{15}$$

$$E(\mu i,\mu j) = \kappa_{\mu}(\phi_{\mu i}|h|\phi_{\mu i}) + (\kappa_{\mu}-1)[\phi_{\mu i}\phi_{\mu j}|\phi_{\mu j}\phi_{\mu i}] \tag{16}$$

and

$$I(\mu,\nu) = \sum_{i,j} C_{\mu i}^2 C_{\nu j}^2 I(\mu i,\nu j) \tag{17}$$

$$I(\mu i,\nu j) = \kappa_{\nu}\{2[\phi_{\mu i}\phi_{\mu i}|\phi_{\nu j}\phi_{\nu j}] - [\phi_{\mu i}\phi_{\nu j}|\phi_{\nu j}\phi_{\mu i}]\} \tag{18}$$

where the definitions

$$(\phi_i|h|\phi_j) = \int dV_1\, \phi_i^*(1)\, h(1)\, \phi_j(1) \tag{19}$$

$$[\phi_i\phi_j|\phi_k\phi_l] = \int dV_1 \int dV_2\, \phi_i^*(1)\, \phi_j(1)\, \phi_k^*(2)\, \phi_l(2)/r_{12} \qquad (20)$$

are used. Eq. 14 shows that the total electronic energy can be considered as the sum of <u>intra</u>geminal contributions, $E(\mu)$, and <u>inter</u>geminal contributions, $I(\mu,\nu)$.

The geminal energy

$$\epsilon_\mu = E(\mu) + \sum_{\nu(\neq\mu)} I(\mu,\nu) \qquad (21)$$

represents the energy of one geminal in the context of the whole system. The total energy may also be written as

$$E = \sum_\mu \epsilon_\mu - \sum_{\mu<\nu} I(\mu,\nu) \quad . \qquad (22)$$

Variational Equations

Two interdependent sets of variational equations may be obtained for the APSG wave function. The first of these requires that the energy be stationary for variations of the occupation coefficients and results in a set of coupled eigenvalue equations (42,43)

$$\sum_j H^\mu_{ij}\, C_{\mu j} = \epsilon_\mu\, C_{\mu i} \quad i = 1,2,\ldots, \mu = 1,2,\ldots,n \qquad (23)$$

where

$$H^\mu_{ij} = E(\mu i,\mu j) + \delta_{ij}\, I(\mu i) \qquad (24)$$

and

$$I(\mu i) = \sum_{\nu(\neq\mu)} \sum_j C^2_{\nu j}\, I(\mu i,\nu j) \quad . \qquad (25)$$

The weighted sum of the $I(\mu i)$, namely

$$\sum_i C_{\mu i}^2 \; I(\mu i) = \sum_{\nu(\neq\mu)} I(\mu,\nu) \tag{26}$$

represents the total interaction energy of the μ'th geminal with all the other geminals.

Making the energy stationary for variations of the natural orbitals yields the second set of variational equations. These are a set of coupled integro-differential equations which have been derived by Kutzelnigg (42). If the natural orbitals are obtained from an orthonormal basis by an isometric transformation, $\underline{\underline{T}}$, as in Eq. 10, variations of the natural orbitals are replaced by variations of the elements of $\underline{\underline{T}}$, and this yields the expression

$$\sum_{k'} G_{kk'}^{\mu i} \; T_{k',\mu i} = \sum_{\nu j} T_{k,\nu j} \; \lambda_{\nu j,\mu i} \tag{27}$$

where

$$\lambda_{\nu j,\mu i} = \lambda_{\mu i,\nu j} \tag{28}$$

are Lagrangian multipliers introduced to guarantee the orthogonality constraints

$$\int dV \; \phi_{\mu i}^* \; \phi_{\nu j} = \delta_{\mu\nu} \; \delta_{ij} \quad ,$$

and furthermore

$$G_{kk'}^{\mu i} = h_{kk'} \; C_{\mu i}^2 + f_{kk'}^{\mu} \; C_{\mu i} + g_{kk'}^{\mu} \; C_{\mu i}^2 \tag{29}$$

with

$$h_{kk'} = (k|h|k') \quad , \tag{30}$$

$$f^{\mu}_{kk'} = (\kappa_{\mu}-1) \sum_{\ell\ell'} [k\ell|k'\ell'] \{\sum_{j} T_{\ell,\mu j} T_{\ell',\mu j} c_{\mu j}\} \tag{31}$$

$$g^{\mu}_{kk'} = \sum_{\ell\ell'} \{2[kk'|\ell\ell'] - [k\ell|k'\ell']\} \cdot \sum_{\nu(\neq\mu)} T_{\ell,\nu j} T_{\ell'\nu j} c^{2}_{\nu j} \quad . \tag{32}$$

If both sides of Eq. 27 are multiplied by $T_{k,\mu i}$ and summed over k and then over i, one obtains the relation

$$\epsilon_{\mu} + (\kappa_{\mu}-1) \sum_{i,j} c_{\mu i} c_{\mu j} [\phi_{\mu i} \phi_{\mu j}|\phi_{\mu j} \phi_{\mu i}] = \kappa_{\mu} \sum_{i} \lambda_{\mu i,\mu i} \tag{33}$$

as the coupling equation between the diagonal elements of $\underline{\underline{\lambda}}$ and the geminal energies.

Determination of Wave Function

Variation of parameters

Three sets of interdependent parameters must be determined to find the optimal form of the APSG wave function. The occupation coefficients are found by solving Eq. 23. The orbital exponents associated with the basis functions, χ^{or}, are determined by varying them until the energy is minimal. The elements of the rotation matrix $\underline{\underline{T}}$ could be found from Eq. 27; however, because of its complex nature this method is replaced by the alternative of minimizing the total energy with respect to the elements of $\underline{\underline{T}}$.

This optimization is accomplished by parametrizing $\underline{\underline{T}}$ in terms of M(M-1)/2 parameters γ_{ν}, i.e.,

$$\underline{\underline{T}}^{M} = \underline{\underline{T}}^{M} (\gamma_{1}, \gamma_{2}, \ldots, \gamma_{M(M-1)/2}) \tag{34}$$

where M is the order of $\underline{\underline{T}}$. These parameters are varied until the energy is minimized. They represent angles for two by two rotations and are limited to the domain $\langle -\pi, \pi \rangle$. The orthogonal matrix $\underline{\underline{T}}$ of degree n is obtained (44) as the n'th step in a recursive sequence of orthogonal matrices $\underline{\underline{T}}^{(n)}$, i.e., $\underline{\underline{T}} = \underline{\underline{T}}^{(n)}$. The n'th matrix $\underline{\underline{T}}^{(n)}$ is obtained from the (n-1)'st matrix $\underline{\underline{T}}^{(n-1)}$ by the following set of recursive steps

$$T_{jk}^{(n)} = t_{jk}^{(n)} \cos \gamma_{jn} - r_{jk} \sin \gamma_{jn} \tag{35}$$

$$r_{j+1,k}^{(n)} = t_{jk}^{(n)} \sin \gamma_{jn} + r_{jk}^{(n)} \cos \gamma_{jn} \tag{36}$$

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

$$\underline{\underline{t}}^{(n)} = \begin{pmatrix} \underline{\underline{T}}^{(n-1)} & 0 \\ 0 & 1 \end{pmatrix} , \tag{37}$$

$$r_{1k}^{n} = -\delta_{kn}, \qquad \gamma_{nn} = 1/2\,\pi , \qquad \underline{\underline{T}}^{(1)} = 1 \quad . \tag{38}$$

By separating the variation of the orbital exponents and the rotation matrix parameters it is not necessary to recompute the atomic integrals when the rotation matrix is being optimized. The entire procedure becomes an iterative scheme which is illustrated in Fig. 1. Each block is essentially independent, and its output serves as input for the next.

Introduction of atomic orbital basis

The orthogonal basis functions, $\vec{\chi}^{or}$, are generated from a non-orthogonal basis set by the symmetric transformation

$$\vec{\chi}^{or} = \vec{\chi}\, \underline{\underline{S}}^{-1/2} \tag{39}$$

where $\underline{\underline{S}}$ is the overlap matrix for the χ's. Introducing Eq. 39 into Eq. 10, the natural basis can be expanded in the non-orthogonal basis set as

$$\vec{\phi} = \vec{\chi}\,\underline{\underline{D}} \tag{40}$$

where

$$\underline{\underline{D}} = \underline{\underline{S}}^{-1/2}\,\underline{\underline{T}} \tag{41}$$

is the transformation which carries the non-orthogonal basis $\vec{\chi}$ into the natural basis $\vec{\phi}$.

When a new basis function is added to a previous set of M basis functions, it is important to construct the initial guess in the (M + 1)-dimensional function space in such a way that it is at least as good as the optimal wave function obtained previously in the M-dimensional space. The proper form of $\underline{\underline{D}}$ for this to be the case is

$$\underline{\underline{D}}^{M+1} = \begin{pmatrix} D^{o}_{11} & \cdots & D^{o}_{12} & \cdots & D_{1i} & \cdots & D^{o}_{1,M+1} \\ \vdots & & \vdots & & \vdots & & \vdots \\ 0 & \cdots & 0 & \cdots & D_{ii} & \cdots & 0 \\ \vdots & & \vdots & & \vdots & & \vdots \\ D^{o}_{M+1,1} & \cdots & D^{o}_{M+1,2} & \cdots & D_{M+1,i} & \cdots & D^{o}_{M+1,M+1} \end{pmatrix} \tag{42}$$

where $D^{o}_{kj} = [(\underline{\underline{S}}^{o})^{-1/2}\,\underline{\underline{T}}^{o}]_{kj}$ is the k,j'th element of the old wave function and $\underline{\underline{D}}^{M+1}$ is of the order (M+1). This form guarantees that the M natural orbitals

$$\phi_j = \sum_{\alpha} \chi_\alpha D_{\alpha j} = \sum_{\alpha(\neq i)} \chi_\alpha D^{o}_{\alpha j} \qquad (j \neq i) \tag{43}$$

are identical with the old natural orbitals. Since the (M+1)'st of the new natural orbitals, viz.,

$$\phi_i = \sum_{\alpha=1}^{M+1} \chi_\alpha D_{\alpha i} \tag{44}$$

is required to be orthogonal to those of Eq. 43, it is completely determined, and its coefficients are

$$D_{ii} = [1 - \sum_{\alpha(\neq i)} S_{\alpha i}\, \theta_{\alpha i}]^{-1/2}$$

$$D_{\alpha i} = - D_{ii}\, \theta_{\alpha i} \qquad (\alpha \neq i) \tag{45}$$

where

$$\theta_{\alpha i} = \sum_{\beta} \sum_{\gamma} D^{o}_{\alpha\beta}\, S_{i\gamma}\, D^{o}_{\gamma\beta} \quad , \qquad (\alpha,\beta,\gamma\neq i) \tag{46}$$

with

$$S_{\alpha\beta} = \int dV\, \chi_{\alpha}\, \chi^{*}_{\beta} \tag{47}$$

whence

$$S_{\alpha\beta} = S^{o}_{\alpha\beta} \quad , \qquad \text{if } \alpha\neq i \text{ and } \beta\neq i \quad . \tag{48}$$

The relation 45 can be derived by a Schmidt-Orthogonalization of the form

$$\phi_{i} = \text{const.} \{\chi_{i} - \sum_{\alpha(\neq i)} (\phi_{\alpha}|\chi_{i})\, \phi_{\alpha}\}$$

and is related to a method suggested by Löwdin (45) for orthogonalizing two internally orthogonal basis sets. If it is desired to add more than one basis function to the previous M basis functions before reoptimizing the parameters, the procedure outlined by Eqs. 42 and 45 is repeated as often as necessary.

To carry out the parameter variation it is necessary to factor $\underline{\underline{D}}^{M+1}$ according to Eq. 41 and to obtain the set of parameters which characterizes $\underline{\underline{T}}^{M+1}$. Since $\underline{\underline{S}}^{M+1}$ is known for the new basis, the orthogonal matrix $\underline{\underline{T}}^{M+1}$ is given by

$$\underline{\underline{T}}^{M+1} = (\underline{\underline{S}}^{M+1})^{1/2}\, \underline{\underline{D}}^{M+1} \quad . \tag{49}$$

The M(M+1)/2 parameters, γ, which characterize $\underline{\underline{T}}^{M+1}$ can be determined by choosing an arbitrary set, γ_a, and varying them until the inequality

$$\sum_{\alpha,\beta} |T_{\alpha\beta}^{M+1} - (T_a^{M+1})_{\alpha\beta}| \lessapprox 10^{-4} \tag{50}$$

is satisfied. The convergence of Eq. 50 is facilitated by choosing initial values of the γ_a's so that those connecting two old basis functions have the optimal value of the corresponding γ in the M-dimensional basis, and setting those γ_a's which connect the new basis orbital with the old ones to zero.

Strategy of optimizing the natural orbitals

In the determination of the APSG wave function for beryllium and the first row four electron ions by MR, the final wave functions were built up from minimal, single determinant wave functions by systematically adding one or more basis orbitals and reoptimizing at each stage. The number of NO's retained throughout the variational procedure was always the maximum, i.e., the same as the number of atomic basis functions. This method was taken over here. Another strategy would be to start with the Hartree-Fock-SCF wave function and determine the APSG wave function from that point of departure. If the latter procedure is used, n(2m-n-1)/2 primary parameters out of a total of m(m-1)/2 parameters are determined initially by the HF-SCF procedure or its equivalent (where n is the number of geminals and m the number of basis functions, and one has m > n). The addition of the remaining natural orbitals, i.e., m-n more, furnishes (m-n)(m-n-1)/2 additional secondary parameters which can be varied.

The method outlined in Eqs. 42 and 45 for adding one basis orbital at a time makes it very convenient to vary all parameters at each level at which the wave function is reoptimized. Since the initial function in the expanded basis remains always very close to the optimal wave function, the variation procedure does not have to move very far in parameter space to find it. Nevertheless the calculation becomes quite time consuming if the number of molecular orbitals goes beyond 15. In the alternative scheme mentioned above the secondary parameters are arbitrary prior to reoptimization, however, the wave function would at least be as good as the HF-SCF wave function, and therefore, the variation procedure would perhaps, here too, not have to move too far in parameter space if a judicious initial choice of the secondary parameters can be made. After the wave function has been expanded to m natural orbitals and optimized in terms of the secondary parameters, the primary parameters may have to be revaried in order to obtain a reasonably optimized wave function. It would be valuable to establish the relative merits of the two schemes by comparitive calculations in the determination of similar wave functions for similar systems.

Computational Considerations

The computer program is logically similar in structure to the diagram in Figure 1. At certain intervals the input data is updated so that the calculation can be stopped and restarted without the loss of intermediate results. Blocks A and C are minimization schemes based on a method suggested by Powell (46) which determine the optimum values of the orbital exponents and rotation matrix parameters. The largest portion of computing time is spent in block B, evaluation of the atomic integrals, and blocks D and E, formation of the geminal matrix elements H^{μ}_{ij}. In the independent particle calculation where the wave function is represented as a single Slater determinant, evaluation of the atomic integrals is usually the rate determining step. In the context of an APSG calculation the single determinant wave function involves evaluation of only one of the geminal matrix elements per geminal, namely

$$[H^1_{PNO}, H^2_{PNO}, \ldots, H^n_{PNO}] \quad .$$

Here the subscript PNO means prinicpal natural orbital. Extension of the geminals beyond the PNO rapidly increases the number of matrix elements which must be calculated. These matrix elements are made up of the molecular integrals, many of which are quadruple sums over the atomic integrals such as

$$[\phi_\alpha \phi_\beta \mid \phi_\gamma \phi_\delta] = \sum_{kk'} \sum_{\ell\ell'} D_{\alpha k} D_{\beta k'} D_{\gamma \ell} D_{\delta \ell'} [kk'|\ell\ell'], \qquad (51)$$

and it is due to the large number of molecular integrals which arise that the time needed to evaluate all of them is about twice as long as that needed to evaluate all the atomic integrals for a calculation of the total energy. For example, in the LiH wave function, which is expanded in terms of 18 basis orbitals, it takes approximately 15 minutes to calculate the energy. The atomic integrals require about five minutes, and the rest of the time, 10 minutes, is spent forming geminal matrix elements. The solution of Eq. 23 proves to be a trivial part of the calculation.

From the computational point of view the new feature of this calculation is the introduction of the rotation matrix and its variational parameters. Within a given symmetry type the number of rotation matrix parameters which arise for m basis functions is m(m-1)/2, whereas only m orbital exponents are needed. Due to the stringent symmetry requirements in atoms the number of rotation matrix parameters is small even for large basis sets. In diatomic molecules, the relaxed symmetry yields a large increase in the number of parameters which can be varied. This can be seen by comparing Li and LiH where seven and seventy parameters are free to be varied respectively. From Eq. 51 it is seen that the molecular integrals must be recomputed each time any of the parameters are varied, while the atomic integrals need to be recalculated <u>only</u> when the orbital exponents are varied. In contrast to the single determinant calculation the time consumed for evaluation of the molecular matrix elements is as important as that used for the evaluation of integrals.

WAVE FUNCTIONS AND ENERGIES AT THE EQUILIBRIUM DISTANCE

Basis Functions in Diatomic Molecules

Atomic orbital basis

The basis functions are taken to be real Slater Type Atomic Orbitals (STAO's) with origins at the nuclei, and have the form

$$\chi = c_n \, r^{n-1} \, e^{-\zeta r} \mathcal{Y}_{\ell m}(\theta,\varphi) \tag{52}$$

where

$$c_n = (2\zeta)^{n+1/2} / [(2n)!]^{1/2} \tag{53}$$

and

$$\mathcal{Y}_{\ell m}(\theta,\varphi) = \mathcal{P}_{\ell}^{|m|}(\theta) \begin{cases} \cos m\varphi / [(1+\delta_{mo})\,\pi]^{1/2} & m \geq 0 \\ \sin |m|\varphi / \pi^{1/2} & m < 0 \end{cases} \tag{54}$$

and the $\mathcal{P}_{\ell m}$ are normalized associated Legendre functions (47). The use of Slater Type Atomic Orbitals rather than elliptic orbitals as basis functions for diatomic molecule wave functions has one important advantage in that it is possible to calculate "corresponding" separated atom wave functions. In the present application of the separated pair model, the conclusions made concerning its efficacy in the general case have been significantly influenced by the separated atom results. Moreover, since a major aim of quantum chemistry is the study of chemical reactions, it is essential that wave functions of comparable degree of approximation can be determined for both reactants and products.

Symmetry considerations

It can be shown (48) that the APSG wave function can be constructed to conform to the desired symmetry state of the system under study by forming it from symmetry adapted geminals. The energy expression Eq. 14 has been restricted to singlets with the spin function

$$\theta(1,2) = [\alpha(1)\ \beta(2) - \alpha(2)\ \beta(1)] / \sqrt{2} \tag{55}$$

and doublets with the spin function

$$\theta(1) = \alpha(1) \text{ or } \beta(1) \quad . \tag{56}$$

The space geminals are constructed from symmetry adapted natural orbitals. The ground state of LiH and BH is $^1\Sigma^+$ and the natural orbitals must be eigenfunctions of L_z such that $L_z = 0$. The natural orbitals for the atoms must be eigenfunctions of $\vec{L}^2$ as well as L_z. The ground states for Li and B are ^2S and ^2P respectively (49). Symmetry adapted natural orbitals are constructed by using a transformation matrix which does not mix basis functions belonging to different symmetry states, i.e., the elements of $\underline{\underline{D}}$ which would mix more than one symmetry type into a natural orbital vanish. Since the STAO's already belong to a given symmetry the orthogonalization matrix $\underline{\underline{S}}^{-1/2}$ will automatically have the proper block diagonal form, and the problem is reduced to constraining $\underline{\underline{T}}$ to reflect the same symmetry. From Eq. 34 it is seen that each of the parameters which determine $\underline{\underline{T}}$ connect two basis functions, and $\underline{\underline{T}}$ can be made block diagonal by requiring that $\gamma_{\alpha\beta} = 0$, if α and β denote states belonging to different symmetries.

As an example consider a six basis function expansion

$$(\sigma_a, \sigma_b, \pi_a, \pi_b, \bar{\pi}_a, \bar{\pi}_b) \tag{57}$$

where a and b indicate the two centers. If the $\gamma_{\alpha\beta}$'s are constrained so that only those which connect functions belonging to the same symmetry state do not vanish, there will be three non-zero parameters $\gamma_{\sigma_a,\sigma_b}$, γ_{π_a,π_b}, $\gamma_{\bar{\pi}_a,\bar{\pi}_b}$, and $\underline{\underline{T}}$ will be in block diagonal form. From Eq. 41 it is seen that $\underline{\underline{D}}$ will then also be in block diagonal form, and therefore six natural orbitals are obtained

$$(\phi_{\sigma_1}, \phi_{\sigma_2}, \phi_{\pi_1}, \phi_{\pi_2}, \phi_{\bar{\pi}_1}, \phi_{\bar{\pi}_2}) \tag{58}$$

where the subscripts denote the symmetry of each natural orbital. Moreover, the π and $\bar{\pi}$ states are made doubly degenerate by choosing $\gamma_{\bar{\pi}_a,\bar{\pi}_b}$ identical in value to γ_{π_a,π_b} to conform to the Σ state.

Selection of basis functions

The choice of type and number of basis functions is dependent on several factors. Enough basis functions must be included to account for the different types of correlation which are present in the hydrides: a description of in-out-correlation is given by s-type orbitals, sigma orbitals yield a description of left-right correlation, and angular correlations are accounted for by pi and delta orbitals. For each basis function added, a new natural orbital can be added, describing one of these correlations. However, each basis function *also* serves to improve the expansions of the natural orbitals already present in the wave function. An example is the addition of the 3dπ orbital to hydrogen in LiH. It generates a natural orbital yielding 0.00058 hartree of correlation energy in the bonding geminal, and it also increases the correlation energy recovered by the π natural orbital already present in the bonding geminal by 0.0010 hartree.

The APSG wave function for LiH is expected to be a closer approximation to the true wave function than the one for BH. This is essentially due to the fact that LiH seems to correspond more closely to a system with well defined pairs than BH, and it is only for such systems that the APSG approximation can be expected to yield good wave functions. Since one of the reasons for constructing these wave functions is to test the capability of the APSG wave function to approximate the true wave function for diatomic molecules, the LiH wave function is refined to a considerably higher degree than the BH wave function.

Separated Pair Approximation in Li and LiH

Geminal expansions

The APSG wave functions for Li and LiH are

$$\Phi_{Li} = \mathcal{A}\,\{\Lambda_k\,[(\alpha\beta-\beta\alpha)/\sqrt{2}]\,\phi_L\,\alpha\}$$

$$\Phi_{LiH} = \mathcal{A}\,\{\Lambda_k\,[(\alpha\beta-\beta\alpha)/\sqrt{2}]\,\Lambda_B\,[(\alpha\beta-\beta\alpha)/\sqrt{2}]\} \tag{59}$$

where Λ_k denotes the K-shell geminal, Λ_B the bonding geminal and ϕ_L is the unpaired electron natural orbital in Li. The LiH wave function is determined at the experimental equilibrium separation of 3.015 bohr (27). The space geminals, Λ_μ, are assumed to be expanded in the natural form according to Eq. 2. Due to the strong orthogonality condition, Eq. 6, the natural orbitals are uniquely assigned to one of the two geminals in LiH, while in Li all except one of the natural orbitals are assigned to Λ_k. Within each geminal the natural orbitals can be arranged in order of decreasing occupancy and, because they are symmetry adapted, assigned to a symmetry class. This suggests, for the natural orbitals, the notation $Mi\alpha j$ with the following meaning:

M is the geminal to which the NO belongs;

i is the order of the NO by decreasing occupancy in the M'th geminal;

α designates the symmetry class of the NO;

j is the order of the NO by decreasing occupancy within its symmetry class in the M'th geminal. Generally the greater j, the more nodes the NO possesses.

In LiH, the APSG wave function is a superposition of 18 natural orbitals, nine in the K-geminal and nine in the B-geminal. The structure of each geminal is schematically represented by the charts:

K-geminal

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	2		3				4	5
Order within Π (j)			1		2		3		
Order within Δ (j)						1			

B-geminal

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	2		3	4			5	6
Order within Π (j)			1			2	3		

. (60)

Thus, the K-geminal has three π natural orbitals, namely $K3\pi1$, $K5\pi2$, and $K7\pi3$. Some of the wave functions for Li and LiH discussed later on have one or more of their natural orbitals omitted. These will be represented by charts similar to those given in 60, with dashes (-) for the omitted NO's.

The Li APSG wave function is expanded in terms of six natural orbitals with five in the K-geminal which has the structure

K-geminal

Overall order (i)	1	2	3	4	5
Order within S (j)	1	2			
Order within P (j)			1	2	
Order within D (j)					1

(61)

.

The unpaired electron occupies one natural orbital and thus needs no further clarification.

Natural orbital expansions

The natural orbitals of the LiH wave function are linear combinations of 18 STAO basis functions, thirteen of which are centered on Li and five on H. The Li natural orbitals are expansions of seven STAO basis functions. The basis orbitals and their orbital exponents are given in Table 1. The separated atom wave function is constructed to correspond as closely as possible to the hydride wave function, so that meaningful estimates of the binding energy can be made. The explicit expansions of the atomic and molecular NO's in terms of the Slater Type Atomic Orbitals, i.e., the D-matrices are given in Tables 2 and 3, which also contain the occupation coefficients.

Transferability of K-geminal

The concept of transferability of certain pair functions, in particular inner shells, is a well known conjecture (50). A great deal of computational effort could be saved if a geminal could be determined once, in the atom for example, and then inserted into the molecular wave function whenever it appears. Moreover, this would imply that such a geminal is only weakly affected and remains essentially constant in structure as the electron environment changes from one system to the other. If this is actually the case, one would furthermore expect that, in the calculation of difference properties, the detailed correlation structure of such a geminal might be omitted without introducing a significant error. It is therefore of considerable interest to investigate this conjecture on the basis of an accurate ab-initio calculation.

For a comparison of the K-shell geminal of LiH with that of Li it is necessary to relate the K-natural orbitals occurring in the two systems. This correspondence is indicated by the following chart:

Atomic K-NO's	σ	π	δ
K1s1	K1σ1		
K2s2	K2σ2		
K3p1	K4σ3	K3π1	
K4p2	K9σ5	K5π2	
K5d1	K8σ4	K7π3	K6δ1

(62)

For example the five (K5d1)-NO's of the Li atom split into one σ-NO, two π-NO's, and two δ-NO's in LiH. Quantitative insight in the similarities is furnished by Table 4, which lists the occupation coefficients for all these orbitals and also the overlap integrals between corresponding atomic and molecular NO's. From the close agreement of the occupation coefficients and the fact that all overlaps are close to one, it is apparent that both geminals have nearly identical structure. An exception is the (K9σ5) NO of LiH which differs markedly in occupation and spatial distribution from the (K4p_z2) NO of Li. However, because of its small weight it does not alter the general similarity and, in fact, the overlap between the two geminals is estimated to be 0.997. By way of comparison it may be mentioned that the PNO of the bonding geminal and the L shell NO of the Li atom have an overlap of only 0.64748.

An even more detailed comparison can be made on the basis of Tables 2 and 3 which confirms the close correspondence. It can also be seen from the contour maps of the NO's. The corresponding maps are as follows:

Atomic NO	Atomic Contour	Molecular NO	Molecular Contour
K1s1	Map No. 19	K1σ1	Map No. 1
K2s2	Map No. 20	K2σ2	Map No. 2
K3p1	Map No. 21	K4σ3, K3π1	Maps No. 3, 4
K4p2	Map No. 22	K9σ5, K5π2	Maps No. 5, 9
K5d1	Map No. 23	K8σ4, K7π3, K6δ1	Maps No. 6, 7, 8

Bonding geminal

The structure of the bonding geminal is also given in Table 3. The PNO is approximately given by

$$(B1\sigma1) \approx 0.17(Li\text{-}L2s) + 0.21(Li\text{-}L2p) + 0.17(Li\text{-}L3s) + 0.66(H\text{-}1s) \qquad (63)$$

and thus exhibits a strong polarization toward the hydrogen as indicated by the magnitude of the coefficient multiplying the H-1s orbital. This also is true for all secondary sigma NO's except for the molecular orbitals (B8σ5) and (B9σ6) which are, however, both very weakly occupied. The pi natural orbitals show the same strong polarization toward the hydrogen as the sigma natural orbitals. In fact the two most strongly occupied pi orbitals are almost entirely hydrogenic, whereas the weakly occupied (B7π3) NO is the only one with significant density near Li. Thus, as has been observed before (51), lithium hydride has considerable Li^+H^- character.

As is the case for the K-shell, the occupancies of the NO's decrease with increasing number of nodes in regions of significant density, which can be easily seen from the contour maps. Two NO's which have the same number of nodes have approximately the same occupancy. The magnitude of the occupancy is of major significance in determining the effectiveness of a natural orbital in recovering correlation energy as will be discussed later.

It is also of interest to compare the PNO's with the SCF NO's. In Li the (Li1s) orbital is essentially the SCF orbital. Its orbital energy of -0.19591 hartree differs only slightly from the SCF result of -0.19632 hartree (52). In LiH, comparison of the (B1σ1) NO with the localized bonding SCF orbital determined by Edmiston and Ruedenberg (53,54), and the canonical HF-SCF orbital, indicates that it is closer to the latter rather than to the former. This situation was also found in MR for the first row beryllium-like ions.

Energy of Li and LiH

Table 5 exhibits various aspects of the energy results obtained for Li and LiH. The total energy recovered by the LiH APSG wave function is -8.0541 hartree, and -7.4694 hartree for Li, which are 99.80% and 99.89% of the total experimental energy (10). This means that about 80% of the correlation energies[a] are recovered for the two systems. The binding energy calculated from the two APSG wave functions is 2.30 e.v. or about 90% of the experimental binding energy. The fact that the wave functions for Li and LiH both recovered about 80% of the correlation energy, and the marked improvement in the predicted binding energy when compared to that predicted by the HF-SCF wave functions, indicates that in Li the three electrons form a discrete pair and a lone electron, and in LiH the electrons form two discrete pairs.

The total energies and the binding energies obtained by the PNO single

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[a] The total correlation energy is defined as E(HF-SCF) - E(exact), and the correlation energy recovered by the APSG wave function is E(HF-SCF)-E(APSG).

determinant wave function and that calculated from the Hartree-Fock SCF wave function are also given. The fact that these results differ by only 0.0008 hartree confirms that the PNO wave function is very close to the HF-SCF wave function. The Hartree-Fock SCF calculations quoted is that of Cade and Huo (10), and also experimental quantities are taken from their tabulations. Their investigation is hereafter referred to as HF-SCF. The SCF result of Clementi (52) is adopted for the lithium atom.

In view of the close similarity of the K-geminals in Li and LiH, it is of interest to know how the binding energy is affected if all natural orbitals except the principal one are omitted from the K-shell geminal in Li as well as in LiH. As is seen from Table 5, this type of calculation yields a binding energy of 2.347 e.v. confirming again that the K-shell plays no essential role in molecule formation.

Comparison with other calculations

The HF-SCF wave function for LiH determined by Cade and Huo (10) has been used extensively throughout the present investigation as the upper bound for comparing correlated APSG wave functions of LiH. Their wave function is expanded in terms of 16 Slater Type Atomic Orbitals; twelve are centered on Li and four on H. It yields an energy of -7.98731 hartree.

Five other calculations on LiH are also included in Table 5. The wave function of Bender and Davidson (55), constructed from a basis of elliptic orbitals, gives the best energy result to date. It is a superposition of 45 configurations which were determined using expansions in the natural orbitals. It is superior in that it contains configurations describing both intrashell and intershell correlations, whereas the APSG wave function contains only configurations describing intrashell correlations. It yields an energy of -8.0606 hartree. The occupation numbers of their principal inner and outer natural orbitals are 0.99705 and 0.9749 which are close to the K- and B-geminal PNO occupancies found for the present wave function.

The APSG wave function of Ebbing and Henderson (17) is extracted from a CI wave function obtained earlier by Ebbing (18). Ebbing's wave function is a linear combination of 53 configurations where the molecular orbitals are expanded in terms of elliptic functions, and it yields an energy of -8.04128 hartree. The geminals of Ebbing and Henderson can be illustrated by the charts:

K-geminal

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	2		3				4	-
Order within Π (j)			-		-		-		
Order within Δ (j)						-			

B-geminal (64)

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	2		3	-			-	-
Order within Π (j)			-			-	-		

which are to be compared with the geminals given in chart 60. In order to relate the present APSG wave function to the one of Ebbing and Henderson, all the NO's not contained in chart 64 were eliminated so that the geminals would be similar in structure to those of Ebbing and Henderson. This wave function yielded an energy of -8.0241 hartree as compared to -8.0179 hartree for their wave function. The difference appears to be due to the considerably extended sigma basis used here and the optimization of the present wave function. In addition their PNO result of -7.98167 hartree is slightly higher than that obtained here. The correlation energy attributed to the inner and outer pairs by Ebbing and Henderson is -0.0186 hartree and -0.0176 hartree respectively, while the corresponding quantities obtained here are -0.0207 hartree and -0.0208 hartree. A comparison of the contour diagrams given by Ebbing and Henderson with those presented here for the NO's enumerated, show the similarities between the sigma natural orbitals of the two wave functions.

Another recent CI calculation by R. Brown (56) using elliptic basis functions yielded an energy of -8.0556 hartree with a 69 term wave function. The occupancies of his principal inner and outer molecular orbitals is 0.9970 and 0.9716. The wave function determined by Brown and Matsen (57) is of the valence bond-configuration interaction (VB-CI) type. Their wave function is made up of 28 configurations constructed from both elliptic and Slater type basis functions. They obtained an energy of -8.0561 hartree and determined values for the spectroscopic constants, ω_e, and $\omega_e x_e$. They also obtained an eight term wave function for Li from which a binding energy of 2.34 e.v. was calculated for LiH. The fifth calculation, by Harris and Taylor (58), is an open shell (VB-CI) type, with a wave function made up of four configurations using elliptic basis functions. They reported an energy of -8.0387 hartree, and also determined a three configuration wave function for Li. From the latter they obtained a binding energy of 2.3 e.v.

Separated Pair Approximation in B and BH

Boron and its hydride are the simplest atomic and diatomic cases where more than one electron pair are situated in the same region of space. They are therefore well suited for studying the applicability of the separated pair model to more complex systems, in that complications which might arise are easily isolated.

Geminal expansions

The APSG wave functions for B and BH have the form

$$\Phi_B = \mathcal{A}\{\Lambda_K[(\alpha\beta-\beta\alpha)/\sqrt{2}]\ \Lambda_{LP}[(\alpha\beta-\beta\alpha)/\sqrt{2}]\ \Phi_L\alpha\}$$

$$\Phi_{BH} = \mathcal{A}\{\Lambda_K[(\alpha\beta-\beta\alpha)/\sqrt{2}]\ \Lambda_{LP}[(\alpha\beta-\beta\alpha)/\sqrt{2}]\ \Lambda_B[(\alpha\beta-\beta\alpha)/\sqrt{2}]\} \tag{65}$$

where the geminal, Λ_{LP}, denotes the lone pair (LP) function. The BH wave function is determined at an internuclear separation of 2.329 bohr, which is 0.005 bohr less than the experimental equilibrium distance of 2.336 bohr (29). Since the NO's are symmetry adapted the notation introduced for them in the discussion of Li and LiH can be adopted.

The APSG wave function for BH is expanded in terms of 18 natural orbitals, and six are assigned to each geminal. The structures of the geminals are as follows:

K-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		2	3	4	5
Order within Π (j)		1				

,

B-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1	2		3	4	
Order within Π (j)			1			2

, (66)

LP-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		2	3	4	5
Order within Π (j)		1				

.

The B wave function is a superposition of seven natural orbitals. The geminals have the structures:

K-geminal

Overall order (i)	1	2	3
Order within S (j)	1	2	
Order within P (j)			1

LP-geminal

Overall order (i)	1	2	3
Order within S (j)	1	2	
Order within P (j)			1

(67)

The odd electron in the B valence shell is represented by a NO with P symmetry. If this orbital has pz character, then it must be orthogonal to the pz' admixture of Λ_K and Λ_{LP}. Since the K and LP geminals are, however, both ^1S, they contain px', py', and pz' orbitals in a symmetric fashion. Consequently the strong orthogonality for pz' indirectly restricts the forms of px' and py' as well.

Natural orbital expansions

The natural orbitals of the BH wave function are linear combinations of 18 STAO basis functions, of which fourteen originate from B and four originate from H. The B natural orbitals are expansions of seven STAO basis functions. The STAO's for the atom and the hydride are exhibited in Table 6 with their orbital exponents. The natural orbital expansions in terms of the STAO's are given in Tables 7 and 8 together with the occupation coefficients.

Transferability of K-geminal

It is of interest to examine the question of the transferability of the K-shell pair in B and BH as well as in Li and LiH. The change in symmetry that BH undergoes upon separation is more drastic than that which LiH experiences. It can therefore be anticipated that the K-shells of the B-BH pair will not be as similar as the K-shells of the Li-LiH pair.

In order to compare the two K-geminals it is necessary to obtain the correspondences between the K-natural orbitals of B and the K-natural orbitals of BH. Comparison of the structures 66 and 67 shows that the BH K-geminal has two more natural orbitals than the B K-geminal. In order that the two K-geminals have equivalent expansions, the two weakest σ NO's of the BH K-geminal are omitted, so that

BH K-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		2	3	-	-
Order within Π (j)		1				

.

The correspondences between the NO's are displayed as follows:

Atomic K-NO's	Molecular K-NO's σ	π
K1s1	K1σ1	
K2s2	K4σ3	
K3p1	K3σ2	K2π1

. (68)

Comparison of the quantitative similarities can be obtained from Table 9 where the occupation coefficients and overlap integrals for these natural orbitals are given. It is seen that the occupation coefficients of the respective NO's are still close and that the overlaps are not very different from one. The main source of difference appears in the overlap between the K-PNO's, which is somewhat smaller than for Li-LiH. The values of the overlaps given in Table 9 yield an estimated overlap of 0.97 for the two geminals.

A more detailed comparison of the K-NO's can be obtained from Tables 7 and 8. The corresponding contour maps are as follows:

Atomic NO	Atomic Contour	Molecular NO	Molecular Contour
K1s1	Map No. 43	K1σ1	Map No. 25
K2s2	Map No. 44	K4σ3	Map No. 28
K3p1	Map No. 45	K3σ2, K2π1	Maps No. 26, 27 .

Bonding geminal

The structure of the bonding geminal shows that BH is less polarized toward the hydrogen than LiH. The bonding PNO is approximately

$$(\mathrm{B1}\sigma 1) \approx 0.22(\mathrm{B\text{-}L2p}\sigma) + 0.33(\mathrm{B\text{-}L2p}\sigma') + 0.52(\mathrm{H\text{-}1s}) \quad , \qquad (69)$$

and the coefficient multiplying the H-1s basis orbital is considerably smaller than in LiH. The contributions to the bonding PNO from Boron are essentially from pσ-type orbitals, whereas Eq. 63 shows that in LiH it is a mixture of s-type and pσ-type orbitals. Most of the secondary natural orbitals have significant density near both nuclei. Only the (B3π1) orbital is predominantly hydrogenic, but this is due to the requirement that it must be orthogonal to the (LP2π1) NO.

The (L1p1) orbital of B is close to the SCF orbital and has an orbital energy of -0.3078 hartree as compared to -0.3099 hartree (52) for the SCF orbital. In contrast to LiH, comparison of the (B1σ1) and (LP1σ1) natural orbitals with the localized SCF orbitals and the canonical SCF orbitals (53,54) shows that they are closer to the localized orbitals.

Lone pair geminal

A comparison of the LP-geminals of the two systems is also of interest since they furnish some insight into the severity of the strong orthogonality constraint and the inherent limitations due to the types of double excitation which can be obtained with a single product of pair functions.

The structure of the BH LP-geminal to be compared with the B LP-geminal is

BH LP-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		2	3	-	-
Order within Π (j)		1				

.

A comparison of the geminals can be obtained by displaying the corresponding LP-NO's as was done for the K-shell NO's. Two such charts are given; the one on the left gives the correspondences in terms of the natural orbital notation, and the one on the right replaces that notation with the occupation coefficients of the NO's so that the electron distributions can be compared:

Atomic LP-NO's	Molecular LP-NO's	
	σ	π
LP1s1	LP1σ1	
LP2s2	LP3σ2	
LP3p1	LP4σ3	LP2π1

Atomic LP-NO's	Molecular LP-NO's	
	σ	π
0.9999	0.9738	
-0.0050	-0.0160	
-0.0050	-0.0102	-0.1600

.

It is seen that the LP-geminals of the two systems differ considerably in structure. The secondary orbitals of the B LP-geminal are very weakly occupied, and it is essentially the PNO orbital. The amount of correlation energy recovered, 0.0009 hartree, is small. In contrast, the (LP2π1) SNO's of BH are strongly occupied and recover a large amount, 0.0445 hartree, of correlation energy.

It is of interest to compare the actual form of the (B-LP3p1) NO with the two corresponding (BH-LP4σ3) and (BH-LP2π1) NO's. This can be done with the help of the explicit expansions given in Tables 7 and 8 which yield approximately

$$(\text{B-LP3p1}) \approx 1.3(\text{L2p}') - 1.6(\text{L2p}) \qquad (70)$$

$$(\mathrm{BH\text{-}4\sigma 3}) \approx 1.5(\mathrm{B\text{-}L2p\sigma}) - 1.4(\mathrm{B\text{-}L2p\sigma'}) \qquad (71)$$

$$(\mathrm{BH\text{-}LP2\pi 1}) \approx -1.1(\mathrm{B\text{-}L2p\sigma'}) \qquad (72)$$

or, more easily, with the help of the contour maps 28, 32, and 48. It is readily recognized that the atomic (LP3p1) orbital and the molecular (LP4σ3) orbital have essentially 3p character (one angular and one radial node), whereas the molecular (LP2π1) orbital has essentially 2p character (one angular node only). The reason for this change in nodal behavior is as follows: In the atom the secondary pσ-type orbital in the LP geminal has to be orthogonal to the pσ-type orbital of the unpaired electron, whence its radial node. For symmetry reasons this character must also be adapted by the secondary pπ-type orbitals of the LP-geminal as was discussed above. In the molecule this symmetry requirement is, however, removed and pσ-type and pπ-type orbitals are no longer tied to each other. Therefore, the secondary pπ-type orbitals of the LP-geminal are not restricted by an orthogonality requirement to any other π orbital with high occupation number. It is clear that a 3p-type orbital, with its additional radial node has a higher kinetic energy and thus a higher promotional energy than a 2p-type orbital. It has therefore a weak occupation number and is much less effective in recovering correlation energy. The removal of this radial node from the (BH-LP2π1) orbital upon molecule formation thus creates a possibility for a stronger occupation and for recovering substantial correlation energy which was not available in boron.

It might be pointed out that even if the strong orthogonality condition is relaxed the (L1p1) NO of boron can only be mixed into the B LP-geminal through triple excitations since doubly excited configurations which would mix this NO into the B LP-geminal would vanish. This fact points out a serious limitation of wave functions built from a single product of geminals.

Energy in B and BH

Various aspects of the energy of B and BH are given in Table 10. The total energy obtained by the boron APSG wave function is -24.5622 hartree and that of BH yields -25.2053 hartree, which is 99.62% and 99.66% of the experimental energy (10). The single determinant and HF-SCF energies are also given. The correlation recovered by the APSG wave functions for these two systems is considerably less than that recovered for Li and LiH. It is 25.69% and 46.47% of the total correlation energy for boron and BH respectively. The reason for the difference in correlation energy recovered by B and BH is due to the loss of a good LP-geminal in B. It may be that the small amount of correlation recovered by BH is also caused by the need for the bonding and lone pair geminals to share certain orbitals for describing intrashell correlation. However, it seems more likely that the intershell terms are important in this case, which also requires going beyond the single product of separated geminals for their recovery. Because of the large difference in correlation energy recovered, the estimated binding energy is greater than the experimental binding energy and has a value of 3.858 e.v.

Since the K-geminals of the two systems are still quite close, the binding energy obtained from the B and BH wave functions with the K-shell correlating NO's removed has also been calculated. It is 4.105 e.v. which again confirms the fact that the inner shells of B and BH are not quite as similar as those of Li and LiH.

Comparison with other calculations

The number of calculations which have been done on BH is surprisingly few. BH seems to be an excellent system for studying the capabilities of various approximations to handle a more complex case while still having few enough electrons to be manageable. In addition, the unusual magnetic properties of BH have been investigated using SCF wave functions (59,60), and it will be of interest to apply correlated wave functions to the calculation of these properties.

The HF-SCF wave function for BH determined by Cade and Huo (10) is used as the upper bound for comparing the correlated APSG wave functions obtained in the present investigation. Their wave function is expanded in terms of sixteen Slater Type Atomic Orbitals, twelve of which are centered on B and four on H. The HF-SCF energy obtained from this wave function is given in Table 10.

The recent calculation by Harrison (61) is the best one prior to the present one. With a VB-CI wave function constructed from Gaussian basis orbitals, an energy of -25.1455 hartree was obtained. Ohno (62) determined a 13 configuration wave function for BH constructed from Slater Type Atomic Orbitals. It yielded an energy of -25.110 hartree, and with a two configuration wave function for B he obtained a binding energy of 2.22 e.v. The calculation of Kaufmann and Burnelle (63) is an SCF type, and an energy of -25.1298 hartree is reported. Their wave function is constructed from Gaussian basis orbitals.

CORRELATION ANALYSIS AT THE EQUILIBRIUM DISTANCE

Formulation of Correlation Energy

In order to obtain some insight into how the separated pair model describes correlation, it is desirable to partition the wave function and the energy into two parts, one being essentially the optimal independent particle contribution, and a remainder, which can be attributed to correlation. Since the PNO wave function is very nearly identical with the Hartree-Fock Self-Consistent-Field wave function, it can be taken as a nearly optimal representation of the independent particle model.

A useful partitioning can be obtained by decomposing each geminal into a PNO part and a correlation term, namely

$$\Lambda_\mu(1,2) = \phi_{\mu o}(1)\ \phi_{\mu o}(2) + \Delta\ \Lambda_\mu(1,2)$$

$$\Delta\ \Lambda_\mu(1,2) = \sum_i C_{\mu i}\ \{\phi_{\mu i}(1)\ \phi_{\mu i}(2) - C_{\mu i}\ \phi_{\mu o}(1)\ \phi_{\mu o}(2)\} \quad . \tag{73}$$

Insertion of these identities into the general formulas 1 and 2 yields the corresponding decomposition of the total separated pair wave function.

$$\Phi = \Phi(\mathrm{PNO}) + \Delta\Phi(\mathrm{corr}) \quad . \tag{74}$$

The overlaps of the correlation term with the PNO term are given by

$$\iint d\tau_1\, d\tau_2\ \phi^*_{\mu o}(1)\ \phi_{\mu o}(2)\ \Delta\ \Lambda_\mu(1,2) = C_{\mu o} - 1$$

$$\int d\tau\ \Phi(\mathrm{PNO})\ \Delta\ \Phi(\mathrm{corr}) = \prod_\mu\ (C_{\mu o} - 1) \quad ,$$

and, in LiH and BH, are found to be 0.00002 and -0.00000 for the latter.

From this division of the wave function the following partitioning of the density matrices of Eqs. 7a and 7b is obtained:

$$\left.\begin{aligned}&\rho_\mu(1,1') = \rho_\mu^o(1,1') + \Delta\rho_\mu(1,1')\\&\Delta\rho(1,1') = \kappa_\mu \sum_i c_{\mu i}^2 \{\phi_{\mu i}(1)\,\phi_{\mu i}(1') - \phi_{\mu o}(1)\,\phi_{\mu o}(1')\}\end{aligned}\right\}\quad, \tag{75a}$$

$$\left.\begin{aligned}&\pi_\mu(1,2;\ 1',2') = \pi_\mu^o(1,2;\ 1',2') + \Delta\,\pi_\mu(1,2;\ 1',2')\\&\Delta\,\pi_\mu(1,2;\ 1',2') = 2(\kappa_\mu - 1)\sum_{i,j} c_{\mu i} c_{\mu j}\,\{\phi_{\mu i}(1)\phi_{\mu i}(2)\phi_{\mu j}(1')\phi_{\mu j}(2') -\\&\qquad\qquad \delta_{ij}\phi_{\mu o}(1)\phi_{\mu o}(2)\phi_{\mu o}(1')\phi_{\mu o}(2')\}\end{aligned}\right\}\quad. \tag{75b}$$

By virtue of Eqs. 8 and 9 for the total density matrices, Eqs. 75a and 75b yield a decomposition of the energy into a PNO part and a correlation contribution

$$E = E(\text{PNO}) + \Delta E \tag{76}$$

where

$$E(\text{PNO}) = \sum_\mu E(\mu o,\mu o) + \sum_{\mu<\nu} I(\mu o,\nu o) \quad . \tag{77}$$

For the correlation energy ΔE, one obtains

$$\Delta E = \sum_\mu \Delta E(\mu) + \sum_{\mu<\nu} \Delta I(\mu,\nu) \tag{78}$$

with

$$\left.\begin{aligned}&\Delta E(\mu) = \sum_{i,j} \Delta E(\mu i,\mu j) = \sum_{i,j} c_{\mu i} c_{\mu j}\,\Delta\mathcal{E}(\mu i,\mu j)\\&\Delta\mathcal{E}(\mu i,\mu j) = E(\mu i,\mu j) - \delta_{ij}\,E(\mu o,\mu o)\end{aligned}\right. \tag{79}$$

$$\left.\begin{aligned}&\Delta I(\mu,\nu) = \sum_{i,j} \Delta I(\mu i,\nu j) = \sum_{i,j} c_{\mu i}^2 c_{\nu j}^2\,\Delta\mathcal{I}(\mu i,\nu j)\\&\Delta\mathcal{I}(\mu i,\nu j) = I(\mu i,\nu j) - I(\mu o,\nu o)\quad .\end{aligned}\right. \tag{80}$$

This energy partitioning is that suggested by MR, and it has thus been shown that it can be derived from a corresponding correlation partitioning of the APSG wave function, namely that of Eq. 74.

It is furthermore of interest that the variational Eq. 23 for the occupation coefficients can be written in the form

$$\sum_j \Delta H^{\mu}_{ij}\, C_{\mu j} = \Delta\epsilon_{\mu}\, C_{\mu i} \quad , \tag{81}$$

where

$$\begin{aligned} \Delta H^{\mu}_{ij} &= H^{\mu}_{ij} - H^{\mu}_{ij}(\mathrm{PNO}) \\ &= \Delta\mathcal{E}(\mu i,\mu j) + \delta_{ij} \sum_{\nu(\neq\mu)} \sum_j C^2_{\nu j}\, \Delta\mathcal{I}(\mu i,\nu j) \quad , \end{aligned} \tag{82}$$

and

$$\begin{aligned} \Delta\epsilon_{\mu} &= \epsilon_{\mu} - \epsilon_{\mu o} \\ &= \epsilon_{\mu} - \{E(\mu o,\mu o) + \sum_{\nu(\neq\mu)} I(\mu o,\nu o)\} \end{aligned} \tag{83}$$

are further quantities characteristic of correlation. Whereas $\Delta E(\mu)$ is the <u>intra</u>geminal correlation contribution, the quantity $\Delta\epsilon_{\mu}$ represents the energy change due to correlation of the geminal within the context of the entire system.

General Results

The correlation analyses resulting for Eqs. 78-80 for Li, LiH, B, and BH are given in Tables 11 through 14. These tables are similar in structure to those given in MR for the 4-electron atomic systems.

A number of conclusions reached by MR are confirmed by the present results. Among these are:

1. The principal source of energy lowering in the separated pair

approximation are the intrageminal correlations $\Delta E(\mu)$. The terms $\Delta I(\mu,\nu)$ are smaller and may be either negative or positive.

2. The main contributions to the intrageminal correlation $\Delta E(\mu)$ come from orbital interactions between the principal NO's and the secondary NO's. Contributions arising from interactions between other strongly occupied NO's and the secondary NO's also lower $\Delta E(\mu)$, but are smaller than the PNO contributions.
3. For each secondary NO, two types of energy quantities occur: The negative 'exchange' energies, $\Delta E(\mu i,\mu j)$, and the positive 'promotion' energies $E(\mu i,\mu i)$. For the weakly occupied NO's the promotion term eliminates approximately one-half of the exchange terms.
4. If Eq. 79 is written in the form

$$\Delta E(\mu) = \sum_i \Delta E(\mu i) \tag{84}$$

with

$$\Delta E(\mu i) = \sum_j \Delta E(\mu i,\mu j) \tag{85}$$

one finds that $\Delta E(\mu o)$ is by far the largest contribution. For the moderately occupied NO's the $\Delta E(\mu i)$ are usually negative, and for the weakly occupied NO's they are very small and may be negative or positive. The $\Delta E(\mu i)$ are the orbital correlation energies, and the $\Delta E(\mu i,\mu j)$ are the orbital interaction energies.

Even in BH, where the separated pair function clearly does not recover all the correlation effects-one finds that whatever is recovered is still mainly due to the terms $\Delta E(\mu o)$. Furthermore, according to Eqs. 79 and 85

$$\Delta E(\mu o) = \sum_{j(\neq o)} C_{\mu o}\, C_{\mu j}\, \Delta\mathcal{E}(\mu o,\mu j) \quad , \qquad (86)$$

and, since the exchange integrals $\Delta\mathcal{E}(\mu o,\mu j)$ are positive, it is seen that $\Delta E(\mu o)$ is appreciable and negative only if there exist one or a few secondary orbitals for which $C_{\mu j}$ is opposite in sign to $C_{\mu o}$ and remains strong enough so that $C_{\mu o}C_{\mu j}\Delta\mathcal{E}(\mu o,\mu j)$ is effective. For the K-shell this implies $C_{\mu j}$ of about -10^{-2}, and for the L-shell it requires $C_{\mu j}$ of about -10^{-1}. It therefore appears that, *even in cases where the separated pair approximation can not recover all correlation effects, it can recover intrashell correlations if geminals can be constructed which contain, in addition to the principal natural orbital, at least one moderately occupied secondary orbital with occupation coefficient opposite in sign to the occupation coefficient of the PNO.*

K-shell Correlation Energies

The main feature of the K-shell geminals is that the bulk of the correlation energy is recovered by two or three moderately occupied NO's. In LiH the K-shell orbital interactions $\Delta E(K1\sigma1, K2\sigma2)$, $\Delta E(K1\sigma1, K3\pi1)$, and $\Delta E(1\sigma1, K4\sigma3)$ recover -0.03164 hartree of a total of -0.03582 hartree. The $(K2\sigma2)$ orbital describes K-shell in-out correlation, and the $(K4\sigma3)$ and $(K3\pi1)$ orbitals describe atomic angular correlation. Most of the K-shell correlation in BH is recovered by the orbital interactions between the $(K3\sigma2)$, $(K4\sigma3)$, and $(K2\pi1)$ secondary NO's and the K-PNO, namely -0.02495 hartree out of a total of -0.0260 hartree. The $(K4\sigma3)$ NO describes in-out correlation and the $(K3\sigma2)$ and $(K2\pi1)$ NO's describe atomic angular correlation in BH. The separated atom K-geminals show similar features.

The difference in the amount of correlation recovered by the K-geminals in the hydrides is not clear, especially since in the separated atoms the correlation recovered is nearly the same. It is seen that the loss of correlation energy in the K-geminal of BH is associated with the σ secondary NO's, whereas the correlation energy recovered by the π SNO's remains about the same in the two systems. It appears therefore that the L-shell electrons in BH are interfering with the K-shell secondary NO's in such a way that the orbital interaction energies of the σ K-NO's are decreased. Moreover, this interference appears to depend only on the electron population of the L-shell, since, if it also depended on the nuclear charge, one would expect to find the decrease in effectiveness of certain K-shell secondary NO's in both BH and B.

Bonding Geminal Correlation Energies

Some of the features of the B-geminals are similar to the K-geminals in that, here again, the bulk of the correlation is recovered by two or three secondary natural orbitals. Another characteristic which can be mentioned for both the K- and B-geminals is that, for those cases where the APSG approximation is effective, one has $\Delta E(\mu) \approx \Delta\epsilon_{\mu}$, while for the less effective ones one finds $\Delta E(\mu) < \Delta\epsilon_{\mu}$.

One of the interesting points brought out by Tables 12 and 14 is that some of the <u>intra</u>geminal correlations of moderately occupied orbitals are positive. In their analysis of the Ebbing and Henderson (17) wave function for LiH, Miller and Ruedenberg already noted this feature for the orbital χ_3^o and wondered whether it would persist for a more accurate wave function. Actually one finds for these positive contributions a sum of 0.00151 hartree, which is greater than the 0.00120 hartree obtained by Ebbing and Henderson.

Such positive contributions seem to be peculiar to the bonding geminals of both LiH and BH and do not appear in the other geminals.

Lone Pair Geminal Correlation Energies

The differences between the LP-geminals of boron and BH have already been discussed. It is seen that the LP-geminal of BH has only one secondary orbital which recovers substantial correlation, namely the $(LP2\pi1)$ NO. As was pointed out in MR the contributions to the *inter*shell interaction are essentially between strongly occupied NO's, i.e., they are mainly non-dynamical interactions (64). This situation is still true here, and, in particular, the large value of $\Delta I(LP,B)$ in BH is almost entirely due to the interaction $\Delta I(LP2\pi1, B1\sigma1)$. On the other hand, Li, LiH, and B have no strongly occupied secondary NO's, and thus the *inter*shell interaction terms are either small or negligible.

In comparing the results for LiH and BH it is seen that the decrease in effectiveness of the separated pair approximation is characterized chiefly by a decrease in magnitude of the $\Delta E(\mu)$ contributions, and the appearance of non-negligible positive contributions in the *inter*geminal interaction terms. In the worst cases, such as the B LP-geminal $\Delta E(LP)$ is nearly zero, and the geminal reverts to the Hartree-Fock orbital.

WAVE FUNCTIONS AND ENERGIES AS FUNCTIONS OF THE INTERNUCLEAR SEPARATION

Determination of Wave Function and Energy

Interpolation of Parameters

In order to find wave functions and energies as functions of the internuclear distance, R, it is necessary to perform the minimization procedure at various values of R. The number of parameters to be varied is 88 and 102 for LiH and BH, respectively, and therefore a complete variation is possible only for relatively few points. On the other hand, it is clear that the optimized parameters will be smooth functions of R, and one might expect that this fact could be exploited to reduce the need for independent minimization at each value of the internuclear distance. This idea is pursued here: A detailed minimization is carried through at selected values of R, and a parameter interpolation procedure is developed for intermediate values of the internuclear distance.

The reasonableness of such an approach is suggested by the fact that the values which the various parameters assume in the separated atoms do not differ greatly from the values which are found for the hydrides at the intermediate distances discussed in the preceding section. Consider first the parameters $\gamma_{\alpha\beta}$ determining the matrix $\underline{\underline{T}}$. Most of them vanish in the atoms since the elements of $\underline{\underline{T}}$ connecting orbitals belonging to different eigenvalues of $\vec{L}^2$ and L_z vanish. In the hydrides the analagous γ's are all close to zero. In LiH there are seven γ's which do not vanish for $R = \infty$ and their maximum change is such that

$$0 < |\gamma(R=3.015) - \gamma(R=\infty)| < \pi/8 \quad . \tag{87}$$

For BH, there are 13 γ's which are non-zero in the separated atom limit and, with one exception, they vary within the range

$$0 < |\gamma(R = 2.329) - \gamma(R = \infty)| < \pi/4 \quad . \tag{88}$$

The exception mentioned is $\gamma_{L\pi,L\pi'}$, as is evident from the following list

	γ(B-Lpσ,B-Lpσ')	γ(B-Lpπ,B-Lpπ')
B	-0.97234	-0.97234
BH	-0.83956	-2.10426

.

The splitting of the atomic γ(B-Lp,B-Lp') parameter into the two molecular parameters, γ(B-Lpσ,B-Lpσ') and γ(B-Lpπ,B-Lpπ'), is of course due to the change from spherical to cylindrical symmetry. However, even γ(B-Lpπ,B-Lpπ') changes only from -2.11004 to -2.11223 as R changes from 2.2 to 2.7 bohr.

Finally, inspection of Tables 1 and 6 shows that the difference between the orbital exponents at $R = R_e$ and $R = \infty$ is also small enough to suggest the possibility of an interpolation.

The approach outlined here is found to yield good results as well as a considerable reduction in computing time. It should therefore be of particular interest in larger systems, where the problem of many parameters is even more severe.

Optimization at reference points

As discussed in the previous section, complete optimizations were carried out at R = 3.015 and 2.329 bohr for LiH and BH respectively. Additional detailed independent minimizations were performed at the internuclear distances R = 2.8, 4.0 and 8.0 bohr in the case of LiH and for R = 2.2, 2.7 and 5.0 bohr in the case of BH. However, these minimizations did not comprise all parameters in each system; only those which could reasonably be expected to show a significant change with the internuclear distance were varied.

In the preceding section, it was pointed out that certain geminals such as the K-shell geminals in LiH and BH are rather insensitive to the changes in electronic environment occurring during molecule formation. It was furthermore found that the binding energy was little affected when the secondary natural orbitals were omitted in these geminals. In view of these results it seems likely that the secondary NO's of such geminals hardly change with R, and the parameters which are most influential in their determination will very nearly keep the values obtained for them at R = 3.015 for LiH and R = 2.329 for BH. If this is the case it should be adequate to reminimize only the remaining parameters and, furthermore, to omit the insensitive secondary NO's during the course of such minimization. If the computer program is appropriately constructed the omission of certain NO's can be accomplished by simply setting the corresponding matrix elements in Eq. 23 equal to zero.

On the other hand, it is important to retain <u>all</u> K-shell <u>basis</u> orbitals because they are required for a good representation of the <u>principal</u> natural orbital of the K-shell. That this is so can be seen by comparison with the K-orbital of the HF-SCF wave function which, as has been seen before, is very close to the K-PNO. Similarly, it seems desirable to retain all outer shell basis orbitals to maintain optimal representations for the retained natural orbitals. Thus, wave functions with geminals of the following natural orbital structure were optimized at the aforementioned values of R:

LiH K-geminal

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	-		-				-	-
Order within Π (j)			-		-		-		
Order within Δ (j)						-			

,

LiH B-geminal

Overall order (i)	1	2	3	4	5	6	7	8	9
Order within Σ (j)	1	2		3	4			-	-
Order within Π (j)			1			2	-		

,

and

BH K-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		-	-	-	-
Order within Π (j)		-				

,

BH LP-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1		2	3	-	-
Order within Π (j)		1				

,

BH B-geminal

Overall order (i)	1	2	3	4	5	6
Order within Σ (j)	1	2		3	-	-
Order within Π (j)			1			

.

It may be noticed that certain very weakly occupied binding and lone pair orbitals are also omitted. Since there are now less natural orbitals than basis orbitals the number of independent parameters γ_{ij} introduced by Eqs. 34-38 for the orthogonal $\underline{\underline{T}}$ matrix are also reduced. The correct number of independent parameters is taken into account if one excludes from variation those γ_{ij} for which <u>both</u> indices, i and j, refer to any one of the omitted NO's.

The reduction in the number of NO's leads therefore to two kinds of calculational economies: A number of matrix elements H^{μ}_{ij} of Eq. 23 are omitted, and the number of γ-variations is reduced. Of these two the former savings is more significant and amounts to about a 50% reduction in computing time.

The orbital exponents were varied for all R values mentioned, except for R = 8 and 5 bohr in LiH and BH respectively. At these large distances the gain of such variation seemed to be too small to justify the investment.

After the described optimizations had been carried out to determine the orbital exponents and the $\underline{\underline{T}}$ matrix, the values of the parameters were then taken as adequate representations for <u>all</u> natural orbitals of the full wave function. Using these orbital exponents and $\underline{\underline{T}}$ matrix elements to calculate the matrix elements H^{μ}_{ij} between all natural orbitals, the occupation coefficients were determined from Eq. 23 to yield the full wave function and energies at the aforementioned points of R. The resulting wave functions are given in Tables 15-20.

<u>Energy as function of R</u>

Graphs 1 and 2 give the energies for LiH and BH as functions of the internuclear distance. They are based on energy values calculated at intervals of 0.05 bohr. The parameters are obtained from a linear interpolation between the previously discussed reference points. A summary of some of the relevant energy results are listed in Tables 21 and 22 respectively.

Graphs 3 and 4 contain a comparison of the PNO energy curves with the HF-SCF energy curves of LiH and BH. The two types of curves are very nearly parallel. In LiH the maximum deviation from being parallel is 0.00018 hartree, and in BH it is 0.0052 hartree. This parallelism seems to confirm that the interpolation optimization scheme used here is indeed satisfactory.

Electronic Structure as Function of Internuclear Distance

Essential features of the dependence of the electronic structure of LiH and BH on the internuclear separation can be obtained from examining the occupancies of the important natural orbitals which are summarized in Tables 23 and 24, and the changes of the _intra_- and _inter_geminal correlation energies displayed in Graphs 5 and 6 as functions of R. Only the occupancies of the PNO's and the moderately occupied SNO's are given in the tables.

Inner shells

It is seen from both the occupancies of the NO's and from the correlation energy plots that the K-shells of both hydrides are essentially independent of R. The maximum change of the occupancy of the K-shell PNO of LiH is only 0.00026, and in BH it is 0.00004. These changes, and the very small changes in occupancy exhibited by the K-shell SNO's have essentially no effect on the overall electronic structure of these hydrides as R increases. In his recent calculation of the $^1\Sigma^+$ states of LiH, R. Brown (56) notes the same trend, and the maximum change in the occupancy of his principal K-shell configuration is 0.00021 which is remarkably similar to that found here. Comparison of the K-shells of the two systems shows that the BH K-shell is less affected by changes in R than LiH. This is perhaps due to the fact that in BH half of the valence shell electrons essentially retain their atomic character.

Character of bonding geminals

The behavior of the bonding geminals is determined by the fact that the (B1σ1) and (B2σ2) NO's must pass to the natural orbitals for the lone electrons of the separated atoms. The other natural orbitals of the bonding geminal become vacant for an APSG wave function. This fact is indicated by the form of Eq. 16 where it is seen that the intrageminal term, $[\phi_{\mu i}\phi_{\mu j}|\phi_{\mu j}\phi_{\mu i}]$, reduces to zero when the bonding geminal is replaced by a natural spin orbital for an odd electron. Furthermore, Eq. 33 shows that ϵ_{μ} and $\sum_i \lambda_{\mu i,\mu i}$ become identical for an unpaired electron and hence the natural spin orbital for it is an approximation to the SCF orbital. In the previous section this was indeed found to be the case for Li and boron.

The detailed nature of the passage of the bonding geminal to the separated atom geminal is given by the following relations (65): Considering only the first two natural orbitals, the bonding geminal is approximately

$$\Lambda_B \approx C_{B1}\, \phi_1(1)\, \phi_1(2) + C_{B2}\, \phi_2(1)\, \phi_2(2) \tag{89}$$

with

$$\phi_1 = A + B$$
$$\phi_2 = A' - B'$$

where A represents the basis expansion originating from center A, and B represents the basis expansion originating from center B. The transition from two strongly interacting valence shells to two weakly interacting separated atoms can be seen by writing Λ_B in the equivalent form

$$\begin{aligned} \Lambda_B \approx\ & (C_{B1} + C_{B2})\ \{\psi_1(1)\ \psi_1(2) + \psi_2(1)\ \psi_2(2)\}\ /\ 2 \\ & + (C_{B1} - C_{B2})\ \{\psi_1(1)\ \psi_2(2) + \psi_2(1)\ \psi_1(2)\}\ /\ 2 \end{aligned} \tag{90}$$

with

$$\left.\begin{aligned} \psi_1 &= (\phi_1 + \phi_2)/\sqrt{2} \\ \psi_2 &= (\phi_1 - \phi_2)/\sqrt{2} \end{aligned}\right\} \quad . \tag{91}$$

For very large R one finds (note that $C_{B1} > 0$, $C_{B2} < 0$)

$$C_{B1} + C_{B2} << C_{B1} - C_{B2}$$

and finally at infinite separation $C_{B1} = -C_{B2}$ so that

$$\Lambda_B = \{\psi_1(1)\ \psi_2(2) + \psi_2(1)\ \psi_1(2)\}/\sqrt{2} \quad . \tag{92}$$

This behavior of the occupation numbers for the (B1σ1) and (B2σ2) orbitals can be seen from Tables 23 and 24. In LiH the occupancy of the (B1σ1) NO has decreased from 0.9712 at R = 3.00 bohr to 0.7908 at R = 7.00 bohr, and at the same points the (B2σ2) NO has increased from 0.0151 to 0.2067 so that $(C_{B1}+C_{B2})$ has decreased from 0.86284 to 0.43457, and $(C_{B1}-C_{B2})$ has increased from 1.10818 to 1.34391. BH shows similar trends as can be seen from Table 24.

The concomitant change in the natural orbitals ϕ_1, ϕ_2, ψ_1 and ψ_2 of Eqs. 89 and 91 is illustrated in Diagrams 1-6 for the LiH molecule. These diagrams are similar to the ones given in Appendix B, and details concerning their use may be found there. (The solid lines denote positive regions of the orbital while the dashed lines denote negative regions and the dotted lines are the nodes). Diagrams 1 and 2 represent the (B1σ1) and (B2σ2) NO's at R = 3.00 bohr; Diagrams 3 and 4 are the same NO's at R = 7.00. Comparison of Diagrams 1 and 3 and 2 and 4 clearly shows the shift of electron density from the bonding region to the regions around the two nuclei with the concomitant formation of the 1s orbital for H and the 2s orbital of Li. The formation of the separated atoms is seen even more clearly from the plots of the separated atom orbitals, ψ_1 and ψ_2 at R = 7.00 bohr, exhibited in Diagrams 5 and 6. It is apparent that at this distance the H orbital ψ_2 has very little admixture from the Li atom, whereas the more diffuse Li orbital still interacts to some extent with the H atom. It is clear from Diagrams 5 and 6 that ψ_1 is approaching the 2s orbital of Li and ψ_2 is approaching the 1s orbital of H.

Correlation in bonding geminals

Further insight into the behavior of the bonding pair is gained from examining the changes in correlation energy as the nuclear separation is increased, and are exhibited in Graphs 5 and 6. The change in character of the (B2σ2) NO from a moderately occupied correlating orbital in the bonding geminal to the strongly occupied orbital A' - B' appears as a rapid increase of the absolute value of ΔE(B) with increasing R. This increase is associated with the (B1σ1, B2σ2) interaction since the orbital interactions of the remaining SNO's are becoming weaker. For example, in LiH the correlation energy associated with the (B1σ1, B3π1) orbital interaction changes from -0.0122 hartree at R = 3.00 bohr to -0.0017 hartree at R = 8.00 bohr, which indicates that the angular correlation is decreasing with increasing R. At $R = R_\infty$, ΔE(B) represents the energetic error due to inappropriate "ionic terms" by which the "MO-approximation" $\phi_1\phi_2$ differs from the "covalent VB approximation" of Eq. 92, which describes more appropriately two weakly interacting separated atoms. The behavior of the total correlation energy as a function of R and the correlation splitting between the (B2σ2) orbital and the (B3π1) orbital is in agreement with that found by Davidson and Jones (66) in their analysis of the correlation splitting in H_2.

The ΔE(B) curve of BH is similar to that of LiH, but its rate of change is slower. This is perhaps due to the fact that because of the higher charge of the boron nucleus it will be less affected by a hydrogen atom over an equal interval of R than Li. Examination of the correlation splitting shows that, here too, the increase of $\Delta E(B)$ is due to $\Delta E(B1\sigma 1, B2\sigma 2)$; whereas $\Delta E(B1\sigma 1, B3\pi 1)$ changes from -0.0067 hartree at R = 2.329 bohr to -0.0039 hartree at R = 4.5 bohr and presumably goes to zero at infinite separation.

The behavior of the intergeminal correlation term $\Delta I(K,B)$ is due almost entirely to the $\Delta I(K1\sigma 1, B2\sigma 2)$ interaction which changes from an interaction between a strongly and moderately occupied natural orbital to an interaction between two strongly occupied natural orbitals. The former interactions are in general small, whereas the latter are found to be fairly large and positive. The magnitude of $\Delta I(K,B)$ is, however, small in comparison to $\Delta E(B)$.

Lone pair geminal

The correlation changes occurring in the LP-geminal in BH are more difficult to assess. The $\Delta E(LP)$ curve passes through a maximum near R_e and then appears to pass through a minimum near R = 4.00 bohr. On the other hand, the $\Delta I(K,LP)$ curve seems to nearly offset the changes in $\Delta E(LP)$ so that the overall result is that the geminal correlation energy, $\Delta\epsilon_{LP}$, is nearly constant. This implies that it would have been possible to omit the lone pair SNO's as well as the K-shell SNO's for this case. The details of the structure of lone pairs and their effect on the total electronic structure appear to need further investigation.

Spectroscopic Constants

The spectroscopic constants for LiH and BH are calculated by using the procedure of Dunham (67). The potential curves are expanded in terms of the reduced coordinates $\rho = (R - R_e)/R_e$ as

$$V = a_o \rho^2 (1 + \sum_k a_k \rho^k) \quad , \tag{93}$$

and Dunham has given the relations between the spectroscopic constants and the expansion coefficients of Eq. 93.

If a polynomial of the type of Eq. 93 is fitted to theoretical curves such as those obtained here, the problem arises under which conditions the coefficients a_k are stable with regard to the choice of (1) the interval chosen for ρ, (2) the number of points used in this interval, and (3) the degree of the expansion polynomial which is fitted. Because, for any given fixed value of R, the numerical minimization can never be complete, there exists a certain random scattering of the computed energies around that E(R) curve corresponding to mathematically perfect minimization at all points. Because of this scattering there is a maximum degree of the polynomial which can be meaningfully determined by a least mean square calculation within a finite interval, $\langle R_1, R_2 \rangle$, no matter how many points are included in the fitting. Conversely, determination of a fourth degree fitting requires a minimum interval length. If the interval length chosen is such that a higher degree polynomial can be determined, only then is it possible to investigate if a fourth order approximation is an adequate representation of E(R) in this interval. In any case, the number of points used in a least mean square fit should be considerably larger than the order of the polynomial to be found.

Another consideration is, however, essential for the present purpose. Since the aim is comparison with experimental data, the curve E(R) should be fitted over that interval which is sampled by the first four to six vibrational levels, in as much as they are necessary to determine the experimental values of a_0, a_1, and a_2.

Since a number of points of the potential curve were obtained over a fairly wide interval by the method outlined in the preceding section, a least mean square program was used to determine polynomials of degree four through eight for four interval sizes including the minimum. The minimum point for each polynomial was determined by finding the value of R for which the linear term vanishes. This minimum was used rather than inserting the actual minimum of the APSG potential curve so that points near it could be used without convergence problems. (The difference between the two is only $\sim 10^{-3}$ bohr). The coefficients of polynomials of the fifth, sixth, and seventh degree fitted to the LiH potential curve are given in Table 25.

From Table 25 it is seen that the first and the second intervals are not sufficient. The coefficients for the two larger intervals appear to have settled down and agree to about two figures. Between the fifth and sixth degree polynomials the agreement is also about two figures for a_0 and a_2, but only one figure for a_1; similar considerations apply to the seventh degree polynomial. In LiH the fifth, sixth and seventh degree polynomials give stable coefficients, in the largest interval, in the sense that the higher order ones, $a_3 \ldots$, are reasonably small. This is also the interval which approximately corresponds to the first four vibrational energy levels. The root mean square deviation of these polynomials is about 2×10^{-5}. Polynomials of higher degree give fluctuating large coefficients for the high order terms, which is indicative of random scattering of the energy values to which the polynomial is being fitted. For BH the fourth, fifth and sixth degree polynomials in the interval R = 1.90 - 3.00 bohr give stable coefficients, and have a root mean square deviation of approximately 1×10^{-4}. Since the choice between stable polynomials seems arbitrary, averages over the fifth, sixth and seventh degree polynomials for LiH, and the fourth, fifth and sixth degree polynomials for BH, are tabulated.

The resulting spectroscopic constants together with the experimental values (29,68) and percentage deviations are given in Table 26. The spectroscopic constants, especially $\omega_e x_e$, are sensitive indicators of the degree of agreement between the theoretical potential curve and the true potential curve, and the results obtained here are quite good. The results calculated from each polynomial for LiH showed less fluctuation about the averages than those for BH. This is not surprising since the potential curve for LiH was determined to a higher degree of optimization than the potential curve for BH. The largest fluctuations are in the anharmonicity term, $\omega_e x_e$, and the closeness of the average value to the estimated value for BH must be interpreted with caution.

It is possible to determine the expansion coefficients of Eq. 93 from the experimental spectroscopic constants and hence construct an "experimental potential curve." For LiH Jorgensen and Crawford (68) have determined all the constants through a_6, and for BH a_0, a_1 and a_2 were determined from the data of Bauer, Herzberg and Johns (29). Using current values for the physical constants (69) and putting a_0 in atomic units the two potential curves

$$V_{LiH} = 0.2995\rho^2(1 - 1.884\rho + 2.378\rho^2 - 2.473\rho^3) \quad , \qquad (94)$$

$$V_{BH} = 0.5313\rho^2(1 - 2.115\rho + 2.873\rho^2) \qquad (95)$$

are obtained from these sources. They are to be compared to the fifth and fourth degree polynomials fitted to the APSG potential curves

$$V_{LiH}(\mathrm{APSG}) = 0.3426\rho^2(1 - 2.409\rho + 4.332\rho^2 - 3.947\rho^3) \tag{96}$$

$$V_{BH}(\mathrm{APSG}) = 0.8609\rho^2(1 - 2.647\rho + 4.038\rho^2) \quad . \tag{97}$$

Graphs 7 and 8 plot the experimental and calculated potential curves of LiH and BH, as well as their differences.

CONCLUSIONS

General Effectiveness of the Separated Pair Approximation

The present investigation has shown that the separated pair model yields good wave functions for some systems but not for others. From the view point of the electron pair interpretation of chemical structure one would have expected that the separated pair model would adequately and completely describe both LiH and BH. In fact, it works well for LiH but only partially for BH. Thus the applicability of the separated pair approximation appears to be more limited than previously realized. It has been shown that the inner shell electrons are in fact adequately described by the separated pair approximation. Valence shell correlations, however, are only incompletely accounted for if the atomic valence shell contains more than one electron pair.

The shortcomings are of two types:

1. The strong orthogonality constraint excludes the secondary natural orbitals from recovering correlation effects in more than one geminal.
2. A single product of separated geminals neglects _inter_shell correlation.

To assess the relative importance of these two shortcomings it must be kept in mind that even if the strong orthogonality constraint is relaxed, a single product of pair functions is still limited in the type of double excitations that can be constructed. As has been shown by Bender and Davidson (70) in a CI-NO calculation of FH, a large part of the correlation is recovered from split-shell excitations of _inter_shell character which cannot be obtained with a simple product of pair functions. It thus appears that the second limitation will prove to be the more serious one. One possible way of describing intershell correlations, which allows one to remain within the pair function framework, is by the split-geminal excitations of the augmented separated pair approximation (71,72).

K-geminals

The application of the separated pair approximation to Li, LiH, B, and BH has shown that the K-shell acts as a separated pair, and is well described within the context of the separated pair approximation. Moreover, it has been quantitatively shown that the K-shell pair is little affected by changes occurring in the valence shell, and therefore the detailed correlation structure of the inner shell can be omitted in the calculation of differences between molecular and atomic properties. The inner shell in the molecule is even less sensitive to small changes in internuclear distance. In fact, the inner shell of BH is less affected by changes in R than the inner shell of LiH.

The source for the decrease in the K-geminal correlation in BH as compared to that in B needs further investigation. Perhaps this problem can be overcome by a more general pair formulation; on the other hand the relative change of the K-shell correlation between them may be less in systems where the L-shells of both the molecule and the separated atom are highly populated.

Determination of APSG Wave Functions for Other Systems

Through the analysis of the present calculations it can be concluded that the effectiveness of the separated pair approximation in a specific case can be determined with a relatively small computational effort. Since the bulk of the correlation is recovered by two or three secondary NO's in each geminal, the energy and other properties calculated from a wave function which includes only these NO's will be nearly as good as the energy calculated from a wave function containing a much larger number of natural orbitals. This is illustrated in LiH where a wave function expanded in terms of the basis given in Table 1, but including only the first four natural orbitals of each geminal given in the structure diagrams of 60, yields an energy of -8.04956 hartree. This is only 0.00462 hartree higher than the energy obtained from the total wave function. The time needed to compute the energy for this wave function is 40% less than the time needed for the total wave function, and the time taken to calculate the geminal matrix elements after the atomic integrals have been calculated is only 40% as long as in the total wave function. It therefore seems reasonable to construct wave functions expanded in terms of the PNO's and one or two secondary NO's in each geminal, which can then be analyzed to determine whether substantial correlation has been recovered. Such wave functions require little computing time for their optimization. In this way it would be possible to rapidly survey a large number of systems to determine if the separated pair model can be fruitfully applied to them.

Determination of Approximate Potential Curves

The results which have been obtained from the approximate potential curves show that the method will give good qualitative results, and it appears that with some additional refinements satisfactory quantitative results can also be obtained. The principal benefit gained from this method is that many points of a potential curve can be determined for many-parameter wave functions without an inordinately large amount of computer time.

The main difficulty encountered in the procedure is matching up the potential curve at the end points of each succeeding segment. In order that the segments are properly matched, the wave function must be carefully optimized to the same degree of accuracy at each value of R where the energy is minimized. Experience indicates that the APSG wave function is more sensitive to variations in the orbital exponents than the HF-SCF wave function, and therefore it is essential that the wave function be reasonably optimized in all its variation parameters if reliable quantitative results are to be obtained. An additional refinement is that the parameters can be fitted to higher order interpolation polynomials than the linear ones used here, which would help smooth out scattering due to slight differences in minimization.

PART II. TWO-CENTER EXCHANGE INTEGRALS BETWEEN SLATER TYPE ATOMIC ORBITALS

INTRODUCTION

Calculation of electronic wave functions for diatomic molecules can be made most effectively if Slater Type Atomic Orbitals are used as a basis set and, in spite of well known difficulties, it may well be that, in the long run, this type of expansion basis will also prove to be practical for polyatomic molecules. In two-center problems, there appear three types of electron repulsion integrals which present mathematical and computational difficulties: The coulomb, hybrid, and exchange integrals and, because efficient methods for their evaluation are essential, various workers have attacked the problem of general methods for their determination (73,74). For all three integral types, new methods were recently developed in this laboratory. While the analyses for the first two were published in previous papers (75,76), the present note deals with some new developments concerning the exchange integrals.

The basis of the method is the analysis which had been given some time ago by one of the authors (77,78). Here we introduce several new developments which greatly increase the effectiveness of the procedure. A particularly useful improvement is an expansion of charge distributions between atomic orbitals in terms of products of powers and Legendre functions of the elliptic coordinates. General formulas are derived for the coefficients appearing in these expansions for the product of any two arbitrary Slater Type Atomic Orbitals. These and other modifications lead to considerable simplification, in particular for implementation on an electronic computer.

GENERAL FORMULA FOR THE EXCHANGE INTEGRAL

Introduction of Neumann Expansion and Integration by Parts

The electron interaction integral under consideration is the two-center exchange integral over arbitrary atomic orbitals

$$I = \int dV_1 \int dV_2 \, \Omega(1) \, \bar{\Omega}(2) \, r_{12}^{-1} \quad , \tag{98}$$

where the charge distribution functions Ω and $\bar{\Omega}$ are two-center functions defined by

$$\Omega(1) = \chi_a \chi_b \quad , \qquad \bar{\Omega}(2) = \bar{\chi}_a \bar{\chi}_b \quad , \tag{99}$$

and the χ_i are atomic orbitals with origin at i.

The integration is carried out in elliptic coordinates. If $\underline{r}_i$ is the radius vector of the electron from origin i, and R is the distance between the nuclei, these coordinates are defined by the relations

$$\begin{aligned} r_a &= \tfrac{1}{2}R(\xi+\eta) & r_b &= \tfrac{1}{2}R(\xi-\eta) \\ z_a &= \tfrac{1}{2}R(1+\xi\eta) & z_b &= \tfrac{1}{2}R(1-\xi\eta) \\ (x_a^2 + y_a^2)^{1/2} &= (x_b^2 + y_b^2)^{1/2} = \tfrac{1}{2}R[(\xi^2-1)(1-\eta^2)]^{1/2} = \tfrac{1}{2}Rd \\ dV &= (\tfrac{1}{2}R)^3(\xi^2-\eta^2)\,d\xi\, d\eta\, d\varphi \end{aligned} \tag{100}$$

where r_i is the magnitude of $\underline{r}_i$ and x_i, y_i, and z_i are its components in cartesian coordinates. It is assumed that the z_a axis points from atom a to atom b whereas the z_b axis points from atom b to atom a, and that the x_a, y_a axes are parallel to the x_b, y_b axes respectively. For the inverse distance $(1/r_{12})$, the Neumann expansion (77) yields the following expression in elliptic coordinates

$$(1/r_{12}) = (4/R) \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-1)^m \frac{(\ell-|m|)!}{(\ell+|m|)!} P_\ell^{|m|}(\xi_1)\, Q_\ell^{|m|}(\xi_2) \cdot \mathcal{Y}_{\ell m}(\eta_1,\varphi_1)\, \mathcal{Y}_{\ell m}(\eta_2,\varphi_2) \tag{101}$$

where $\xi_1 < \xi_2$, and ξ_1, ξ_2 must be interchanged in the product PQ if $\xi_1 > \xi_2$. The Q_ℓ^m are the Legendre functions of the second kind, and the P_ℓ^m are the Legendre functions of the first kind (47). The real spherical harmonics, $\mathcal{Y}_{\ell m}$, are taken to be

$$\mathcal{Y}_{\ell m}(\eta,\varphi) = \mathcal{P}_\ell^{|m|}(\eta)\ f(m)\ [\pi(1+\delta_{m0})]^{-1/2} \tag{102}$$

where the definitions

$$\begin{aligned} \mathcal{P}_\ell^m(\eta) &= \left[\frac{2\ell+1}{2}\,\frac{(\ell-m)!}{(\ell+m)!}\right]^{1/2} P_\ell^m(\eta) \\ P_\ell^m(\eta) &= (1-\eta^2)^{m/2}\, P_\ell^{(m)}(\eta) \\ P_\ell^{(m)}(\eta) &= (d/d\eta)^m\, P_\ell(\eta) \end{aligned} \tag{103}$$

are used for the Legendre functions, and f(m) is defined as

$$f(m) = \begin{cases} \cos |m|\,\varphi & \text{if } m \geq 0 \\ \sin |m|\,\varphi & \text{if } m < 0 \end{cases} . \tag{103'}$$

Introduction of the Neumann expansion into I yields

$$I = \sum_{\ell m} (-1)^m \frac{(\ell-|m|)!}{(\ell+|m|)!} \int_1^\infty d\xi\, Q_\ell^{|m|}(\xi) \cdot [\Omega_{\ell m}(\xi) \int_1^\xi dx\, P_\ell^{|m|}(x)\, \bar{\Omega}_{\ell m}(x) + \bar{\Omega}_{\ell m}(\xi) \int_1^\xi dy\, P_\ell^{|m|}(y)\, \Omega_{\ell m}(y)] \tag{104}$$

where the second term in brackets has been obtained by an interchange in the order of integration. The functions $\Omega_{\ell m}(\xi)$ are found from Eqs. 100 and

101 to be

$$\Omega_{\ell m}(\xi) = \int_{-1}^{1} d\eta \int_{0}^{2\pi} d\varphi (\tfrac{1}{2}R)^3 (\xi^2-\eta^2)\, \mathcal{Y}_{\ell m}(\eta,\varphi)\, \Omega(\xi,\eta,\varphi) \quad . \tag{105}$$

Since the total bracket term in Eq. 104 is of the form

$$f(x)dg(x) + g(x)df(x) = d[f(x)g(x)] \quad , \tag{106}$$

the integral I can be written as

$$\begin{aligned} I = \sum_{\ell m} (-1)^m \frac{(\ell-|m|)!}{(\ell+|m|)!} \int_1^\infty d\xi [Q_\ell^{|m|}(\xi)/P_\ell^{|m|}(\xi)] \\ \frac{d}{d\xi} [\int_1^\xi dx\, P_\ell^{|m|}(x)\, \Omega_{\ell m}(x) \int_1^\xi dy\, P_\ell^{|m|}(y)\, \bar{\Omega}_{\ell m}(y) \quad , \end{aligned} \tag{107}$$

and then integrated by parts, the integrated part vanishing (78). Making use of the relation

$$QP' - PQ' = (-1)^m \frac{(\ell+|m|)!}{(\ell-|m|)!} [1-x^2]^{-1} \tag{108}$$

for the Wronskian of Q and P, I is reduced to the form

$$I = \sum_{\ell m} \int_1^\infty f_{\ell m}(\xi)\, \bar{f}_{\ell m}(\xi) \tag{109}$$

where

$$f_{\ell m} = [(\xi^2-1)^{1/2} P_\ell^{|m|}(\xi)]^{-1} \int_1^\xi dx\, P_\ell^{|m|}(x)\, \Omega_{\ell m}(x) \tag{110}$$

with $\Omega_{\ell m}$ defined by Eq. 105.

The principal result of Eq. 109 is that the functions $f_{\ell m}(\xi)$ can be evaluated separately and then combined in pairs to yield the integrals I, as was pointed out previously (78). This results in a significant saving of computational effort since the number of $f_{\ell m}$ arising from a given basis set of atomic orbitals is very much smaller than the number of exchange integrals.

Introduction of Charge Distribution Expansions

In order to evaluate the functions $f_{\ell m}(\xi)$ and obtain a general formula for the exchange integral, it is assumed that the charge distributions of Eq. 99 are expanded in the following way:

$$(\tfrac{1}{2}R)^3\ (\xi^2-\eta^2)\Omega(\xi,\eta,\varphi) = \sum_{\lambda mk} \omega^m_{\lambda k}(\xi-1)^k(\xi^2-1)^{m/2}\, e^{-\alpha\xi}\, Y_{\lambda m}(\eta,\varphi) \qquad (111)$$

where $\omega^m_{\lambda k}$ are constants to be discussed later on. From Eqs. 105, 110, and 111 one then obtains

$$f_{\ell m}(\xi) = \sum_k \omega^m_{\ell k}\ [(\xi^2-1)^{1/2}P_\ell^{|m|}]^{-1} \int_1^\xi dx(x^2-1)^{|m|/2}P_\ell^{|m|}(x)\,(x-1)^k e^{-\alpha x}\ . \qquad (112)$$

Using Rodrigues' formula for the Legendre functions one finds for $m \geq 0$,

$$\begin{aligned}(x^2-1)^{m/2}P_\ell^m(x) &= \frac{1}{2^\ell \ell!}\ (x^2-1)^m(d/dx)^{\ell+m}(x^2-1)^\ell \\ &= \frac{1}{2^\ell \ell!}\,\frac{(\ell+m)!}{(\ell-m)!}\ (d/dx)^{\ell-m}(x^2-1)^\ell \qquad (113)\\ &= \frac{(\ell+m)!}{(\ell-m)!}\sum_{\nu=0}^{\ell} c_\nu^{\ell m}\ t^{\nu+m}\end{aligned}$$

where

$$\begin{aligned}c_\nu^{\ell m} &= (\ell+\nu)!/(\ell-\nu)!\nu!\ (\nu+m)!\ 2^\nu \\ t &= x-1\end{aligned} \qquad (114)$$

and similarly

$$(x^2-1)^{1/2}P_\ell^m(x) = \frac{(\ell+m)!}{(\ell-m)!}\ t^{(1+m)/2}\ (t+2)^{(1-m)/2} \sum_{\nu=0}^{\ell} c_\nu^{\ell m}\ t^\nu\ . \qquad (115)$$

Combining the results of Eqs. 113 and 115, and setting $s=t/(\xi-1)=(x-1)/(\xi-1)$

one obtains the result

$$f_{\ell m}(\xi) = e^{-\alpha} \sum_{k} \sum_{\nu} \omega^{m}_{\ell k} \, c^{\ell m}_{\nu} \, \tau^{(1+m)/2} \, (\tau+2)^{(m-1)/2} \, \tau^{k+\nu} \cdot q_{\nu+k+m}(\alpha\tau) \Big/ \sum_{\nu} c^{\ell m}_{\nu} \, \tau^{\nu} \quad , \tag{116}$$

where

$$\tau = \xi - 1 \tag{117}$$

and

$$q_j(z) = \int_0^1 ds \; e^{-zs} \, s^j \quad . \tag{118}$$

Inserting the right hand side of Eq. 116 into Eq. 109 for $f_{\ell m}$ and $\bar{f}_{\ell m}$, one obtains the following final formula for the exchange integral

$$I = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \int_0^{\infty} d\tau \; W_{\ell m}(\tau) \, \bar{W}_{\ell m}(\tau) \tag{119}$$

where

$$W_{\ell m}(\tau) = e^{-\alpha} \tau^{(1+m)/2} \, (\tau+2)^{(m-1)/2} \sum_{n} \tau^{n} q_{n+m}(\alpha\tau) \, b^{\ell m}_{n} \Big/ \sum_{\nu} c^{\ell m}_{\nu} \, \tau^{\nu} \tag{120}$$

and

$$b^{\ell m}_{n} = \sum_{k} c^{\ell m}_{n-k} \, \omega^{m}_{\ell k} / (1+\delta_{m0}) \quad . \tag{121}$$

The summations over n, ν, and k are limited by

$$0 \le \nu \le \ell \quad , \qquad k_{min} \le n \le k_{max} + \ell \quad ,$$
$$\max \begin{Bmatrix} k_{min} \\ n-\ell \end{Bmatrix} \le k \le \min \begin{Bmatrix} k_{max} \\ n \end{Bmatrix} \tag{122}$$

where k_{min} and k_{max} are the limits of the summation over k in Eq. 111.

These results depend on the form of Eq. 111 assumed for the charge distribution. It remains to show that this is indeed the case for Slater Type Atomic Orbitals, and to derive general formulas for the coefficients $\omega^{m}_{\ell k}$.

CHARGE DISTRIBUTIONS BETWEEN SLATER TYPE ORBITALS

Decomposition According to Irreducible Representations of $C_{\infty v}$

The charge distributions are chosen to be products of real Slater Type Atomic Orbitals (STAO's) which have the form

$$\chi = c_n \, r^{n-1} \, e^{-\zeta r} \, \mathcal{Y}_{\ell m}(z/r,\varphi) \tag{123}$$

where

$$c_n = (2\zeta)^{n+1/2}/[(2n)!]^{1/2} \quad . \tag{124}$$

If the components of the radius vectors $\underline{r}_a$ and $\underline{r}_b$ in χ_a and χ_b, originating from centers a and b respectively, are transformed to elliptic coordinates as in Eq. 100, the product $\chi_a(\xi,\eta,\varphi)\chi_b(\xi,\eta,\varphi)$ can be written as

$$\Omega = c_n c_{n'} \, [\tfrac{1}{2}R(\xi+\eta)]^{n-1} \, [\tfrac{1}{2}R(\xi-\eta)]^{n'-1} \, e^{-\alpha\xi-\beta\eta}$$

$$\mathcal{P}_{\ell}^{|m|}\left(\frac{1+\xi\eta}{\xi+\eta}\right) \, \mathcal{P}_{\ell'}^{|m'|}\left(\frac{1-\xi\eta}{\xi-\eta}\right) \, f(m)f(m')/\pi[(1+\delta_{m0})(1+\delta_{m'0})]^{1/2} \tag{125}$$

with

$$\alpha = \tfrac{1}{2}R(\zeta_a+\zeta_b) \qquad\qquad \beta = \tfrac{1}{2}R(\zeta_a-\zeta_b) \quad . \tag{126}$$

From the relations between the trigonometric functions, one obtains, for the functions defined by Eq. 103', the relation

$$2f(m)f(m') = ps(1-\delta_{p,-1}\delta_{M_+,0})f(pM)_+) + f(pM_-) \tag{127}$$

with the definitions

$$p = \text{sign}(m)\,\text{sign}(m') \quad , \qquad s = \text{sign}(m+m') \quad , \qquad \text{sign}(0) \equiv 1 \quad ,$$

$$M_+ = |m + m'| \quad , \qquad\qquad M_- = |m - m'| \quad . \tag{128}$$

Using Eq. 127, the expression 125 can be rearranged in the form

$$\pi(\tfrac{1}{2}R)^3 \ (\xi^2-\eta^2) \ \Omega = ps(1-\delta_{p,-1}\delta_{M_+0}) f(pM)_+) \ w_{q_+M_+} + f(pM_-) \ w_{q_-M_-} \tag{129}$$

with

$$w_{qM} = K \ d^{2q} d^{M} g(\xi,+\eta) g(\xi,-\eta) e^{-\alpha\xi-\beta\eta} \tag{130}$$

where

$$q_+ = 0 \quad ,$$

$$q_- = \text{minimum} \ (|m|, \ |m'|) \quad , \tag{131}$$

$$K = [2(1+\delta_{m0})(1+\delta_{m'0})]^{-1/2} \ (R\zeta_a)^{n+1/2} \ (R\zeta_b)^{n'+1/2}$$

$$\left[\frac{2\ell+1}{(2n)!} \frac{2\ell'+1}{(2n')!} \binom{\ell}{m}^{-1} \binom{\ell'}{m'}^{-1} \binom{\ell+m}{m} \binom{\ell'+m'}{m'} \right]^{1/2} \tag{132}$$

and the functions g are defined as

$$g(\xi,\eta) = (\xi+\eta)^{n-\ell} \left\{ \frac{\ell!}{(\ell+m)!} (\xi+\eta)^{\ell-m} P_\ell^{(m)} \left(\frac{1+\xi\eta}{\xi+\eta}\right) \right\} \quad . \tag{133}$$

Expansion of w_{qM}

Expanding $P_\ell^{(m)}(t)$ as (79,80)

$$P_\ell^{(m)}(t) = \frac{(\ell+m)!}{2^\ell \ell!} \sum_{\nu=0}^{\ell-m} \binom{\ell}{\nu} \binom{\ell}{m+\nu} (t-1)^\nu (t+1)^{\ell-m-\nu} \tag{134}$$

and using algebraic identities such as

$$(t+1) = (1+\xi\eta)/(\xi+\eta) + 1 = (\xi+1)(1+\eta)/(\xi+\eta)$$

one finds by substitution and expansion in Eq. 133

$$d^{2q} \ g(\xi,\eta) = (\xi+\eta)^{n-\ell} \sum_{\nu=0}^{\ell-m} \sum_{\alpha=\nu}^{\ell-m} (-1)^\nu A_{\nu mq}^{\alpha\ell} \cdot (\xi-1)^{\alpha+q} (1+\eta)^{\ell-m-\nu+q} (1-\eta)^{\nu+q} \tag{135}$$

with

$$A^{\alpha\ell}_{\nu mq} = 2^{-m-\alpha-q} \binom{\ell}{\nu}\binom{\ell}{m+\nu}\binom{\ell-m+q-\nu}{\ell-m+q-\alpha} \quad . \tag{136}$$

Expanding furthermore $(\xi+\eta)^{n-\ell}$ and interchanging summations in Eq. 135 one has

$$\begin{aligned} d^{2q}\, g(\xi,\eta) = &\sum_{\rho=\ell}^{n} \sum_{\lambda=0}^{\ell-m+q} \binom{n-\ell}{\rho-\ell}(\xi-1)^{\lambda+n-\rho+q} \\ &\cdot \sum_{r=0}^{\lambda} (-1)^r A^{\lambda\ell}_{rmq}(1+\eta)^{\rho-m-r+q}(1-\eta)^{r+q} \quad . \end{aligned} \tag{137}$$

By virtue of these expansions, the product $d^M d^{2q} g(\xi,\eta)\, g(\xi,-\eta)$ contains terms of the form $(1-\eta^2)^{M/2}(1+\eta)^{\sigma}(1-\eta)^{\sigma'}$, which in turn can be expanded in terms of the Legendre functions $\mathcal{P}^M_L(\eta)$, the expansion coefficients being given by

$$\begin{aligned} B^{\sigma\sigma'}_{LM} &= \int_{-1}^{1} d\eta\,(1-\eta^2)^{M/2}\, \mathcal{P}^M_L(\eta)\,(1+\eta)^{\sigma}(1-\eta)^{\sigma'} \\ &= \left[\frac{2L+1}{2}\binom{L}{M}^{-1}\binom{L+M}{M}\right]^{1/2}\left[2^{\sigma+\sigma'+M+1}/(L+\sigma+\sigma'+M+1)\right] \\ &\quad \cdot \sum_{\rho=0}^{L-M} (-1)^{\rho}\binom{L}{\rho}\binom{L}{M+\rho}\binom{L+\sigma+\sigma'+M}{\sigma'+M+\rho}^{-1} \quad . \end{aligned} \tag{138}$$

Substituting the resulting expressions for $d^M d^{2q} g(\xi,\eta)\, g(\xi,-\eta)$ in Eq. 130 one finally obtains

$$\begin{aligned} w_{qM} = &(\xi^2-1)^{M/2}\, e^{-\alpha\xi-\beta\eta} \sum_{k=q}^{n+n'-M} (\xi-1)^k \\ &\cdot \sum_{L=M}^{n+n'} a_{Lk}(n\ell m;n'\ell' m';q,M)\, \mathcal{P}^M_L(\eta) \end{aligned} \tag{139}$$

where the coefficients are given by

$$a_{Lk} = K \sum_{\rho} \sum_{\lambda} \sum_{\rho'} \sum_{\lambda'} \binom{n-\ell}{\rho-\ell} \binom{n'-\ell'}{\rho'-\ell'}$$

$$\cdot \sum_{rr'} (-1)^{r+r'} A^{\lambda\ell}_{rmq} A^{\lambda'\ell'}_{r'm'q} B^{(\rho+r'-r-m+q),\ (\rho'+r-r'-m'+q)}_{LM} \quad . \tag{140}$$

The sum extends over all values of $\rho,\rho',\lambda,\lambda'$, for which $n+n'+q+\lambda+\lambda'-\rho-\rho'=k$, with $\rho,\rho',\lambda,\lambda'$ and r,r' limited by

$$\ell \leq \rho \leq n \quad , \qquad \ell' \leq \rho' \leq n'$$

$$0 \leq \lambda \leq \ell-m+q \quad , \qquad 0 \leq \lambda' \leq \ell'-m'+q \quad , \tag{141}$$

$$0 \leq r \leq \lambda \quad , \qquad 0 \leq r' \leq \lambda' \quad .$$

The constants K, A, and B are defined in Eqs. 132, 136, and 140.

Expressions for the $\omega^{m}_{\ell k}$

With the preceding results, the constants $\omega^{m}_{\ell k}$ appearing in Eq. 111 can be evaluated. To this end Eq. 111 is inserted into Eq. 105, which yields

$$\Omega_{\ell m}(\xi) = (\xi^2-1)^{m/2}\, e^{-\alpha\xi} \sum_{k} \omega^{m}_{\ell k}(\xi-1)^{k} \tag{142}$$

as an alternative definition for the $\omega^{m}_{\ell k}$.

Substituting now Eq. 129 into Eq. 105 and integrating over φ one finds

$$\Omega_{\ell m}(\xi) = ps[(1+p\delta_{m,0})/\pi]^{1/2}\, \delta_{pM_+,m} \int_{-1}^{1} d\eta\, \Theta_{\ell}^{|m|}\, w_{q_+,m}$$

$$+ [(1+\delta_{m,0})/\pi]^{1/2}\, \delta_{pM_-,m} \int_{-1}^{1} d\eta\, \Theta_{\ell}^{|m|}\, w_{q_-,m} \quad . \tag{143}$$

The integrals $\int d\eta\, \Theta^{m}_{L}(\eta) \Theta^{m}_{\ell}(\eta)\, e^{-\beta\eta}$ which occur in this equation, can be evaluated with the help of the expansion theorem for spherical harmonics, and the relation (79,81,82)

$$\int_{-1}^{1} dt\, \mathcal{P}_J(t)\, e^{-\beta t} = (-1)^J\, [\pi(2J+1)/\beta]^{1/2}\, I_{J+1/2}(\beta)$$

where the $I_{J+1/2}$ are modified Bessel functions. Thus, one finds

$$\int_{-1}^{1} d\eta\, \mathcal{P}_L^m(\eta),\, \mathcal{P}_\ell^m(\eta)\, e^{-\beta\eta} = [\pi(2L+1)(2\ell+1)/2\beta]^{1/2} \cdot \sum_J (-1)^{J+m}\, (2J+1) \begin{pmatrix} L & \ell & J \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} L & \ell & J \\ 0 & 0 & 0 \end{pmatrix} I_{J+1/2} \tag{144}$$

where the $\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are the Wigner 3-J symbols (81). Substitution of Eq. 139 and Eq. 144 in Eq. 143 yields in fact an expression of the type of Eq. 142.

It is seen that the $\omega_{\ell k}^m$ are different from zero only if $m=pM_+$ or $m=pM_-$, and these coefficients are found to be

$$\omega_{\ell k}^m = (ps\, \delta_{pM_+,m} + \delta_{pM_-,m})(1 + p\delta_{m,0})^{1/2} \cdot \left[\frac{(2\ell+1)}{2\beta}\right]^{1/2} \sum_{L=|m|}^{n+n'} (2L+1)^{1/2}\, a_{Lk} \sum_{J=|L-\ell|,2}^{L+\ell} (-1)^{J+m}(2J+1) \cdot \begin{pmatrix} L & \ell & J \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} L & \ell & J \\ 0 & 0 & 0 \end{pmatrix} I_{J+1/2}(\beta) \tag{145}$$

where the constants a_{Lk} are given by Eq. 140. Consequently the summations over m in Eq. 119 contain only the terms $\pm M_+$ and $\pm M_-$.

DISCUSSION

Coefficient Matrices

The Eqs. 129, 134, and 139 together yield expansions for the charge distributions in terms of products of the type

$$a_{Lk}(\xi^2-1)^{m/2}(\xi-1)^k \mathcal{P}_L^m(\eta)\ e^{-\alpha\xi-\beta\eta}\begin{cases} f(pM_+) \\ f(pM_-) \end{cases} \qquad (146)$$

where the coefficients a_{Lk} are characterized by the quantum numbers of the orbitals in the charge distribution, and a symmetry designation, M. For example, the charge distribution made up from a 1s function and a 2s function is characterized by the label $(1s,2s,\Sigma^+)$ (77). Since the matrices are determined completely when the quantum numbers have been specified, they can be evaluated once and for all, and stored in a convenient manner.

From Eq. 138 it is seen that the relation between charge distributions which differ only in that the centers have been interchanged is given by

$$a_{Lk}(\chi_b,\chi_a,q,M) = (-1)^{L-M}\, a_{Lk}(\chi_a,\chi_b,q,M) \quad . \qquad (147)$$

Reference to Eqs. 100, 133, and 140 further yields the result that if the quantum numbers from the two orbitals are related as

$$n-\ell = n'-\ell' \qquad \text{and} \qquad \ell-m = \ell'-m' \quad , \qquad (148)$$

then

$$a_{Lk}(\chi_b,\chi_a,q,M) = a_{Lk}(\chi_a,\chi_b,q,M) \quad , \qquad (149)$$

and

$$a_{Lk} = 0 \quad , \qquad \text{if } (L-M) \text{ odd} \quad . \qquad (150)$$

The number N_a of unique charge distribution matrices $\{a_{Lk}\}$ which arise for all combinations of orbital types from n=1 to n=N, is found by noting that each combination in which one or both of the m's are zero gives rise to one charge distribution matrix, whereas if both m's are ≠0, two charge distribution matrices are formed. In this way one finds for N_a the formula

$$N_a = N(N+1)\ [\{N(N+1)\ (2N^2 + 2N + 5) + 6(2N+1)\}]/72 \quad . \qquad (151)$$

Numerical Integration

The final integration indicated in Eq. 119 is done by Gauss-Legendre quadrature (83) in terms of the integration variable σ given by

$$\sigma = (\tau-1)/(\tau+1) \quad , \qquad -1 \leq \sigma \leq 1 \quad . \qquad (152)$$

The numerical integration is carried out over enough points to insure a minimum accuracy of six decimal places. The number of points, N_I, needed for this accuracy is given by the relation

$$N_I = 0.75\alpha_0^2 - 8\alpha_0 + 33.25 \qquad (153)$$

where α_0 is the smallest value of $\frac{1}{2}R(\zeta_a+\zeta_b)$ in a given basis set. In addition the number of terms needed in the infinite series must be determined. It is found to be less than or equal to eleven terms for all integrals involving 1s through 3d6 orbitals and the maximum, ℓ_{max}, is 10 even in those cases where the lowest value ℓ=M is different from zero.

Once N_I has been determined, the values of all the integrands $W_{\ell m}(\tau)$ are determined over the integration grid for all charge distributions and stored. Then the integrals are computed from two charge distributions at a time. Table 27 gives the time needed to compute all the integrals arising from a given basis set.

Computation of Special Functions

The functions $q_j(x)$ introduced in Eq. 118 are computed as follows: The recursion formula

$$x\, q_j(x) = j\, q_{j-1}(x) - e^{-x} \tag{154}$$

with

$$q_0(x) = (1-e^{-x})/x \tag{155}$$

may be used for all x except in a region $x<f(j)$ where too many figures are lost due to the subtraction in Eq. 154. In the latter region the infinite series

$$q_j(x) = j!\, e^{-x} \sum_{k=0}^{\infty} \frac{x^k}{(j+1+k)!} \tag{156}$$

is used for the highest value of j needed, and the recurrence formula 154 is then used in the downward direction.

The maximum value of j is found from Eqs. 116 and 139 to be

$$j_{max} = \ell_{max} + n+n' \tag{157}$$

where n,n' are the principal quantum numbers of the orbitals in the charge distribution. For all charge distributions including STAO's through 3dδ, one has $j_{max} = 16$. The exact form of f(j) is machine dependent. For an IBM series 360 computer using double precision arithmetic

$$f(j) = 3(1+j/11) \tag{158}$$

is sufficient to maintain eight significant figures in $q_j(x)$. For very large x the approximation

$$q_j(x) = j!/x^{j+1} \qquad (x \geq 81) \tag{159}$$

is sufficient.

The modified Bessel functions appearing in Eqs. 144 and 145 are evaluated by noting that they are related to the diagonal elements of the $I_{\alpha\beta}$ functions which have been discussed elsewhere (84).

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APPENDIX A

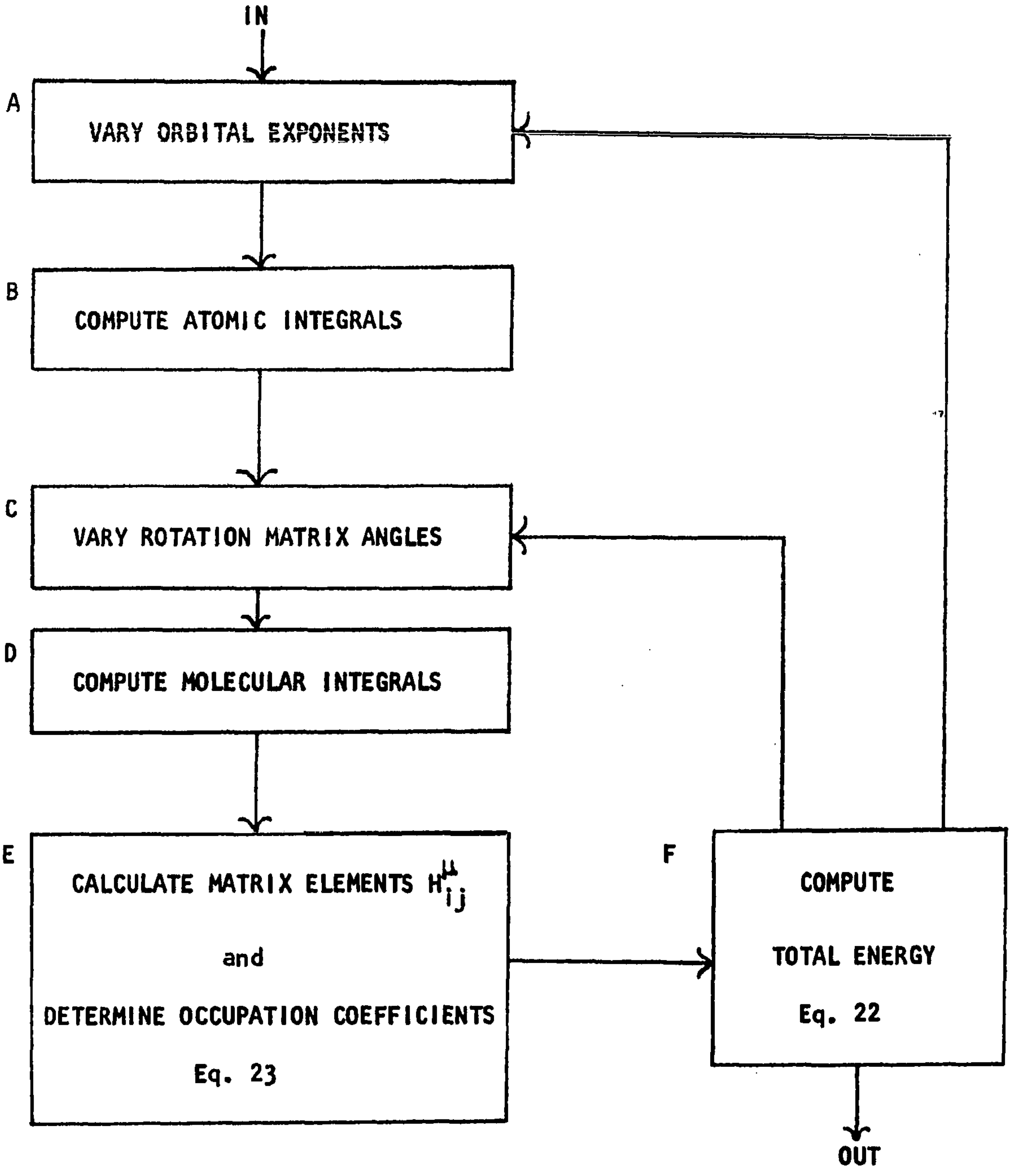

FIGURE 1. SCHEMATIC DIAGRAM OF LOGIC FLOW FOR DETERMINATION OF OPTIMAL APSG WAVE FUNCTION

TABLE 1. BASIS FUNCTIONS FOR LI AND LIH

LITHIUM		LITHIUM HYDRIDE	
ORBITALS	ORBITAL EXPONENTS	ORBITALS	ORBITAL EXP (R=3.015)
K1S	2.44741	LI-K1S	2.48169
K2S	3.19356	LI-K2S	3.29233
K2P	4.24204	LI-K2Pσ	4.09184
		LI-K2Pπ	4.21650
K3P	4.66054	LI-K3Pσ	5.68493
		LI-K3Pπ	4.73995
K3D	5.70550	LI-K3Dσ	5.71936
		LI-K3Dπ	5.69243
		LI-K3Dδ	5.67957
L2S	0.49152	LI-L2S	0.67828
L3S	0.53297	LI-L3S	1.02091
		LI-L2Pσ	0.75366
		LI-L2Pπ	0.76258
		H-1S	1.02951
		H-2S	1.13376
		H-2Pσ	1.18804
		H-2Pπ	1.16849
		H-3Dπ	1.45935

TABLE 2. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF LITHIUM

	K1S1	K2S2	L1S1
K1S	1.20118	-3.13509	-0.17445
K2S	-0.21171	3.36868	-0.00440
L2S	-0.01101	-0.15837	1.90367
L3S	0.00756	-0.01768	-0.99065
O.C.	0.99871	-0.02650	1.00000

	K3P1	K4P2
K2P	0.58489	-3.16509
K3P	0.42740	3.19018
O.C.	-0.02420	-0.00405

	K5D1
K3D	1.00000
O.C.	-0.00381

TABLE 3. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF LIH AT R = 3.015 BOHR

Σ	K1σ1 (K1S1)	K2σ2 (K2S2)	K4σ3 (K3P1)	K8σ4 (K5D1)	K9σ5 (K4P2)
LI-K1S	1.18046	-3.28409	0.06427	-0.02563	0.03070
LI-K2S	-0.18782	3.48834	-0.08232	0.05680	-0.05530
LI-K2P	-0.00207	0.00832	0.69621	0.24335	-8.40608
LI-K3P	-0.00248	0.00936	0.33480	-0.23811	8.37892
LI-K3D	-0.00021	-0.00096	-0.00846	1.00096	0.02733
LI-L2S	0.00498	0.06547	-0.19280	-0.11589	0.15093
LI-L2P	-0.01152	-0.20859	-0.42008	0.08111	0.22750
LI-L3S	-0.01542	-0.21465	-0.04265	0.21330	-0.12555
H-1S	-0.00957	-0.01134	-0.09830	0.02962	0.02319
H-2S	0.00276	0.14763	0.44003	-0.15814	-0.08944
H-2P	-0.00067	-0.03595	0.02786	-0.07459	0.09717
O.C.	0.99883	-0.02463	-0.02158	-0.00383	-0.00142

Σ	B1σ1	B2σ2	B4σ3	B5σ4	B8σ5	B9σ6
LI-K1S	-0.11159	-0.06425	-0.06640	0.08820	-0.54080	-0.43068
LI-K2S	-0.00205	-0.01589	-0.11964	-0.28318	1.10980	0.65767
LI-K2P	0.00353	-0.00212	-0.00334	-0.00081	-0.04719	-0.02178
LI-K3P	0.00230	0.00575	-0.00101	-0.00963	0.01654	0.03482
LI-K3D	0.00050	0.00025	0.00230	0.00132	-0.00179	-0.00244
LI-L2S	0.16953	0.55051	-0.22159	-1.18359	-7.34995	0.91454
LI-L2P	0.21296	0.58765	0.00971	-0.96281	0.72548	1.48596
LI-L3S	0.16863	0.45787	-0.07519	-0.60934	7.98468	-0.52409
H-1S	0.66120	-1.47778	0.31235	-1.98857	0.12258	0.21325
H-2S	0.02475	0.42943	-0.22961	3.77949	-1.11643	-1.38849
H-2P	0.02121	-0.05818	1.05159	0.61603	-0.57099	-0.43310
O.C.	0.98545	-0.12319	-0.05695	-0.01232	-0.00198	-0.00094

TABLE 3. (CONTINUED)

Π	K3π1 (K3P1)	K5π2 (K4P2)	K7π3 (K5D1)	B3π1	B6π2	B7π3
LI-K2P	0.58208	-2.38791	-2.53682	0.00500	-0.00017	0.10783
LI-K3P	0.43349	2.41641	2.58840	-0.01358	-0.08327	-0.30859
LI-K3D	-0.00666	-0.72798	0.68593	0.00083	0.00506	0.04236
LI-L2P	-0.01686	-0.07911	-0.11449	0.06496	-0.00906	1.27397
H-2P	-0.05197	0.01168	0.00410	0.95237	-0.17731	-0.61469
H-3D	-0.01143	-0.00270	-0.05385	0.16284	0.99179	-0.46074
O.C.	-0.02411	-0.00386	-0.00383	-0.07104	-0.00947	-0.00482

Δ	K6δ1 (K5D1)
LI-K3D	1.00000
O.C.	-0.00384

TABLE 4. OVERLAPS BETWEEN K-GEMINAL NATURAL ORBITALS OF LI AND LIH AT R=3.015 BOHR

LI		LIH		NO
NO	O.C.	NO	O.C.	OVERLAP
K1S1	0.99871	$K1\sigma1$	0.99883	0.99979
K2S2	-0.02650	$K2\sigma2$	-0.02463	0.97813
K3P(Z)1	-0.02420	$K4\sigma3$	-0.02158	0.95816
K3P(X)1	-0.02420	$K3\pi1$	-0.02411	0.99791
K4P(Z)2	-0.00405	$K9\sigma5$	-0.00142	0.37677
K4P(X)2	-0.00405	$K5\pi2$	-0.00386	0.98740
$K5D(Z^2)1$	-0.00381	$K8\sigma4$	-0.00383	0.99799
K5D(XZ)1	-0.00381	$K7\pi3$	-0.00383	0.99885
$K5D(X^2-Y^2)1$	-0.00381	$K6\delta1$	-0.00384	0.99998

TABLE 5. ENERGY RESULTS FOR LIH AND THE SEPARATED ATOM

TOTAL ENERGY OF PRESENT CALCULATION AT R=3.015 BOHR			
	LI+H	LIH	(LI+H)-LIH EV
E(PNU)	-7.93194	-7.98469	1.4353
E(PNO)-E(EXP)	0.04606	0.08554	-1.0742
E(PNO)-E(SCF)	0.00079	0.00262	-0.0498
E(APSG')[a]	-7.93194	-8.01823	2.3480
E(APSG')-E(EXP)	0.04527	0.05227	-0.1905
E(APSG)	-7.96943	-8.05418	2.3060
E(APSG)-E(EXP)	0.00857	0.01632	-0.2108
E(EXP)	-7.9780	-8.0705	2.5169
CORRELATION ENERGY RECOVERED BY PRESENT CALCULATION			
ΔE(CORR)=E(SCF)-E(EXP)	0.04527	0.08319	
E(SCF)-E(APSG')	-0.00079	0.03092	
PERCENT RECOVERED		37.17	
E(SCF)-E(APSG)	0.03670	0.06687	
PERCENT RECOVERED	81.07	80.38	
OTHER CALCULATIONS			
E(SCF)	-7.93273[b]	-7.98731[c]	1.4851
B+D[d] (CI-NO, R=3.015)	_[e]	-8.0606	_[e]
B+M[f] (VB-CI, R=3.046)	-7.9700	-8.0561	2.343
B[g] (CI, R=3.060)	_[e]	-8.0556	_[e]
H+T[h] (VB-CI, R=3.2)	-7.9574	-8.0387	2.212
E+B[i] (APSG-NO, R=3.0)	_[e]	-8.0179	_[e]

[a] APSG WITH CORRELATION K-NO S OMITTED

[b] CLEMENTI REF. (52)

[c] CADE AND HUO REF. (10)

[d] BENDER AND DAVIDSON REF. (55)

[e] LI+H WAS NOT CALCULATED

[f] BROWN AND MATSEN REF. (57)

[g] R. BROWN REF. (56)

[h] HARRIS AND TAYLOR REF. (58)

[i] EBBING AND HENDERSON REF. (17)

TABLE 6. BASIS FUNCTIONS FOR B AND BH

BORON		BORON HYDRIDE	
ORBITALS	ORBITAL EXPONENTS	ORBITALS	ORBITAL EXP (R=2.329)
K1S	4.23977	B-K1S	4.44380
K2S	5.28416	B-K2S	5.55292
K2P	6.96675	B-K2Pσ	6.33261
		B-K2Pπ	6.39500
		B-K3Pσ	6.24836
		B-K3Dσ	8.49277
L2S	1.27652	B-L2S	1.35277
L2P	1.96288	B-L2Pσ	1.96917
		B-L2Pπ	2.05102
		B-L3Pσ	2.00045
		B-L3Dσ	2.24698
L2S'	2.08748	B-L2S'	2.05631
L2P'	0.96345	B-L2Pσ'	0.91141
		B-L2Pπ'	1.33187
		H-1S	1.24835
		H-2S	1.97523
		H-2P σ	2.00664
		H-2P π	1.50634

TABLE 7. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF BORON

	K1S1	K2S2	LP1S1	LP2S2
K1S	1.21228	-2.86099	-0.02107	1.13008
K2S	-0.19022	3.21683	-0.04508	-2.09217
L2S	-0.16221	-0.29871	0.95108	-2.11668
L2S'	-0.03513	-0.12184	0.07766	2.86786
O.C.	0.99959	-0.01680	0.99995	-0.00499

	K3P1	LP3P1	L1P1
K2P	1.01608	0.48653	0.00567
L2P	-0.04231	-1.62190	0.27398
L2P'	-0.17596	1.29969	0.78040
O.C.	-0.01344	-0.00496	0.57735

TABLE 8. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF BH AT R = 2.329 BOHR

Σ	K1σ1 (K1S1)	K3σ2 (K3P1)	K4σ3 (K2S2)	K5σ4	K6σ5
B-K1S	1.10613	0.35058	-2.93794	0.03848	-0.12210
B-K2S	-0.11572	-0.41124	3.73420	-0.05214	0.16796
B-K2P	0.00009	1.16409	0.16919	0.00147	-2.37934
B-K3P	0.00157	0.02119	-0.05853	-0.06240	3.33303
B-K3D	-0.00015	0.02321	0.01077	0.98679	0.00656
B-L2S	-0.01081	-0.06344	1.42154	0.07219	-0.12353
B-L2P	0.00368	-0.87173	-0.02559	0.09234	-1.66332
B-L3P	-0.00339	0.08257	-0.02150	0.01221	0.03590
B-L3D	0.00048	-0.01072	-0.00928	0.05759	-0.01722
B-L2S'	0.01150	0.09059	-2.04002	0.02932	-0.13886
B-L2P'	0.00301	0.35345	0.07987	0.01969	0.54482
H-1S	-0.00067	-0.21267	-0.29893	0.12028	-0.27287
H-2S	-0.00052	0.25682	0.19869	-0.24439	0.52619
H-2P	0.00035	0.04172	0.02023	-0.10766	0.34832
O.C.	0.99969	-0.01181	-0.00968	-0.00271	-0.00264

Σ	LP1σ1	LP3σ2	LP4σ3	LP5σ4	LP6σ5
B-K1S	-0.20529	-0.82166	0.15181	0.16336	0.06411
B-K2S	-0.01440	0.26487	-0.20729	-0.18981	-0.07884
B-K2P	-0.00342	0.03043	-0.04863	-0.09714	-1.02327
B-K3P	0.00394	0.00890	-0.06482	0.59978	3.22289
B-K3D	0.00069	-0.00363	-0.01617	-0.35105	0.03813
B-L2S	1.00459	-2.25689	-0.39206	1.38232	0.34045
B-L2P	-0.09005	-0.09976	1.53306	-2.13993	-7.16247
B-L3P	0.01342	0.07812	-0.09490	3.22428	8.07031
B-L3D	-0.01059	0.00973	0.05127	1.46601	-0.05750
B-L2S'	-0.03924	2.60107	0.35086	-0.18953	-0.00843
B-L2P'	-0.26671	-0.14159	-1.43702	-0.20807	-2.18820
H-1S	0.03923	0.07945	0.61547	0.62028	0.25970
H-2S	-0.02988	0.19218	-0.21862	-2.43258	-0.72843
H-2P	0.00829	-0.21422	-0.40793	-1.08379	-0.34577
O.C.	0.97386	-0.01595	-0.01018	-0.00235	-0.00086

TABLE 8. (CONTINUED)

Σ	B1σ1	B2σ2	B4σ3	B5σ4
B-K1S	-0.04804	0.10041	-0.30994	0.04768
B-K2S	-0.01624	0.01719	0.36497	0.01533
B-K2P	0.00443	-0.00915	0.16253	0.00113
B-K3P	0.00179	0.01086	0.12085	0.02359
B-K3D	-0.00139	0.00777	-0.01555	-0.00045
B-L2S	-0.05363	-0.63379	-0.62983	0.27367
B-L2P	0.21548	-0.59113	-0.71241	-0.19590
B-L3P	0.05393	-0.13245	0.45606	0.06172
B-L3D	0.03958	-0.03810	0.17430	0.03692
B-L2S'	0.08135	-0.10003	-0.07662	-0.31919
B-L2P'	0.33367	-0.49328	-0.54035	-0.08364
H-1S	0.51777	0.84820	0.38953	-5.18775
H-2S	0.05440	0.41126	0.19245	5.29632
H-2P	0.02330	-0.03423	1.07235	0.03784
O.C.	0.99377	-0.09615	-0.02065	-0.00492

Π	K2π1 (K3P1)	LP2π1	B3π1	B6π1
B-K2P	1.08657	-0.00852	-0.01503	-0.60435
B-L2P	-0.21944	0.07203	0.25761	2.70184
B-L2P'	-0.07750	-1.09135	-0.60908	-2.30290
H-2P	0.02534	0.07856	1.11425	0.16136
O.C.	-0.01364	-0.16004	-0.03694	-0.00067

TABLE 9. OVERLAPS BETWEEN K-GEMINAL NATURAL ORBITALS OF B AND BH AT R=2.329 BOHR

B		BH		NO
NO	O.C.	NO	O.C.	OVERLAP
K1S1	0.99959	K1σ1	0.99969	0.9849
K2S2	-0.01680	K4σ3	-0.00968	0.7604
K3P(Z)1	-0.01344	K3σ2	-0.01181	0.9043
K3P(X)1	-0.01344	K2π1	-0.01364	0.9935

TABLE 10. ENERGY RESULTS FOR BH AND THE SEPARATED ATOM

TOTAL ENERGY OF PRESENT CALCULATION AT R=2.329 BOHR

	B+H	BH	(B+H)-BH EV
E(PNO)	-25.0273	-25.1220	2.577
E(PNO)-E(EXP)	0.1307	0.1680	-1.014
E(PNO)-E(SCF)	0.0018	0.0094	-0.207
E(APSG')[a]	-25.0281	-25.1790	4.106
E(APSG')-E(EXP)	0.1299	0.1110	0.514
E(APSG'')	-25.0622	-25.2040	3.858
E(APSG'')-E(EXP)	0.0958	0.0860	0.267
E(APSG)	_[b]	-25.2053	_[b]
E(APSG)-E(EXP)	_[b]	0.0847	_[b]
E(EXP)	-25.1580	-25.290	3.592
CORRELATION ENERGY RECOVERED BY PRESENT CALCULATION			
ΔE(CORR)=E(SCF)-E(EXP)	0.1289	0.1586	
E(SCF)-E(APSG')	-0.0010	0.0476	
PERCENT RECOVERED		30.01	
E(SCF)-E(APSG)	0.0331	0.0726	
PERCENT RECOVERED	25.68	45.77	
E(SCF)-E(APSG)		0.0739	
PERCENT RECOVERED		46.60	
OTHER CALCULATIONS			
E(SCF)	-25.0291[c]	-25.1314[d]	2.784
H[e] (CI, R=2.50)	_[f]	-25.1455	_[f]
K+B[g] (SCF, R=2.336)	_[f]	-25.1298	_[f]
O[h] (CI, R=2.329)	-25.0289	-25.1105	2.22

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[a] APSG WITH CORRELATING K-NO S OMITTED

[b] B+H WAVE FUNCTION WAS NOT DETERMINED FOR CORRESPONDING BH WAVE FUNCTION

[c] CLEMENTI REF. (52)

[d] CADE AND HUO REF. (10)

[e] HARRISON REF. (61)

[f] B+H WAVE FUNCTION WAS NOT DETERMINED

[g] KAUFMANN AND BURNELLE REF. (63)

[h] OHNO REF. (62)

TABLE 11. CORRELATION ANALYSIS FOR LI

CONTRIBUTOR	ORBITAL[a] INTERACTION	ORBITAL[b] CORRELATIONS	TOTAL GEMINAL[c] CONTRIBUTIONS	GEMINAL[d] ENERGIES
K1S1,K1S1			-7.23604	-6.61157
K1S1,K2S2	-0.01182			
K1S1,K3P1	-0.02090			
K1S1,K4P2	-0.00222			
K1S1,K5D1	-0.00245			
K1S1		-0.03739		
K,OTHER		-0.00010		
K			-0.03749	-0.03749
L1S1,L1S1			-0.82037	-0.19591
K1S1,L1S1			0.62447	
ΔI(K,L)		0.00000	0.00000	
ΔE		-0.03749		
E			-7.46943	

[a] QUANTITY DEFINED BY EQ. 79
[b] QUANTITY DEFINED BY EQ. 85
[c] QUANTITY DEFINED BY EQS. 76, 77 AND 78
[d] QUANTITY DEFINED BY EQ. 81

TABLE 12. CORRELATION ANALYSIS FOR LIH (R=3.015)

CONTRIBUTOR	ORBITAL[a] INTERACTION	ORBITAL[b] CORRELATIONS	TOTAL GEMINAL[c] CONTRIBUTIONS	GEMINAL[d] ENERGIES
K1σ1,K1σ1			-7.89569	-6.54489
K1σ1,K2σ2	-0.01128			
K1σ1,K4σ3	-0.00645			
K1σ1,K8σ4	-0.00050			
K1σ1,K9σ5	-0.00021			
K1σ1,K3π1	-0.01394			
K1σ1,K5π2	-0.00122			
K1σ1,K7π3	-0.00122			
K1σ1,K6δ1	-0.00100			
K1σ1		-0.03582		
K,OTHERS		-0.00007		
K			-0.03589	-0.03852
B1σ1,B1σ1			-2.43482	-1.08403
B1σ1,B2σ2	-0.01424			
B1σ1,B4σ3	-0.00473			
B1σ1,B5σ4	-0.00066			
B1σ1,B8σ5	-0.00001			
B1σ1,B9σ6	-0.00000			
B1σ1,B3π1	-0.01226			
B1σ1,B6π2	-0.00058			
B1σ1,B7π3	-0.00007			

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[a] QUANTITY DEFINED BY EQ. 79
[b] QUANTITY DEFINED BY EQ. 85
[c] QUANTITY DEFINED BY EQS. 76, 77 AND 78
[d] QUANTITY DEFINED BY EQ. 81

TABLE 12. (CONTINUED)

CONTRIBUTOR	ORBITAL INTERACTION	ORBITAL CORRELATIONS	TOTAL GEMINAL CONTRIBUTIONS	GEMINAL ENERGIES
B1σ1		-0.03261		
B2σ2		+0.00099		
B4σ3		+0.00016		
B3π1		+0.00044		
B,OTHERS		+0.00006		
B			-0.03096	-0.03360
K1σ1,B1σ1			1.35079	
K1σ1,B2σ2	-0.00149			
K1σ1,B3π2	-0.00078			
OTHERS	-0.00037			
ΔI(K,B)		-0.00263	-0.00263	
ΔE		-0.06954		
E			-8.05418	

TABLE 13. CORRELATION ANALYSIS FOR BORON

CONTRIBUTOR	ORBITAL[a] INTERACTION	ORBITAL[b] CORRELATIONS	TOTAL GEMINAL[c] CONTRIBUTIONS	GEMINAL[d] ENERGIES
K1S1,K1S1			-21.52053	-17.86940
K1S1,K2S2	-0.01268			
K1S1,K3P1	-0.02136			
K1S1		-0.03405		
K,OTHERS	-0.00002			
K			-0.03405	-0.03402
LP1S1,LP1S1			-5.17363	-1.91269
LP1S1,LP2S2	-0.00028			
LP1S1,LP3P1	-0.00057			
LP1S1		-0.00085		
LP,OTHERS		-0.00006		
LP			-0.00091	-0.00086
L1P1,L1P1			-2.27056	-0.30775
K1S1,LP1S1			2.47463	
ΔI(K,LP)		+0.00005		
K1S1,L1P1			1.17650	
ΔI(K,L)		-0.00001		
LP1S1,L1P1			0.78631	
ΔI(LP,L)		0.00000		
TOTAL 1			0.00004	
ΔE		-0.03492		
E			-24.5622	

[a] QUANTITY DEFINED BY EQ. 79
[b] QUANTITY DEFINED BY EQ. 85
[c] QUANTITY DEFINED BY EQS. 76, 77 AND 78
[d] QUANTITY DEFINED BY EQ. 81

TABLE 14. CORRELATION ANALYSIS FOR BH (R=2.329)

CONTRIBUTOR	ORBITAL[a] INTERACTION	ORBITAL[b] CORRELATIONS	TOTAL GEMINAL[c] CONTRIBUTIONS	GEMINAL[d] ENERGIES
K1σ1,K1σ1			-22.8443	-18.2303
K1σ1,K3σ2	-0.0056			
K1σ1,K4σ3	-0.0055			
K1σ1,K5σ4	-0.0005			
K1σ1,K6σ5	-0.0005			
K1σ1,K2π1	-0.0138			
K1σ1		-0.0260		
K,OTHERS		+0.0000		
K			-0.0259	-0.0196
LP1σ1,LP1σ1			-5.3071	-1.4113
LP1σ1,LP3σ2	-0.0012			
LP1σ1,LP4σ3	-0.0003			
LP1σ1,LP5σ4	-0.0000			
LP1σ1,LP6σ5	-0.0000			
LP1σ1,LP2π1	-0.0302	-0.0318		
LP1σ1				
LP2π1,LP1σ1	-0.0302			
LP2π1,LP2π1	+0.0143			
LP2π1,OTHERS	+0.0016			
LP2π1		-0.0142		
LP,OTHERS		-0.0005		
LP			-0.0465	-0.0329
B1σ1,B1σ1			-5.1179	-1.6275
B1σ1,B2σ2	-0.0138			
B1σ1,B4σ3	-0.0022			
B1σ1,B5σ4	-0.0003			
B1σ1,B3π1	-0.0067			
B1σ1,B6π2	-0.0000			

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[a] QUANTITY DEFINED BY EQ. 79
[b] QUANTITY DEFINED BY EQ. 85
[c] QUANTITY DEFINED BY EQS. 76, 77 AND 78
[d] QUANTITY DEFINED BY EQ. 81

TABLE 14. (CONTINUED)

CONTRIBUTOR	ORBITAL INTERACTION	ORBITAL CORRELATIONS	TOTAL GEMINAL CONTRIBUTIONS	GEMINAL ENERGIES
B1σ1		-0.0232		
B2σ2,B1σ1	-0.0138			
B2σ2,B2σ2	+0.0080			
B2σ2,OTHERS	+0.0005			
B2σ2		-0.0054		
B3π1		+0.0022		
B,OTHERS		+0.0000		
B			-0.0263	-0.0146
K1σ1,LP1σ1			2.5097	
K1σ1,LP2π1	0.0037			
OTHERS	0.0005			
ΔI(K,LP)		+0.0042		
K1σ1,B1σ1			2.1043	
K1σ1,B2σ2	+0.0039			
K1σ1 B3π1	-0.0017			
OTHERS	-0.0000			
ΔI(K,B)		+0.0021		
LP1σ1,B1σ1			1.3861	
LP1σ1,B2σ2	+0.0012			
LP1σ1,B3π1	-0.0005			
LP2π1,B1σ1	+0.0086			
OTHERS	+0.0001			
ΔI(LP,B)		+0.0095		
TOTAL ΔI			+0.0158	
ΔE		-0.0831		
E			-25.2053	

TABLE 15. ORBITAL EXPONENTS FOR THE APSG WAVE FUNCTION OF LIH AS A FUNCTION OF R

ORBITALS		ORBITAL EXPONENTS	
	R = 2.80	R = 3.015	R = 4.00
LI-K1S	2.47066	2.48169	2.46973
LI-K2S	3.29233	3.29233	3.28359
LI-K2Pσ	4.09384	4.09184	4.03478
LI-K2Pπ	4.26156	4.21650	4.26061
LI-K3Pσ	5.67795	5.68493	5.58527
LI-K3Pπ	4.76716	4.73995	5.70326
LI-K3Dσ	5.84102	5.71936	4.95792
LI-K3Dπ	5.65041	5.69243	5.60553
LI-K3Dδ	5.67957	5.67957	5.62025
LI-L2S	0.68950	0.67828	0.63774
LI-L3S	1.01435	1.02091	1.02810
LI-L2Pσ	0.77678	0.75366	0.68099
LI-L2Pπ	0.83268	0.76258	0.74672
H-1S	1.02733	1.02951	0.94576
H-2S	1.14166	1.13376	1.06624
H-2P σ	1.23243	1.18804	1.15064
H-2P π	1.18244	1.16849	1.09741
H-3D π	1.47935	1.45935	1.24182

TABLE 16. ORBITAL EXPONENTS FOR THE APSG WAVE FUNCTION OF BH AS A FUNCTION OF R

ORBITALS	ORBITAL EXPONENTS		
	R = 2.20	R = 2.329	R = 2.70
B-K1S	4.39679	4.44380	4.40669
B-K2S	5.54900	5.55292	5.55394
B-S2Pσ	6.34899	6.33261	6.24406
B-K2Pπ	6.46035	6.39500	6.43341
B-K3Pσ	6.26168	6.24836	6.26168
B-K3Dσ	8.51087	8.49277	8.51087
B-L2S	1.32414	1.35277	1.36074
B-L2Pσ	1.96304	1.96917	1.98446
B-L2Pπ	2.05250	2.05102	2.07080
B-L3Pσ	2.00471	2.00045	2.00471
B-L3Dσ	2.25177	2.24698	2.25177
B-L2S'	2.07562	2.05631	2.07564
B-L2Pσ'	0.94889	0.91141	0.82329
B-L2Pπ'	1.34093	1.33187	1.37077
H-1S	1.25839	1.24835	1.19805
H-2S	1.97944	1.97523	1.95129
H-2Pσ	2.02316	2.00664	1.92821
H-2Pπ	1.53939	1.50634	1.38736

TABLE 17. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF LIH AT R = 2.80 BOHR

Σ	K1σ1	K2σ2	K4σ3	K8σ4	K9σ5
LI-K1S	1.18865	-3.33789	0.06323	-0.02812	0.03649
LI-K2S	-0.19514	3.56649	-0.07668	0.07026	-0.07005
LI-K2P	-0.00090	0.01851	0.70030	0.24397	-8.40883
LI-K3P	-0.00273	0.00105	0.33392	-0.23861	8.37766
LI-K3D	-0.00003	0.00080	-0.00815	1.00109	0.02647
LI-L2S	0.01174	-0.07449	-0.28448	-0.13150	0.15133
LI-L2P	-0.01326	-0.17197	-0.42840	0.08642	0.22133
LI-L3S	-0.02759	-0.03401	0.03113	0.23762	-0.13305
H-1S	-0.02156	0.00090	-0.09579	0.02304	0.03818
H-2S	0.00464	0.07691	0.45137	-0.16651	-0.08624
H-2P	0.00052	-0.08952	-0.00259	-0.08437	0.11466
O.C.	0.99886	-0.02418	-0.02146	-0.00375	-0.00144

Σ	B1σ1	B2σ2	B4σ3	B5σ4	B8σ5	B9σ6
LI-K1S	-0.11658	-0.38574	-0.09512	0.17185	-0.65408	-0.42734
LI-K2S	0.00252	0.03620	-0.13743	-0.36234	1.36951	0.68222
LI-K2P	0.00330	0.01817	0.00158	-0.00936	-0.07522	-0.02046
LI-K3P	0.00370	-0.00951	-0.00247	-0.00651	0.03200	0.02631
LI-K3D	0.00059	0.00310	0.01018	0.00236	-0.00241	-0.00250
LI-L2S	0.12100	0.56015	-0.13005	-1.25685	-8.46795	0.99655
LI-L2P	0.20883	0.64575	0.00259	-0.98582	0.72412	1.51056
LI-L3S	0.19518	0.50637	-0.11264	-0.63428	9.07057	-0.56429
H-1S	0.67544	-1.52485	0.31008	-1.98889	0.13237	0.19595
H-2S	0.02071	0.39967	-0.23986	3.90978	-1.17245	-1.44968
H-2P	0.03035	-0.07791	1.05691	0.62210	-0.44017	-0.40168
O.C.	0.98633	-0.11548	-0.05557	-0.01250	-0.00144	-0.00077

TABLE 17. (CONTINUED)

Π	K3π1	K5π2	K7π3	B3π1	B6π2	B7π3
LI-K2P	0.55364	-3.43770	0.09509	-0.00533	0.03988	0.14147
LI-K3P	0.46604	3.49663	-0.08900	0.01552	-0.07618	-0.38372
LI-K3D	-0.00439	0.02815	1.00126	0.00133	-0.00130	0.02342
LI-L2P	-0.00829	-0.14945	0.02191	0.02350	0.01280	1.34670
H-2P	-0.06855	0.00387	-0.03176	0.97117	-0.18401	-0.64554
H-3D	-0.08703	-0.05299	-0.05056	0.16981	0.98393	-0.53343
O.C.	-0.02384	-0.00380	-0.00387	-0.07188	-0.01006	-0.00451

Δ	K6δ1
LI-K3D	1.00000
O.C.	-0.00385

TABLE 18. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF LIH AT R = 4.00 BOHR

Σ	K1σ1	K2σ2	K4σ3	K8σ4	K9σ5′
LI-K1S	1.18465	-3.28950	0.01258	-0.03577	0.06702
LI-K2S	-0.19557	3.49022	-0.01314	0.04505	-0.07408
LI-K2P	0.00110	-0.13295	0.68727	0.24911	-8.30391
LI-K3P	-0.00597	0.13446	0.33603	-0.22036	8.28907
LI-K3D	-0.00031	-0.00848	-0.03151	0.99921	0.02961
LI-L2S	0.00254	0.21535	-0.07575	-0.03242	0.10863
LI-L2P	-0.00195	-0.25895	-0.35766	0.06198	0.23558
LI-L3S	-0.00157	-0.41987	-0.07914	0.10747	-0.04166
H-1S	0.01717	-0.05792	-0.10728	0.04073	0.02886
H-2S	0.00080	0.25885	0.35588	-0.12450	-0.15061
H-2P	0.00104	0.05873	0.06646	-0.08226	0.00840
O.C.	0.99896	-0.02432	-0.02201	-0.00429	-0.00151

Σ	B1σ1	B2σ2	B4σ3	B5σ4	B8σ5	B9σ6
LI-K1S	-0.12548	-0.09985	-0.09111	0.04068	-0.32891	-0.41820
LI-K2S	0.01139	-0.02819	0.03890	-0.03470	0.50987	0.51620
LI-K2P	0.00478	-0.02031	0.04054	0.06369	-0.07379	-0.04275
LI-K3P	-0.00113	0.02005	-0.02699	-0.05892	0.07530	0.06327
LI-K3D	0.00003	-0.00696	0.02345	0.01353	-0.01068	-0.01136
LI-L2S	0.19727	0.52979	-0.29174	-1.11411	-4.87423	0.99335
LI-L2P	0.18832	0.40172	-0.14564	-0.69574	0.42458	1.34194
LI-L3S	0.18008	0.32581	-0.07074	-0.18347	5.14225	-0.83254
H-1S	0.69968	-1.42201	0.46287	-2.07363	0.04065	0.29356
H-2S	0.00030	0.60736	-0.30754	3.27378	-0.39708	-1.13927
H-2P	0.01332	0.03376	1.05236	0.51782	-0.51027	-0.32000
O.C.	0.97977	-0.16663	-0.05405	-0.01315	-0.00307	-0.00123

TABLE 18. (CONTINUED)

Π	K3π1	K5π2	K7π3	B3π1	B6π2	B7π3
LI-K2P	0.97575	-7.49013	0.01567	0.02235	-0.24865	0.06881
LI-K3P	0.03110	7.53463	-0.00995	-0.02101	0.26219	-0.22993
LI-K3D	-0.00650	0.00141	1.00017	0.00021	0.00113	0.00213
LI-L2P	-0.04131	0.11471	0.00835	0.11306	-0.25340	1.13327
H-2P	-0.02215	-0.01960	-0.00887	0.92961	-0.13096	-0.50775
H-3D	-0.00458	-0.04060	-0.02097	0.19642	1.04667	-0.22680
O.C.	-0.02145	-0.00165	-0.00391	-0.06700	-0.00895	-0.00497

Δ	K6δ1
LI-K3D	1.00000
O.C.	-0.00391

TABLE 19. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF BH AT R = 2.20 BOHR

Σ	K1σ1	K3σ2	K4σ3	K5σ4	K6σ5
B-K1S	1.12539	0.35303	-3.00802	0.04284	-0.13420
B-K2S	-0.13121	-0.41226	3.79935	-0.05686	0.18550
B-K2P	-0.00024	1.15914	0.16509	0.00320	-2.38175
B-K3P	0.00342	0.02796	-0.05299	-0.06646	3.33206
B-K3D	-0.00030	0.02506	0.01519	0.98585	0.01079
B-L2S	-0.01312	-0.07992	1.27858	0.08272	-0.15603
B-L2P	-0.00160	-0.88767	-0.01733	0.10098	-1.67504
B-L3P	0.00373	0.03691	-0.08552	0.02275	-0.06757
B-L3D	0.00155	-0.02493	-0.03675	0.06588	-0.05021
B-L2S'	0.00312	0.07441	-1.93413	0.04279	-0.18905
B-L2P'	0.00125	0.38422	0.08598	0.02074	0.59368
H-1S	-0.00005	-0.20184	-0.28207	0.11598	-0.23997
H-2S	-0.00365	0.28719	0.25284	-0.26722	0.59818
H-2P	-0.00128	0.07323	0.07339	-0.12209	0.39672
O.C.	0.99970	-0.01179	-0.00951	-0.00271	-0.00263

Σ	LP1σ1	LP3σ2	LP4σ3	LP5σ4	LP6σ5
B-K1S	-0.19849	0.87892	0.18654	0.19607	0.06931
B-K2S	-0.01454	0.33327	-0.24740	-0.23372	-0.08690
B-K2P	-0.00311	0.02782	-0.06571	-0.08167	-1.03365
B-K3P	0.01286	0.01690	-0.03474	0.57271	3.26892
B-K3D	0.00041	-0.00648	-0.02669	-0.36075	0.03899
B-L2S	0.96990	-2.05216	-0.31788	1.46227	0.32191
B-L2P	-0.13157	-0.13056	1.46897	-2.18257	-7.35229
B-L3P	0.09521	0.12266	0.13732	3.44997	8.46228
B-L3D	-0.00468	0.03252	0.09585	1.55088	-0.05490
B-L2S'	0.00022	2.43296	0.39877	-0.01130	0.03816
B-L2P'	-0.31934	-0.12457	-1.53360	-0.18762	-2.36823
H-1S	-0.04123	0.05427	0.55519	0.51897	0.23133
H-2S	0.00937	0.15079	-0.28460	-2.63560	-0.74675
H-2P	0.03997	-0.26932	-0.61910	-1.14162	-0.30360
O.C.	0.97426	-0.01518	-0.00820	-0.00241	-0.00085

TABLE 19. (CONTINUED)

Σ	B1σ1	B2σ2	B4σ3	B5σ4
B-K1S	-0.05469	0.10974	-0.30971	0.00349
B-K2S	-0.01574	0.01638	0.36179	0.07707
B-K2P	0.00326	-0.02911	0.13972	0.02192
B-K3P	0.00528	0.01616	0.14292	0.05387
B-K3D	-0.00073	0.02208	-0.01337	-0.00223
B-L2S	-0.07670	-0.64537	-0.75611	0.07337
B-L2P	0.22753	-0.48104	-0.64879	-0.38015
B-L3P	0.02998	-0.32816	0.45737	0.12342
B-L3D	0.03131	-0.13306	0.13789	0.04229
B-L2S'	0.09186	-0.17186	-0.10585	-0.37687
B-L2P'	0.32103	-0.33900	-0.72283	-0.23941
H-1S	0.52574	1.09024	1.24609	-4.96016
H-2S	0.06723	0.25606	-0.45136	5.34425
H-2P	0.03172	-0.02993	1.05382	0.24253
O.C.	0.99466	-0.08590	-0.02299	-0.00441

Π	K2π1	LP2π1	B3π1	B6π1
B-K2P	1.08834	-0.01166	-0.01993	-0.58868
B-L2P	-0.23314	0.06835	0.28312	2.71794
B-L2P'	-0.07072	-1.09094	-0.66401	-2.33063
H-2P	0.03039	0.08211	1.12958	0.14751
O.C.	-0.01351	-0.15891	-0.03695	-0.00077

TABLE 20. TRANSFORMATION MATRIX AND OCCUPATION COEFFICIENTS OF BH AT R = 2.70 BOHR

Σ	K1σ1	K3σ2	K4σ3	K5σ4	K6σ5
B-K1S	1.12003	0.34452	-2.99951	0.03370	-0.10712
B-K2S	-0.12983	-0.41435	3.79575	-0.04643	0.14348
B-K2P	-0.00121	1.20077	0.17819	-0.00020	-2.47328
B-K3P	0.00190	-0.00656	-0.06665	-0.05535	3.43598
B-K3D	0.00025	0.02056	0.00537	0.98894	-0.00456
B-L2S	-0.00020	-0.06203	1.47460	0.04951	-0.02836
B-L2P	0.00717	-0.89489	-0.04775	0.07969	-1.68507
B-L3P	-0.00970	0.19408	0.05877	-0.00894	0.28367
B-L3D	-0.00198	0.00857	0.02166	0.04119	0.05605
B-L2S'	0.00367	0.13248	-2.03499	0.01367	-0.08629
B-L2P'	0.00239	0.29310	0.07694	0.01735	0.44903
H-1S	0.00105	-0.23394	-0.36265	0.12498	-0.32116
H-2S	0.00503	0.22255	0.18019	-0.20472	0.37875
H-2P	0.00253	-0.00133	-0.06658	-0.08025	0.22775
O.C.	0.99970	-0.01176	-0.00950	-0.00270	-0.00266

Σ	LP1σ1	LP3σ2	LP4σ3	LP5σ4	LP6σ5
B-K1S	-0.22175	-0.87068	0.16325	0.10035	0.04375
B-K2S	-0.01142	0.30982	-0.24183	-0.09252	-0.04953
B-K2P	-0.00312	0.01612	-0.06956	-0.12544	-1.05865
B-K3P	-0.01562	0.01098	-0.08974	0.66997	3.18147
B-K3D	0.00135	-0.00347	-0.02815	-0.31865	0.04448
B-L2S	0.98805	-2.22691	-0.32825	1.09944	0.28221
B-L2P	-0.03877	-0.12732	1.58645	-2.19408	-6.79887
B-L3P	-0.09972	0.06371	-0.37635	2.72018	7.22551
B-L3D	-0.02665	-0.00082	0.07104	1.24532	-0.10551
B-L2S'	-0.02731	2.56232	0.34541	-0.39571	-0.06742
B-L2P'	-0.19908	-0.08584	-1.14340	-0.08508	-1.80324
H-1S	0.07018	0.13095	0.58861	0.72848	0.37844
H-2S	-0.03167	0.15461	-0.20397	-1.96470	-0.65498
H-2P	0.01184	-0.12066	-0.41375	-0.88106	-0.39229
O.C.	0.97352	-0.01623	-0.00833	-0.00249	-0.00086

TABLE 20. (CONTINUED)

Σ	B1σ1	B2σ2	B4σ3	B5σ4
B-K1S	-0.03943	0.11102	-0.28070	0.06688
B-K2S	-0.01000	-0.01602	0.31059	-0.00401
B-K2P	0.00644	0.01657	0.17142	0.00954
B-K3P	0.00801	-0.01393	0.03365	-0.01525
B-K3D	-0.00407	-0.01321	-0.02448	-0.00306
B-L2S	0.00813	-0.47352	-0.65350	0.45779
B-L2P	0.16570	-0.57727	-0.36406	-0.12501
B-L3P	0.14520	0.11631	0.33213	0.03879
B-L3D	0.06247	0.08917	0.24094	0.07677
B-L2S'	0.03662	-0.03626	0.14514	-0.30497
B-L2P'	0.31544	-0.50323	-0.62824	0.06840
H-1S	0.52829	0.98553	0.45764	-5.40740
H-2S	0.03139	0.00271	0.00443	5.32834
H-2P	0.00802	-0.16217	0.93649	-0.08970
O.C.	0.99171	-0.11412	-0.02314	-0.00410

Π	K2π1	LP2π1	B3π1	B6π1
B-K2P	1.09293	-0.01056	-0.00945	-0.61233
B-L2P	-0.24366	0.08247	0.16493	2.84440
B-L2P'	-0.06373	-1.09086	-0.44791	-2.44954
H-2P	0.02872	0.06393	1.07454	0.22017
O.C.	-0.01346	-0.16111	-0.03833	-0.00047

TABLE 21. ENERGY QUANTITIES OF LIH AS FUNCTIONS OF R

R	−E	−E(PNO)	−ϵ(K)	−ϵ(B)	I(K,B)
2.600	8.04374	7.97614	6.53413	1.17042	1.49304
2.800	8.05155	7.98277	6.55896	1.14441	1.41961
3.000	8.05415	7.98470	6.58180	1.11945	1.35290
3.015	8.05418	7.98469	6.58342	1.11763	1.34816
3.050	8.05421	7.98467	6.58656	1.11349	1.33776
3.100	8.05411	7.98449	6.59097	1.10765	1.32323
3.200	8.05342	7.98368	6.59945	1.09622	1.29525
3.400	8.05059	7.98064	6.61519	1.07439	1.24336
3.600	8.04642	7.97631	6.62937	1.05398	1.19641
4.000	8.03570	7.96533	6.65350	1.01711	1.11509
5.000	8.00518	7.92706	6.68182	0.93971	0.98371
7.000	7.97037	7.85833	6.67639	0.84722	0.87533
∞	7.96943	7.93194	6.64906	0.19591	0.62446

TABLE 22. ENERGY QUANTITIES OF BH AS FUNCTIONS OF R

R	$-E$	$-E(PNO)$	$-\epsilon(K)$	$-\epsilon(B)$	$-\epsilon(LP)$	I(K,B)	I(K,LP)	I(B,LP)
1.800	25.1259	25.0514	18.1744	1.3982	1.9294	2.4649	2.4539	1.4829
2.000	25.1823	25.1035	18.2079	1.4143	1.8153	2.3223	2.4722	1.4503
2.200	25.2034	25.1213	18.2348	1.4317	1.7077	2.1388	2.4958	1.4173
2.300	25.2054	25.1224	18.2468	1.4413	1.6567	2.1247	2.5094	1.4035
2.329	25.2053	25.1223	18.2499	1.4442	1.6422	2.1064	2.5138	1.3956
2.350	25.2053	25.1221	18.2512	1.4452	1.6335	2.0961	2.5152	1.3918
2.400	25.2050	25.1214	18.2536	1.4476	1.6131	2.0719	2.5192	1.3828
2.600	25.1974	25.1127	18.2630	1.4576	1.5350	1.9798	2.5372	1.3478
3.500	25.1061	25.0177	18.2772	1.4455	1.2796	1.7538	2.5481	1.2303
4.500	25.0236	24.9283	18.2888	1.4441	1.0934	1.5964	2.5692	1.1427
∞	25.0622	25.0200	17.9034	1.9136	0.3078	1.1765	2.4747	0.7863

TABLE 23. OCCUPATION NUMBERS OF LIH AS FUNCTIONS OF R

R	K1σ1	K2σ1	K3π2	K4σ3	B1σ1	B2σ2	B3π1	B4σ3
2.600	0.99778	0.00110	0.00056	0.00046	0.97466	0.01164	0.01038	0.00288
2.800	0.99772	0.00114	0.00058	0.00046	0.97284	0.01334	0.01033	0.00309
3.000	0.99766	0.00116	0.00061	0.00047	0.97123	0.01505	0.01011	0.00323
3.200	0.99770	0.00112	0.00061	0.00047	0.96954	0.01690	0.00988	0.00328
3.500	0.99778	0.00104	0.00061	0.00047	0.96656	0.02027	0.00954	0.00321
4.000	0.99792	0.00092	0.00059	0.00048	0.95995	0.02777	0.00898	0.00292
5.000	0.99792	0.00092	0.00058	0.00048	0.93244	0.05914	0.00623	0.00183
7.000	0.99794	0.00092	0.00058	0.00048	0.79075	0.20672	0.00203	0.00034
∞	0.99742	0.00117	0.00070	0.00059	0.50000	0.50000	0.0	0.0

TABLE 24. OCCUPATION NUMBERS OF BH AS FUNCTIONS OF R

R	K1σ1	K2π1	LP1σ1	LP2π1	B1σ1	B2σ2	B3π1
2.000	0.99942	0.00035	0.95064	0.04912	0.99253	0.00410	0.00279
2.200	0.99940	0.00037	0.94918	0.05050	0.98935	0.00738	0.00273
2.300	0.99938	0.00037	0.94858	0.05107	0.98790	0.00891	0.00273
2.400	0.99938	0.00037	0.94834	0.05128	0.98653	0.01026	0.00275
2.600	0.99940	0.00037	0.94799	0.05166	0.98424	0.01237	0.00286
3.000	0.99940	0.00036	0.94630	0.05335	0.98131	0.01544	0.00271
3.500	0.99940	0.00036	0.94363	0.05600	0.97808	0.01910	0.00237
4.500	0.99940	0.00036	0.93962	0.06001	0.96865	0.02931	0.00177
∞	0.99918	0.00036	0.99990	0.00005	0.50000	0.50000	0.0

TABLE 25. DUNHAM[a] POLYNOMIAL APPROXIMATION FOR THE POTENTIAL CURVE OF LIH

DEGREE	$E(R_1)$	$E(R_2)$	NUMBER OF POINTS	MIN R	a_0	a_1	a_2
5	-8.05261(2.85)	-8.05221(3.30)	10	3.042	0.3277	-2.2341	13.797
5	-8.05017(2.75)	-8.04965(3.45)	15	3.043	0.3403	-2.4141	5.1934
5	-8.04631(2.65)	-8.04642(3.60)	20	3.042	0.3441	-2.3798	3.8896
5	-8.02765(2.40)	-8.02832(4.25)	16	3.042	0.3426	-2.4089	4.3316
6	-8.02765(2.40)	-8.02832(4.25)	16	3.045	0.3393	-2.2169	4.2101
7	-8.02765(2.40)	-8.02832(4.25)	16	3.045	0.3367	-2.254	4.709
EXP[b]				3.015	0.2995	-1.884	2.378

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[a] REF. (67)
[b] CRAWFORD AND JORGENSEN REF. (27)

TABLE 26. SPECTROSCOPIC CONSTANTS CALCULATED FROM APSG POTENTIAL CURVES

LIH

CONSTANT		CALCULATED	EXPERIMENT[a]	PERCENT DEVIATION
B_e	1/CM	7.381	7.513	-1.75
ω_e	1/CM	1483	1405.6	5.5
$\omega_e x_e$	1/CM	24.45	23.20	5.4
α_e	1/CM	0.2849	0.213	33.7
R_e	A	1.611	1.595	0.96

BH

CONSTANT		CALCULATED	EXPERIMENT[b]	PERCENT DEVIATION
B_e	1/CM	12.085	12.016	0.57
ω_e	1/CM	2928	2367.5	23.7
$\omega_e x_e$	1/CM	45.40	(49)[c]	
α_e	1/CM	0.4887	0.408	19.77
R_e	A	1.230	1.236	-0.49

[a] CRAWFORD AND JORGENSEN REF. (27)

[b] BAUER, ET AL. REF. (29)

[c] ESTIMATED FROM $\omega_e x_e/\omega_e = 0.6\ \alpha_e/B_e$ SEE REF. (29)

TABLE 27. COMPUTATION TIME FOR ALL EXCHANGE INTEGRALS ARISING FROM A GIVEN BASES SET[a,b]

BASIS SET	NO. OF AO'S PER CENTER	TOTAL NO. OF INTEGRALS	TOTAL TIME IN MINUTES
1s	1	1	0.05
+2s	2	10	0.05
+2pσ	3	45	0.08
+2pπ	4	136	0.10
+2p$\bar{\pi}$	5	325	0.10
+3s	6	666	0.14
+3pσ	7	1225	0.21
+3pπ	8	2080	0.32
+3p$\bar{\pi}$	9	3321	0.32
+3dσ	10	5050	0.42
+3dπ	11	7381	0.56
+3d$\bar{\pi}$	12	10440	0.63
+3dδ	13	14365	0.76
+3d$\bar{\delta}$	14	19300	0.89

[a] $\zeta_a \neq \zeta_b$ for all orbitals, but $\zeta\bar{\pi} = \zeta\pi$, $\zeta\bar{\delta} = \zeta\delta$

[b] Times quoted apply to an IBM 360/65

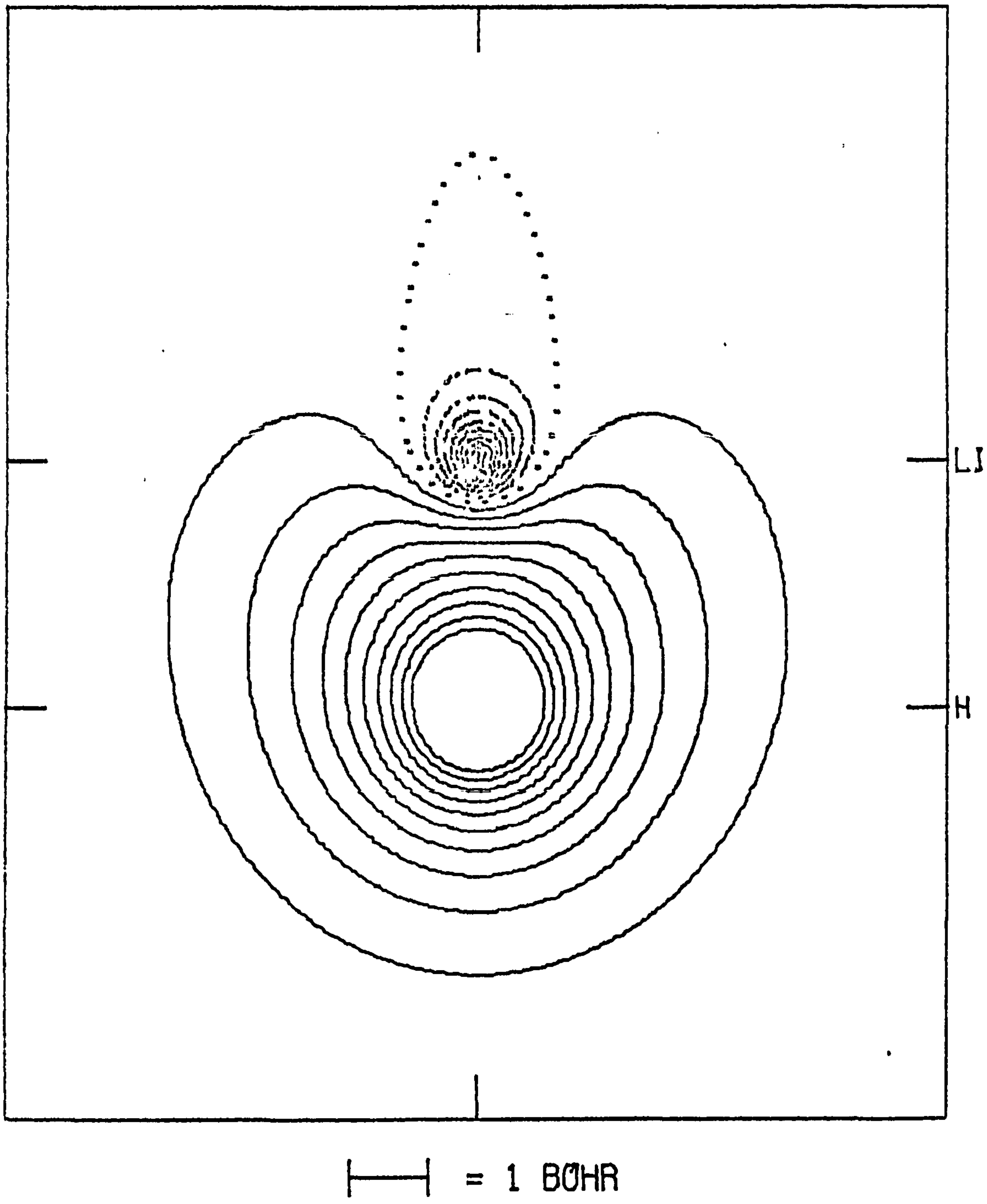


DIAGRAM 1. CONTOUR MAP OF B 1 SIGMA 1 NO OF LIH AT R=3.00 BOHR

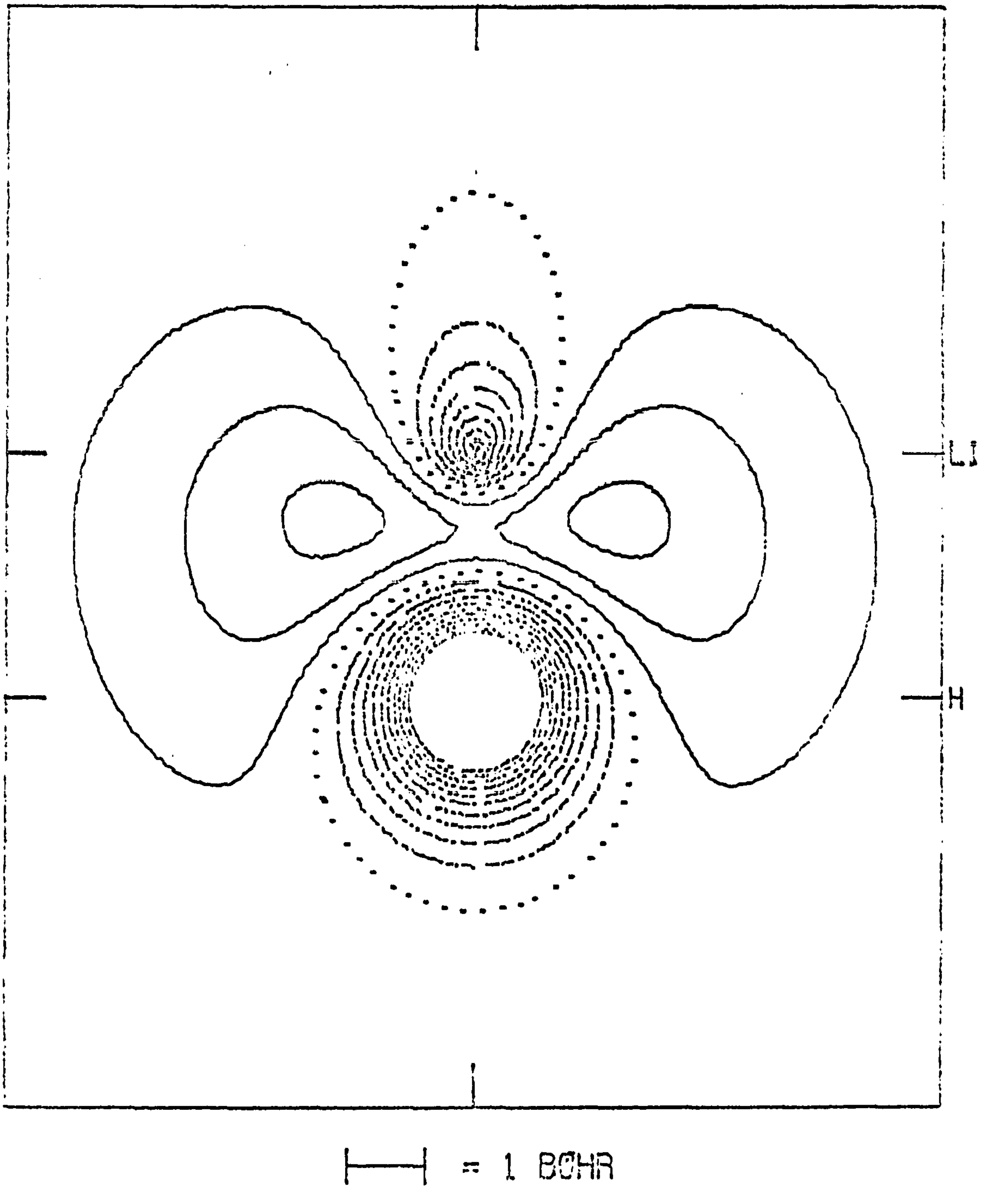


DIAGRAM 2. CONTOUR MAP OF B 2 SIGMA 2 NO OF LIH AT R=3.00 BOHR

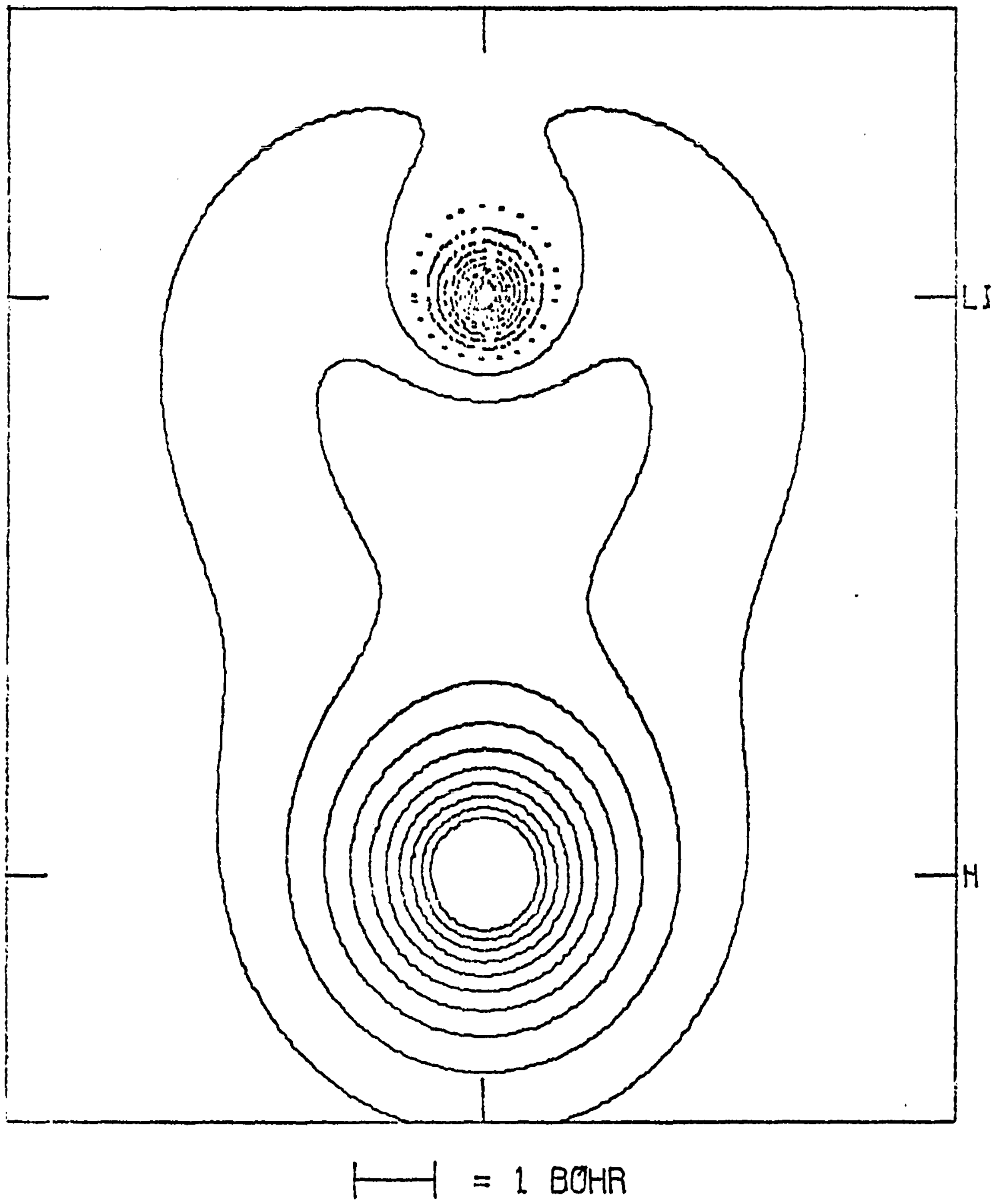


DIAGRAM 3. CONTOUR MAP OF B 1 SIGMA 1
NO OF LIH AT R=7.00 BOHR

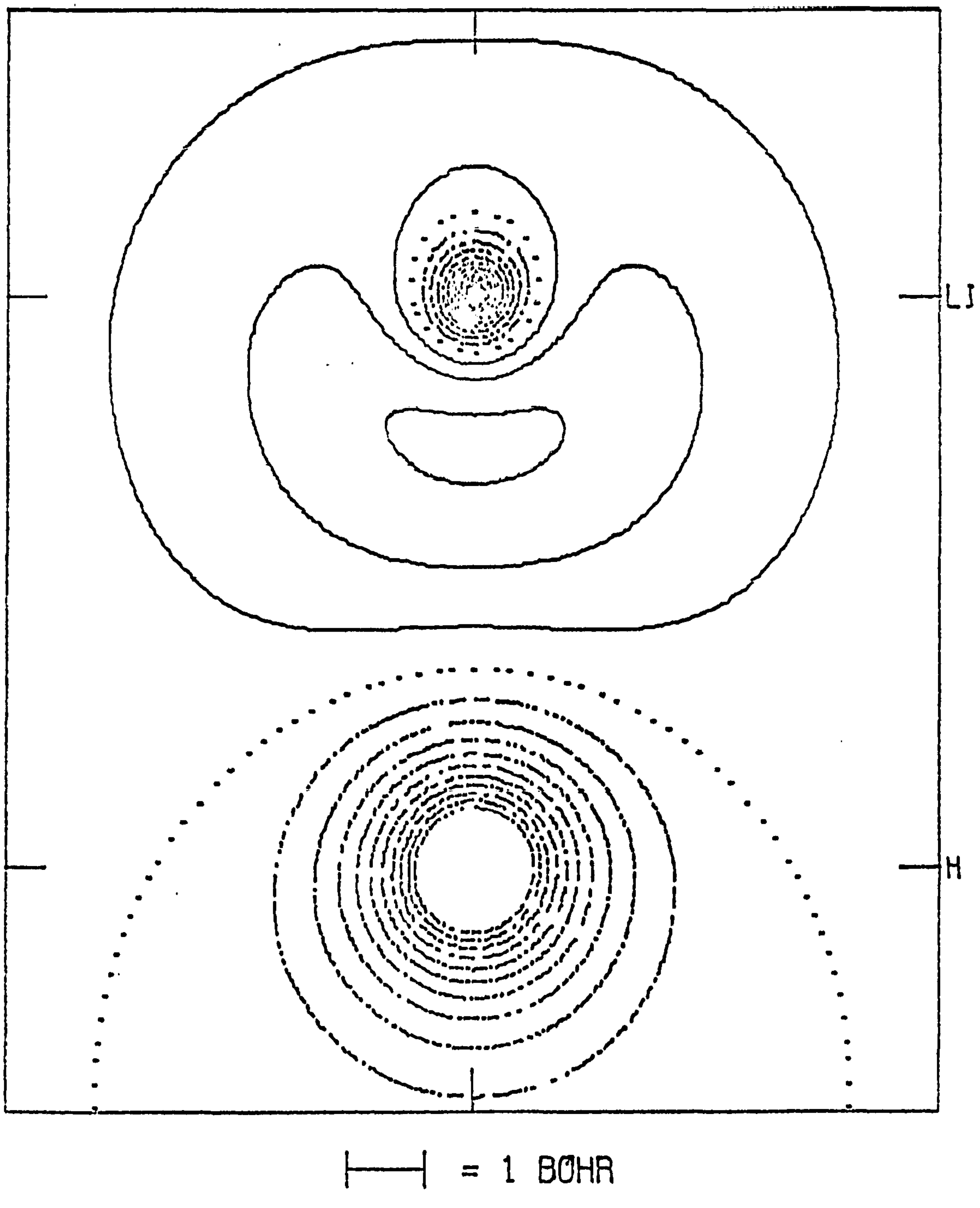


DIAGRAM 4. CONTOUR MAP OF B 2 SIGMA 2
NO OF LIH AT R=7.00 BOHR

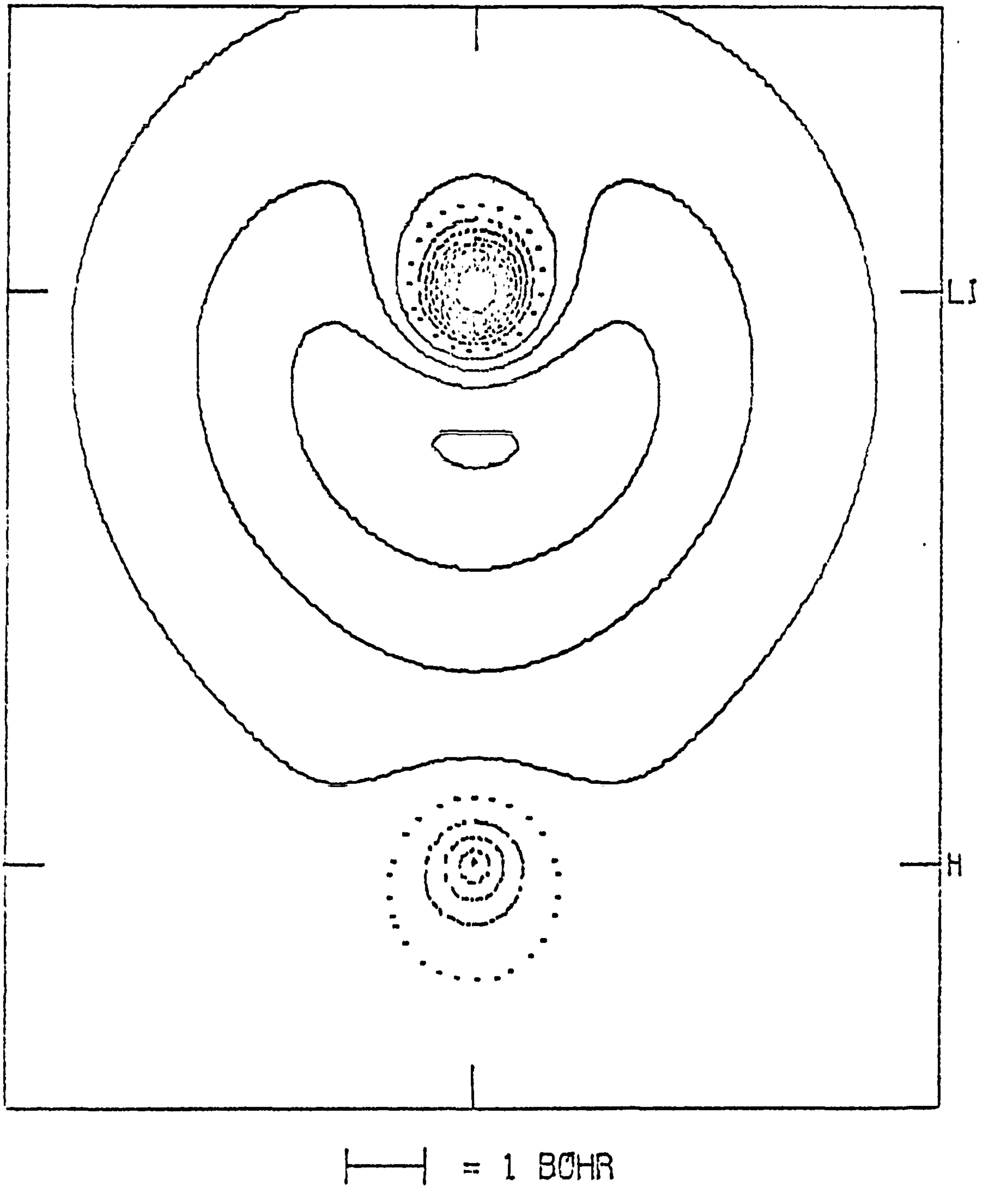


DIAGRAM 5. CONTOUR MAP OF B 1 SIGMA 1 + B 2 SIGMA 2 NO'S OF LIH AT R=7.00 BOHR

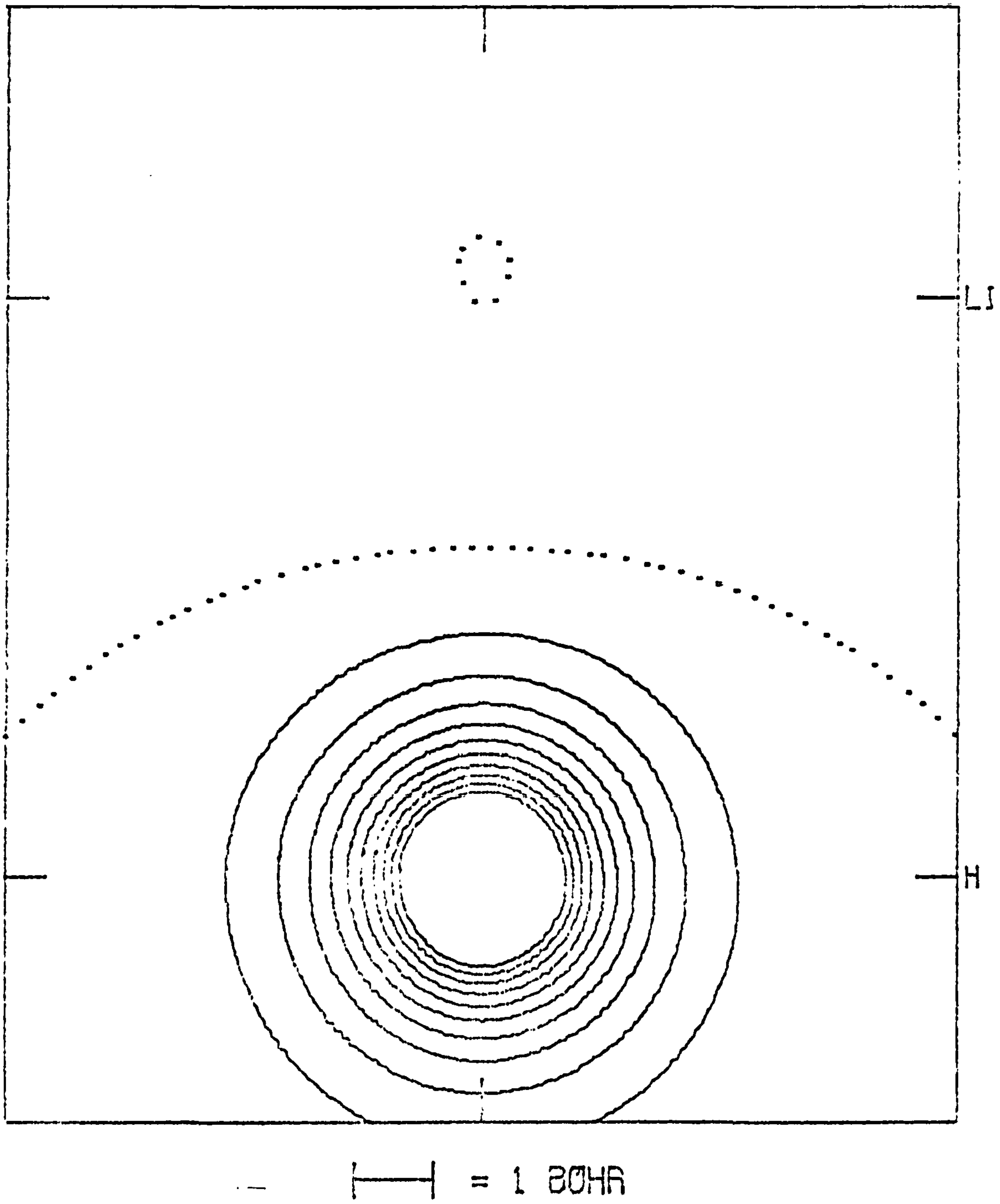
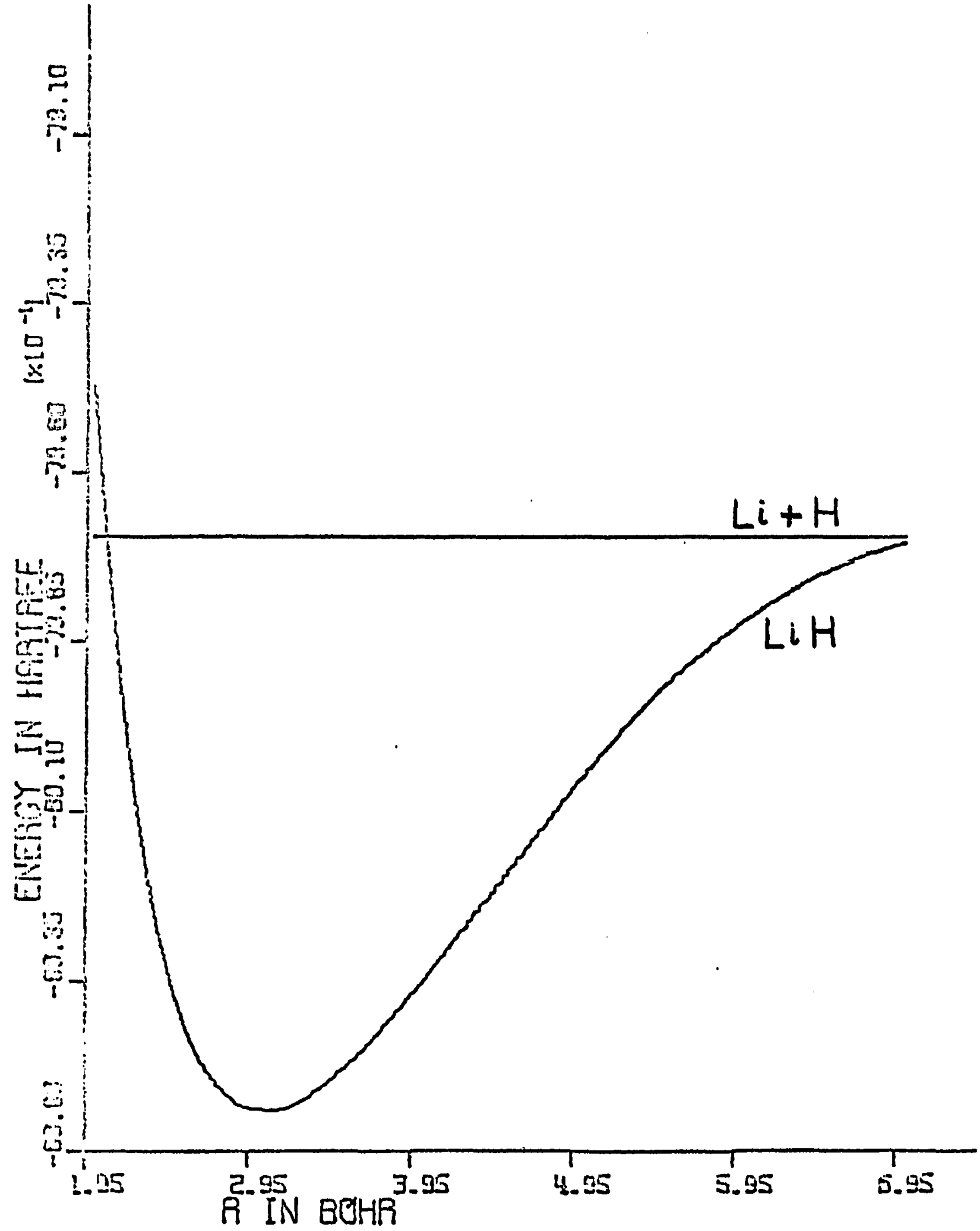
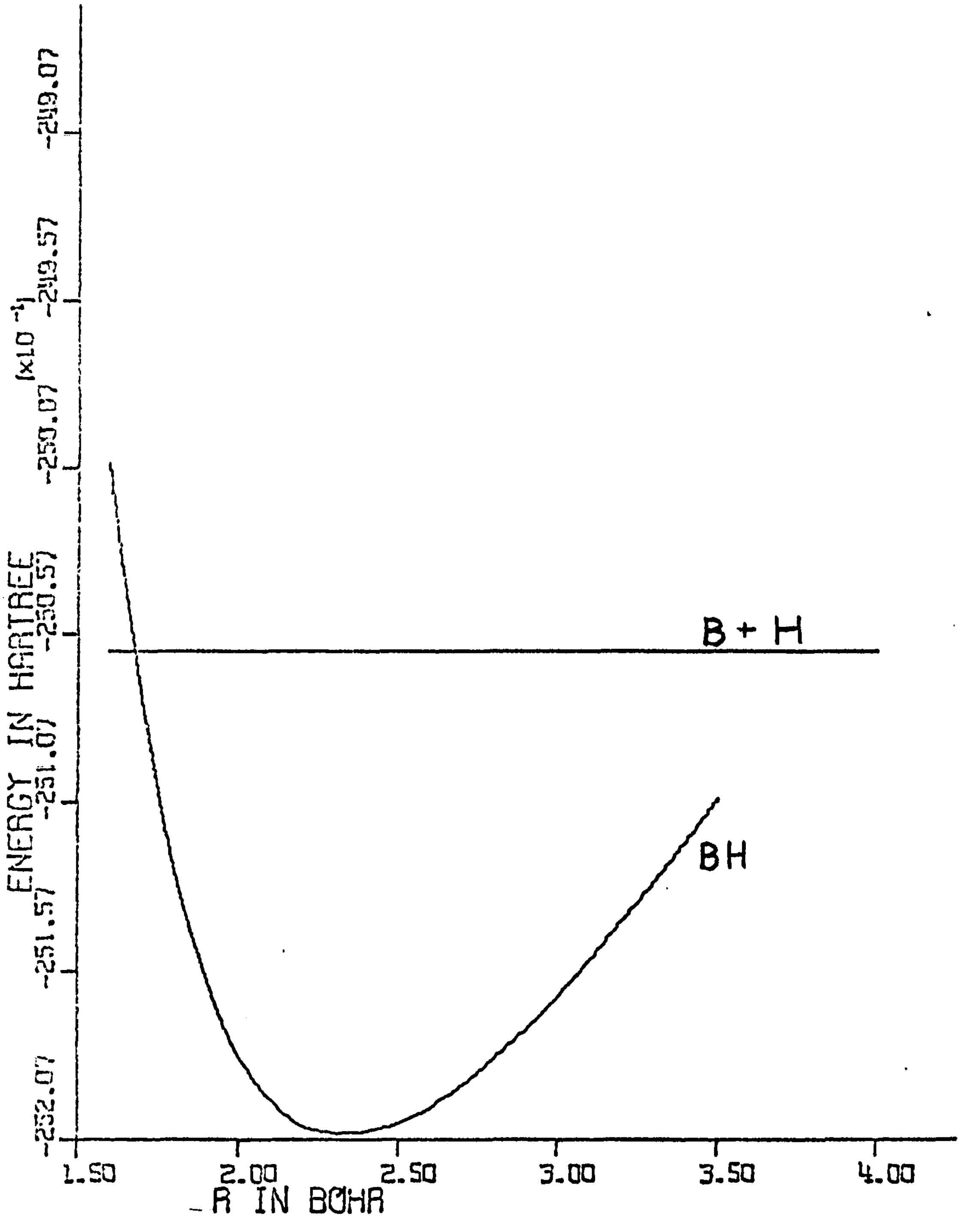


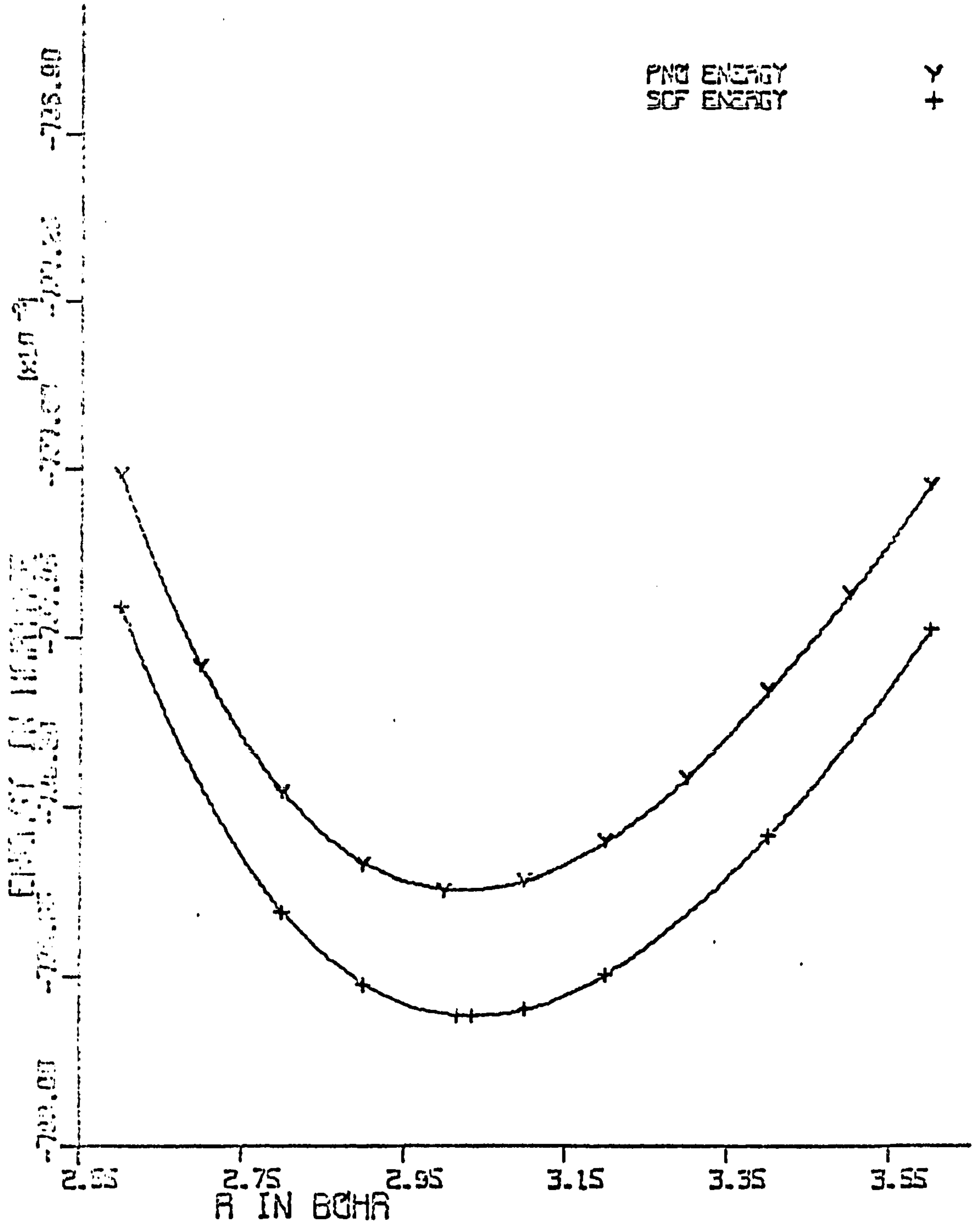
DIAGRAM 6. CONTOUR MAP OF B 1 SIGMA 1 - B 2 SIGMA 2 NO'S OF LIH AT R=7.00 BOHR



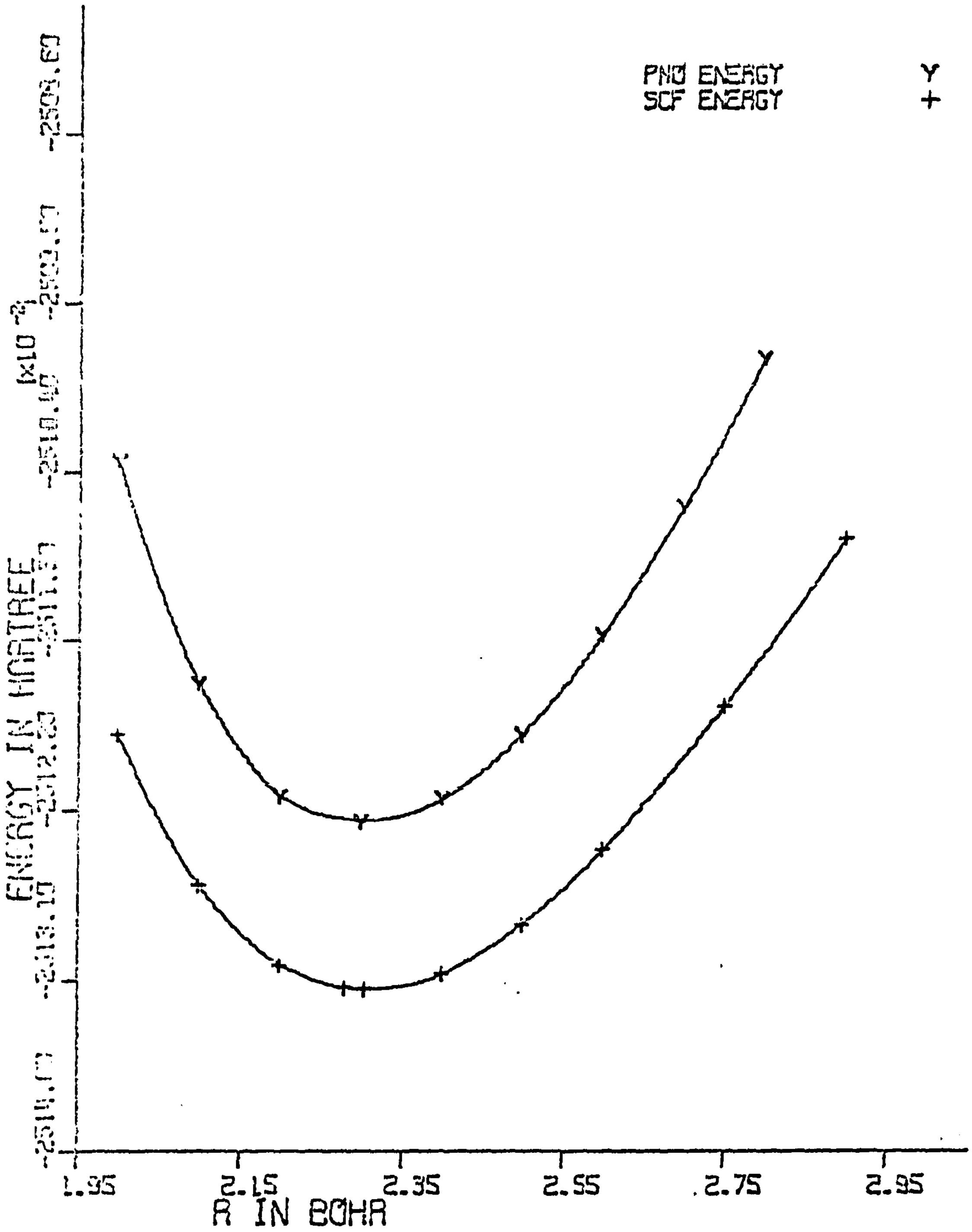
GRAPH 1. POTENTIAL CURVE OF THE SEPARATED PAIR ENERGY OF LIH



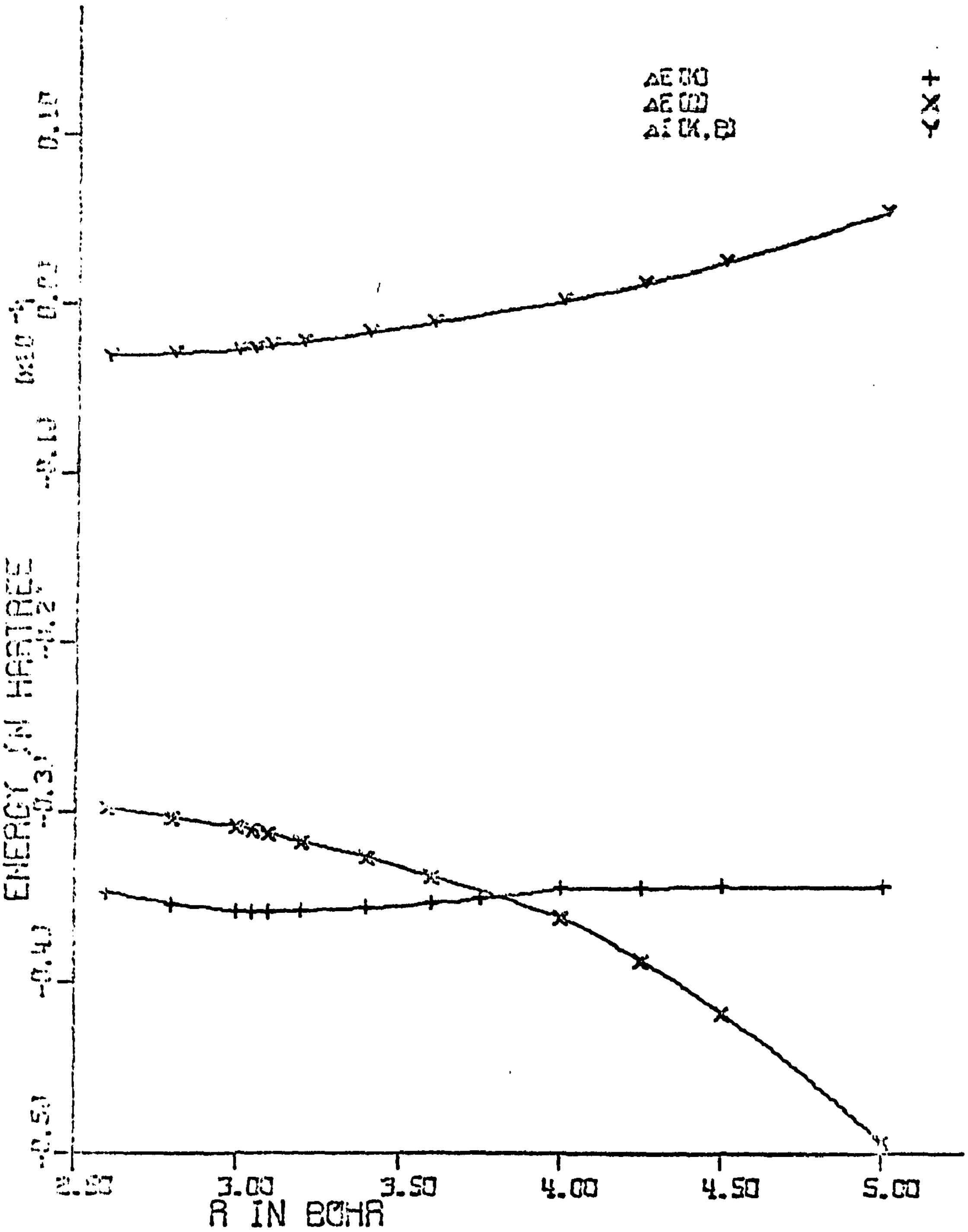
GRAPH 2. POTENTIAL CURVE OF THE SEPARATED PAIR ENERGY OF BH



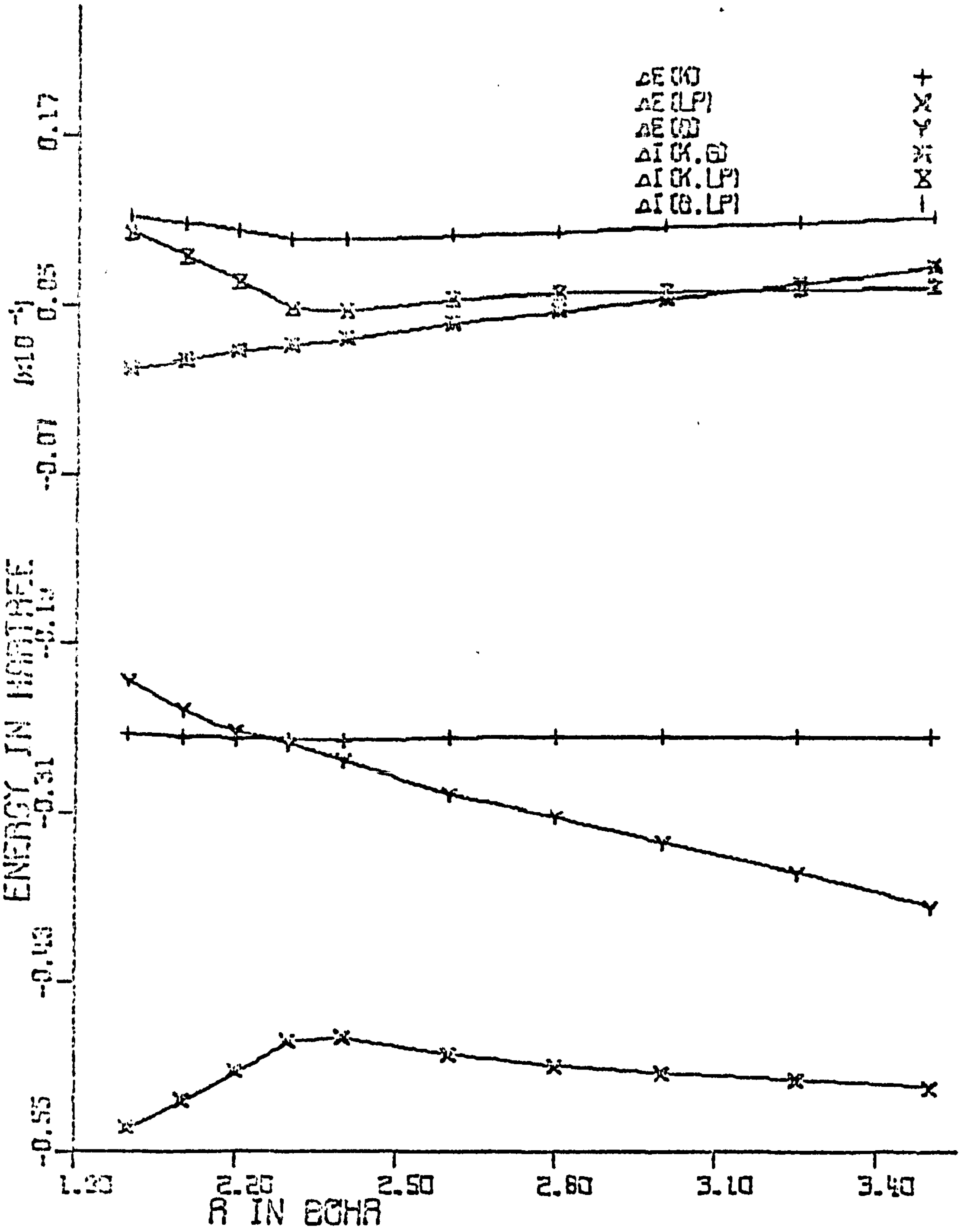
GRAPH 3. POTENTIAL CURVES FOR THE PNO AND SCF ENERGIES OF LIH



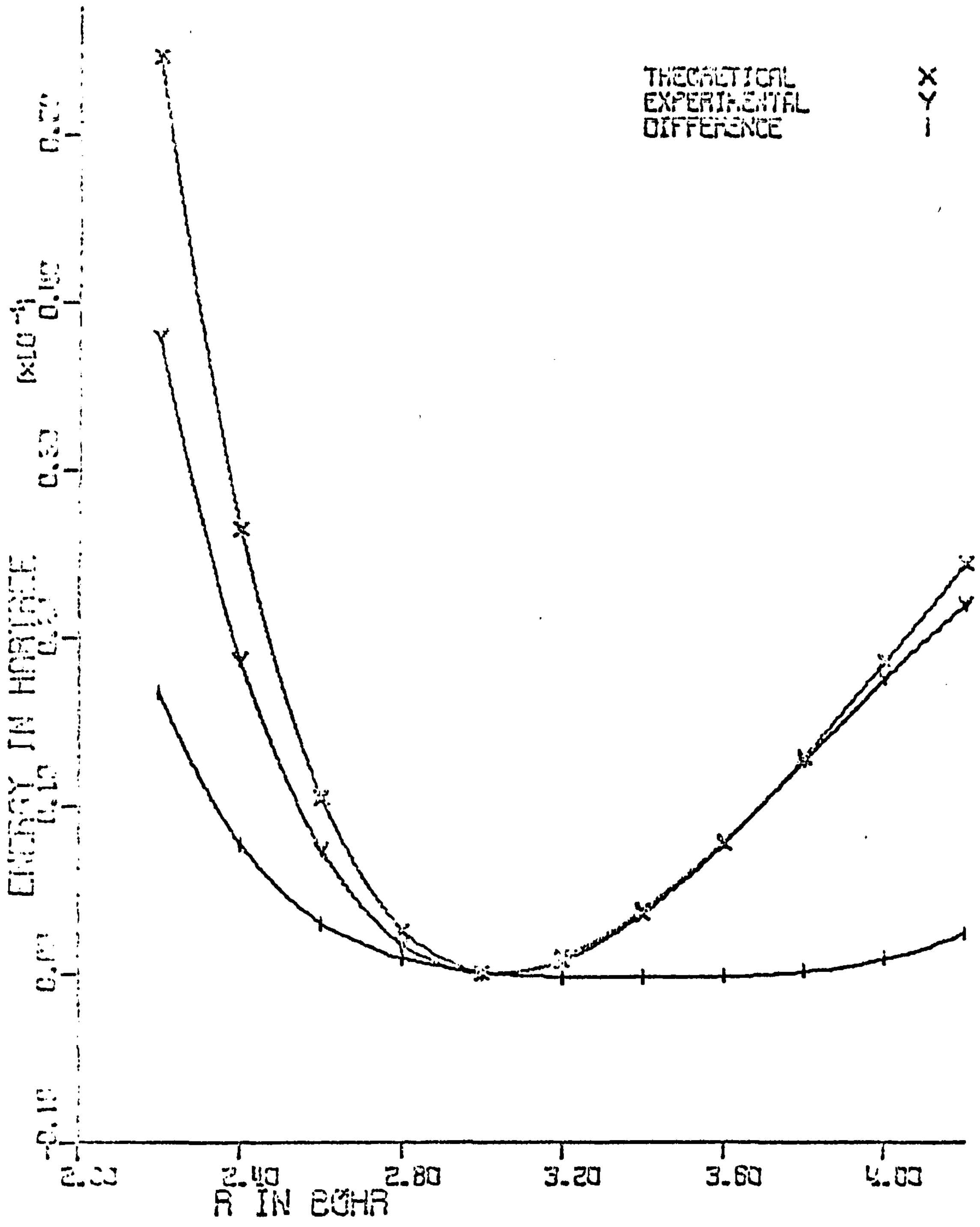
GRAPH 4. POTENTIAL CURVES FOR THE PNO AND SCF ENERGIES OF BH



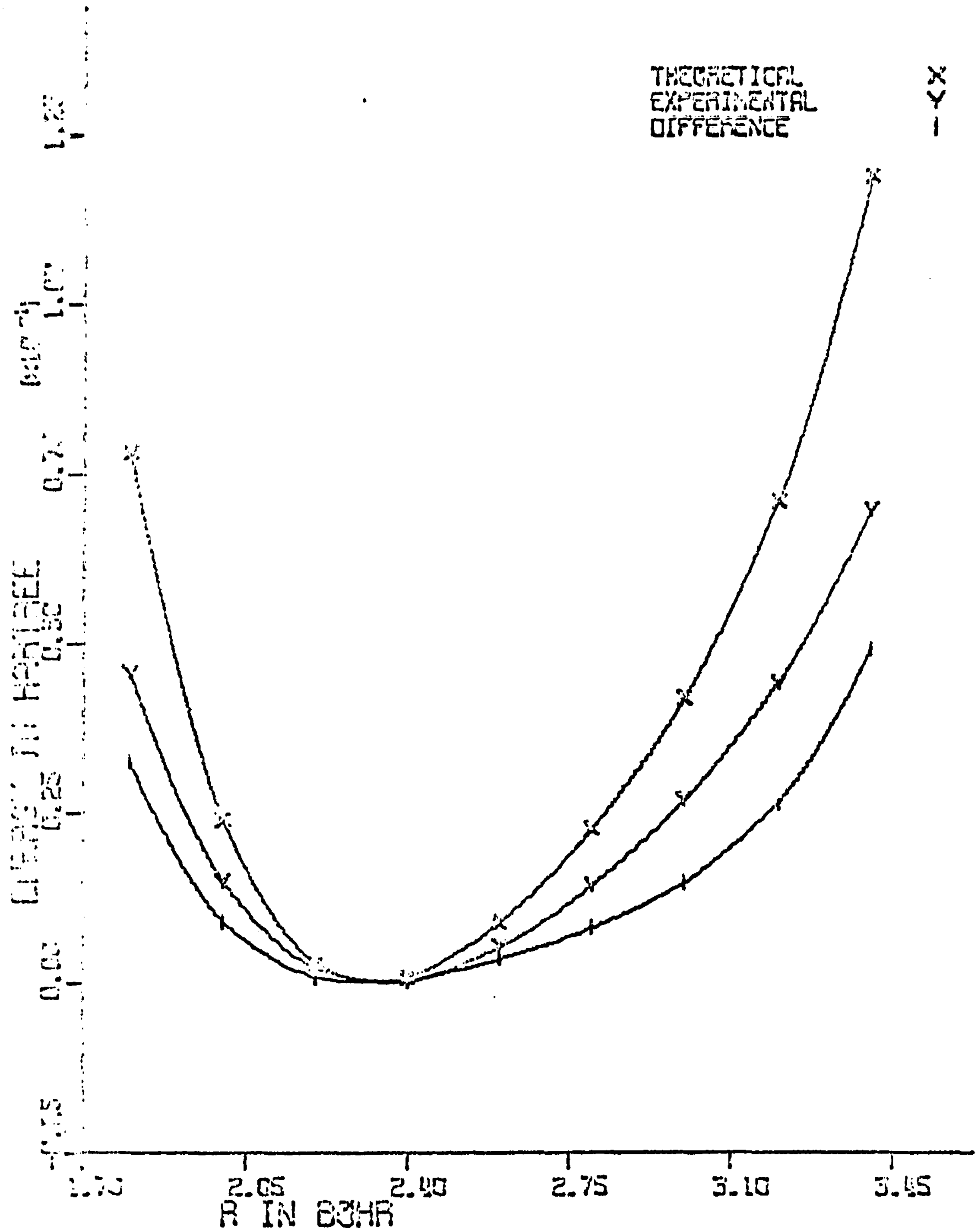
GRAPH 5. INTRA- AND INTER- GEMINAL CORRELATION ENERGIES FOR LIH



GRAPH 6. INTRA- AND INTER- GEMINAL CORRELATION ENERGIES FOR BH



GRAPH 7. EXPERIMENTAL AND THEORETICAL DUNHAM POTENTIAL CURVES FOR LIH



GRAPH 8. EXPERIMENTAL AND THEORETICAL DUNHAM POTENTIAL CURVES FOR BH

APPENDIX B

Contour maps for all the natural orbitals which form the bases of the APSG wave functions determined for Li, LiH, B, and BH are presented. The LiH and BH contour maps are chosen at the equilibrium distance of 3.015 and 2.329 bohr respectively. The contour maps are drawn to the same scale in units of $R^{-3/2}$.

Contours which are positive are drawn with solid lines, and contours which are negative are drawn with dashed lines. The nodes are drawn with dotted lines. Contours, C, are drawn in increments of 0.04 $\text{bohr}^{-3/2}$ in the interval[a]

$$-0.4 \leq C \leq 0.4 \quad .$$

Thus in a region enclosed by a node the contour nearest it has a value of $|0.04|\ \text{bohr}^{-3/2}$. The nuclei are located at the intersections of the straight lines which would connect the vertical tick marks and the horizontal tick marks.

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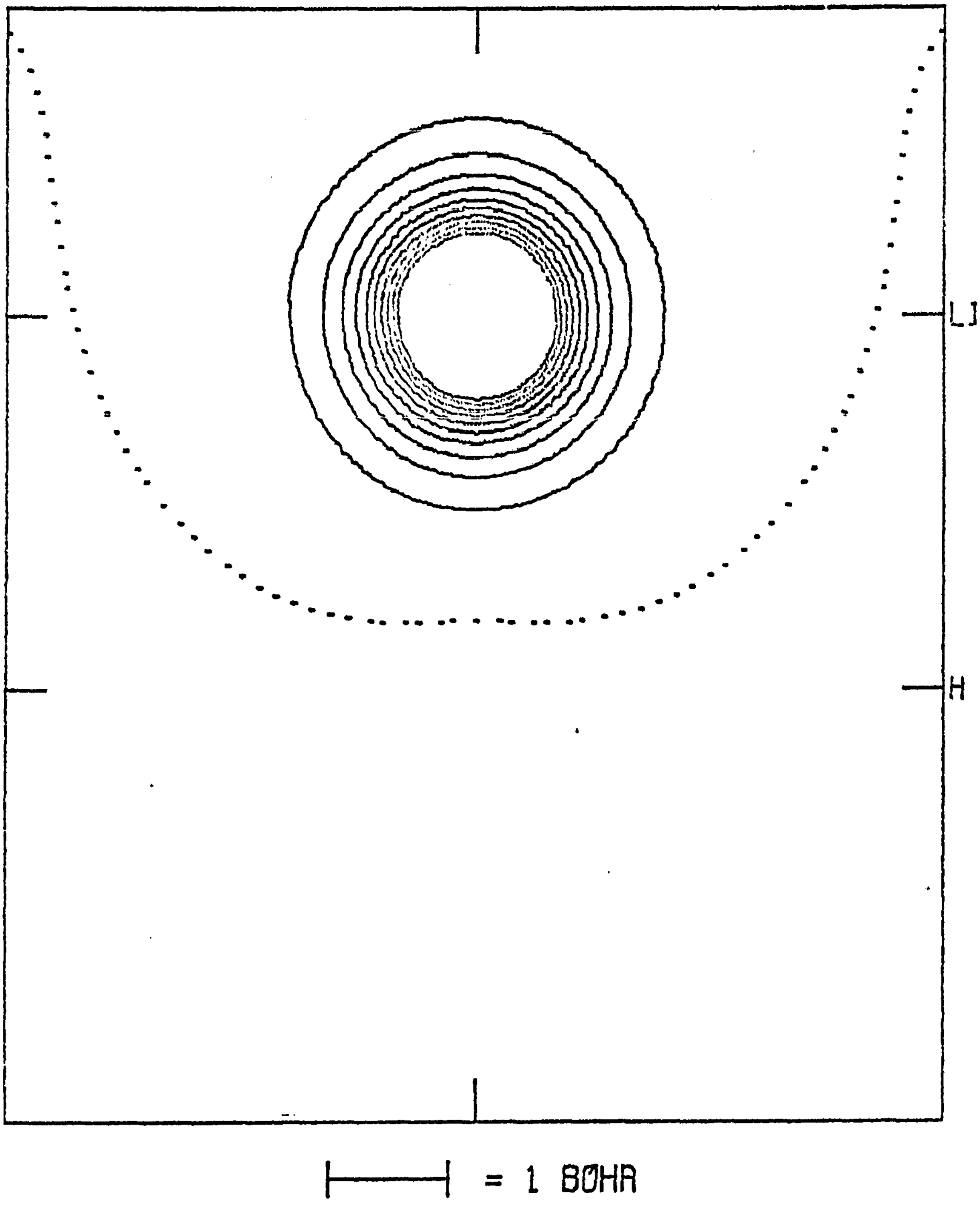
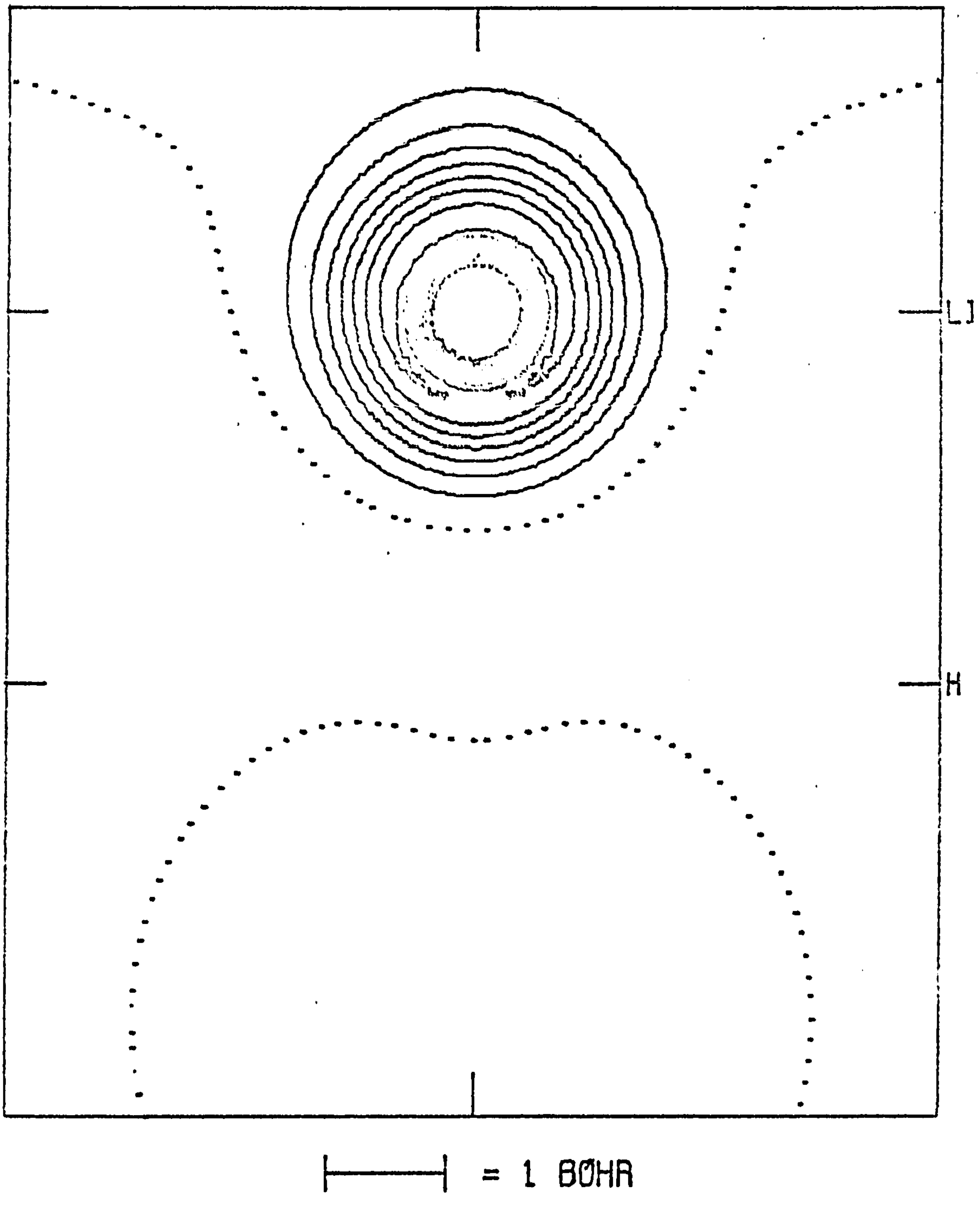
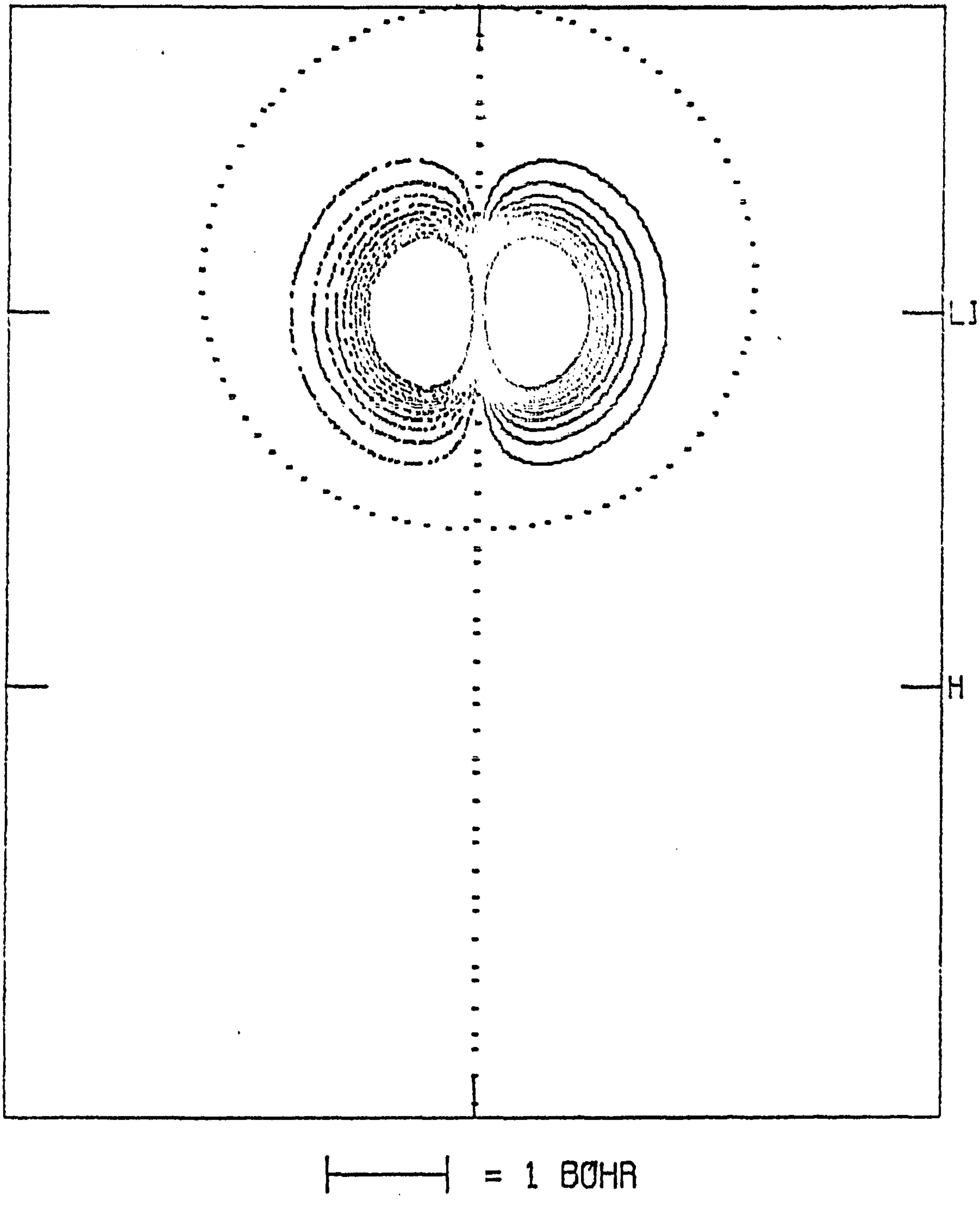
[a] The contour maps of Diagrams 1-6 are drawn in increments of 0.02 $\text{bohr}^{-3/2}$ in an interval $-0.2 \leq C \leq 0.2$.



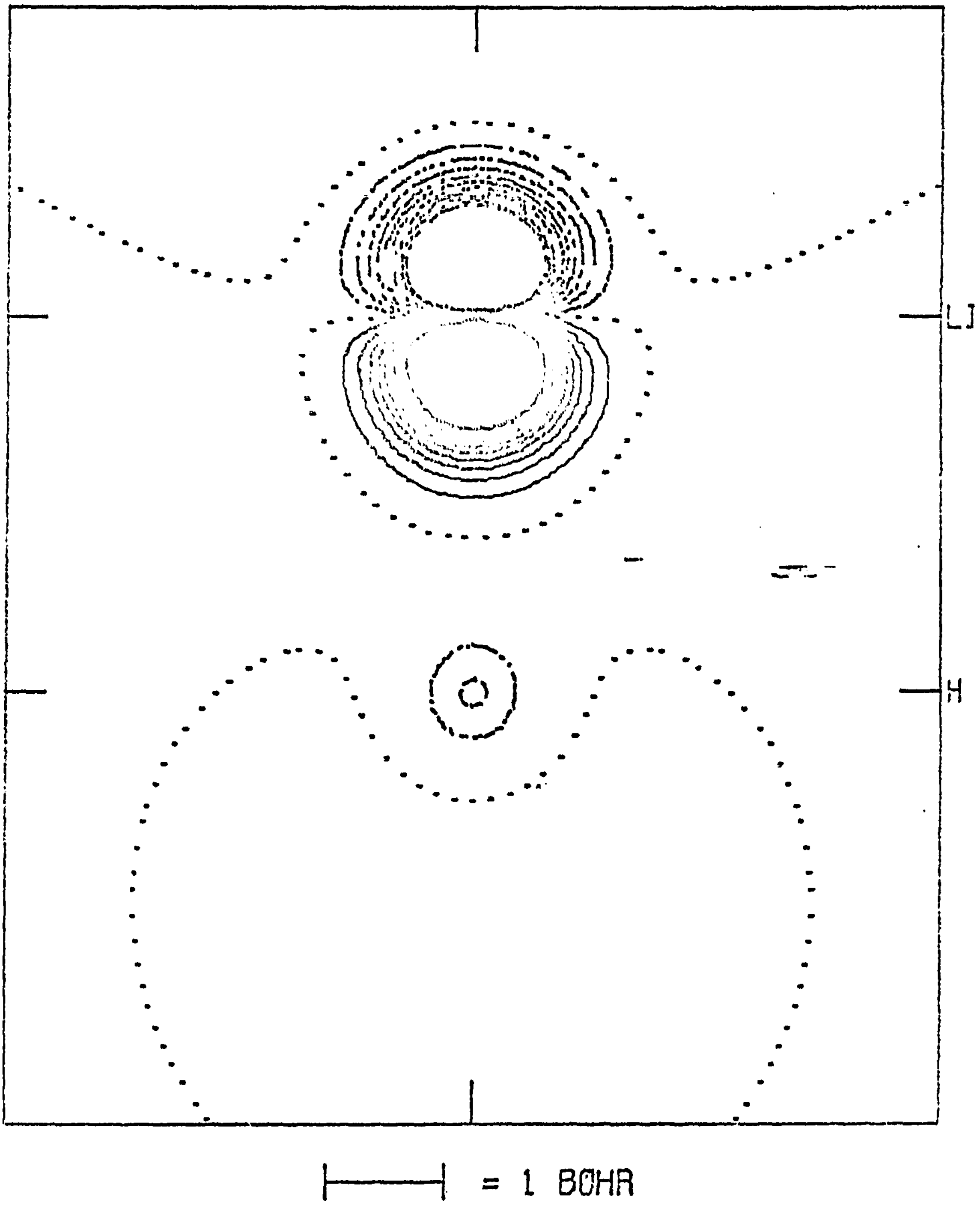
NATURAL ORBITAL CONTOUR MAP 1.
LIH K SHELL 1 SIGMA 1 (OC= .99882)



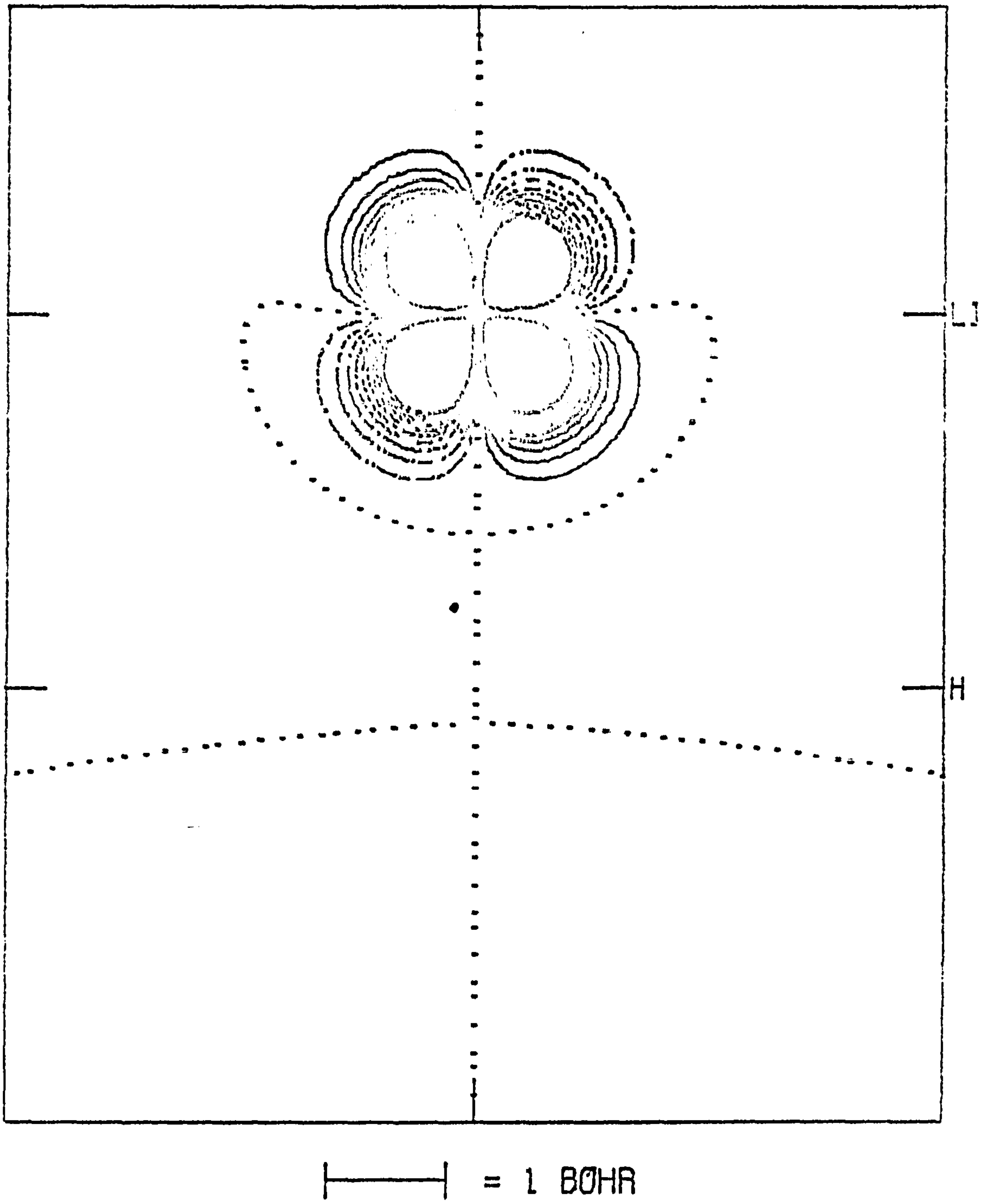
NATURAL ORBITAL CONTOUR MAP 2.
LIH K SHELL 2 SIGMA 2 (OC=-.02463)



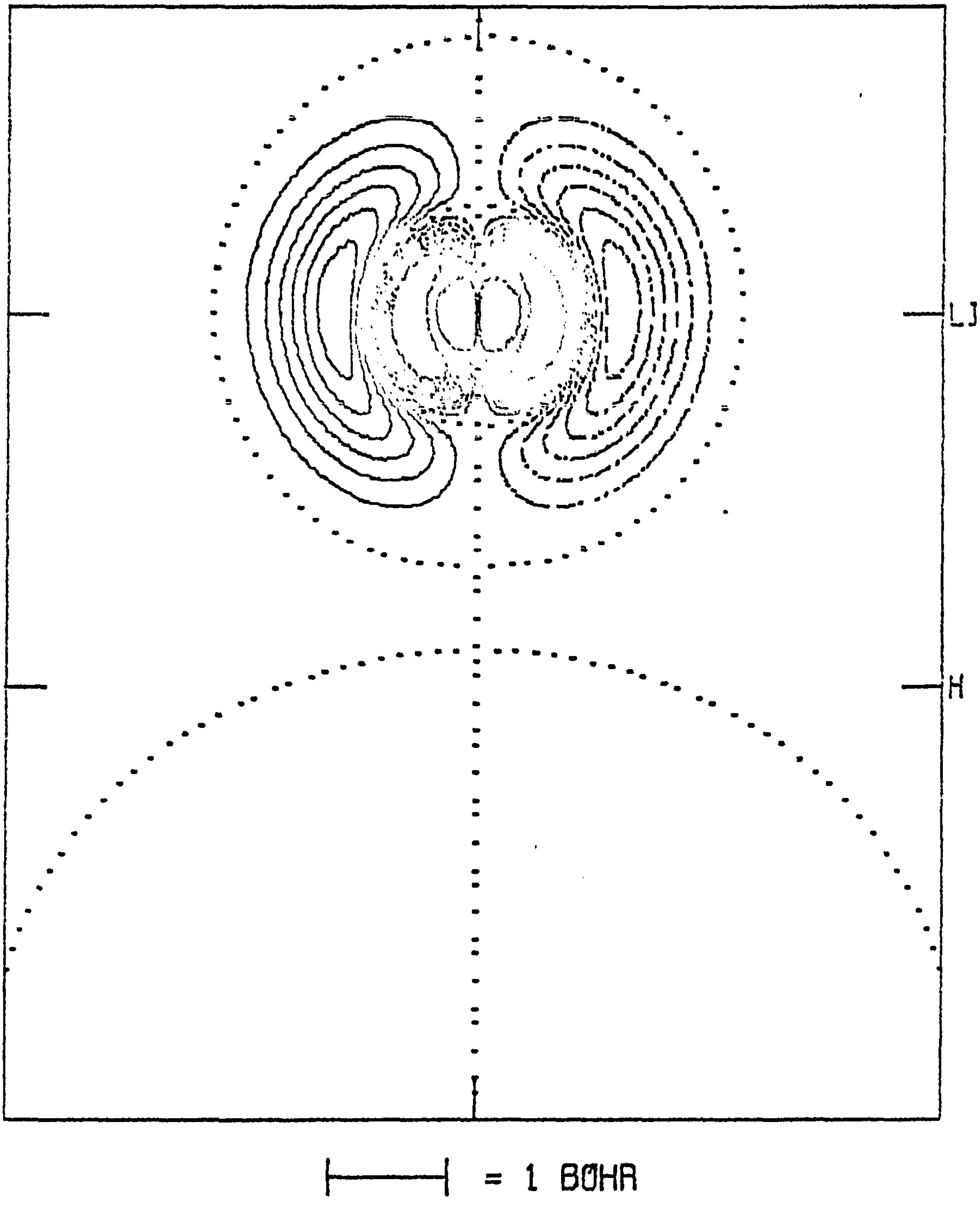
NATURAL ORBITAL CONTOUR MAP 3.
LIH K SHELL 3 PI 1 (OC=-.02421)



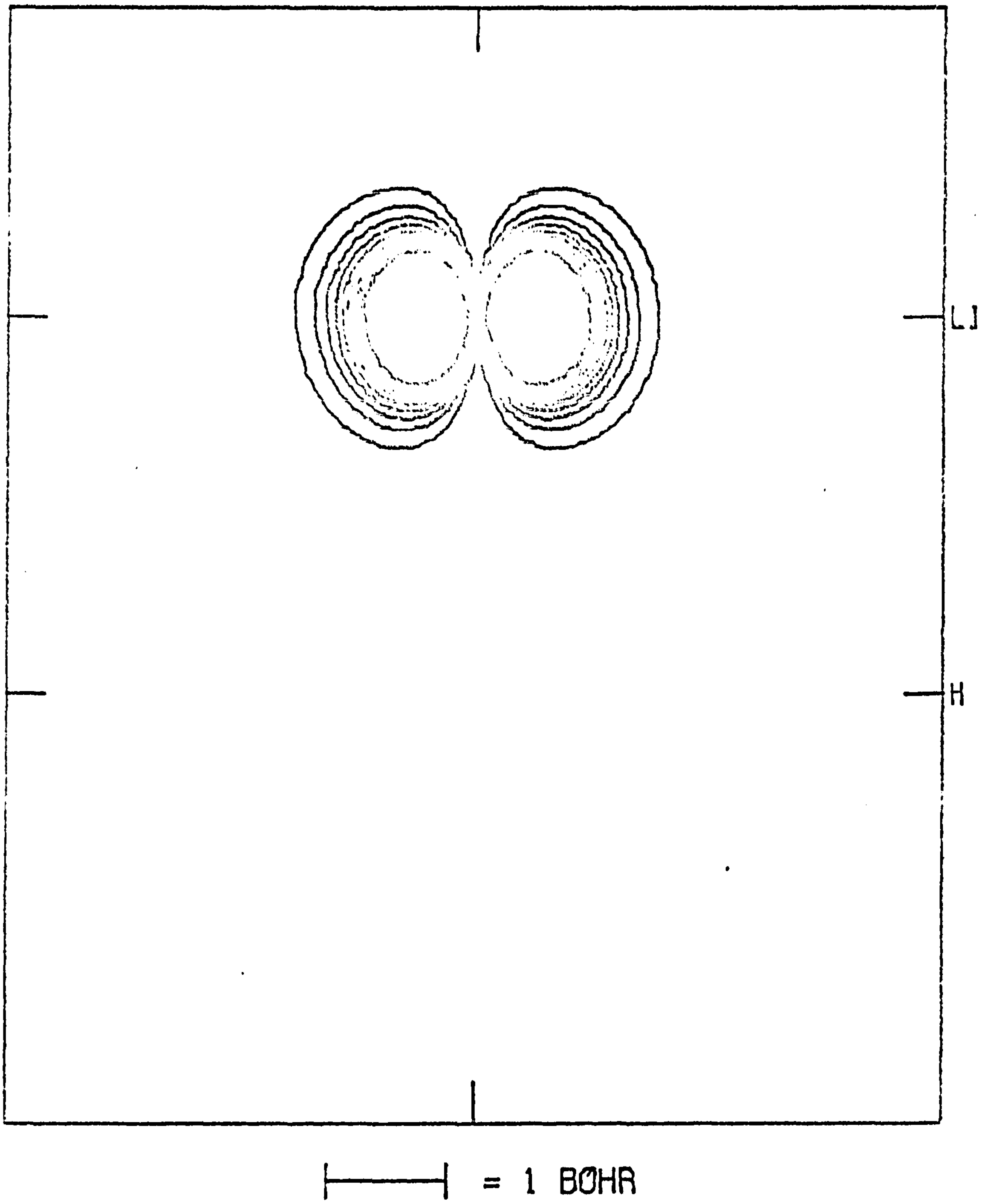
NATURAL ORBITAL CONTOUR MAP 4.
LIH K SHELL 4 SIGMA 3 (OC=-.02158)



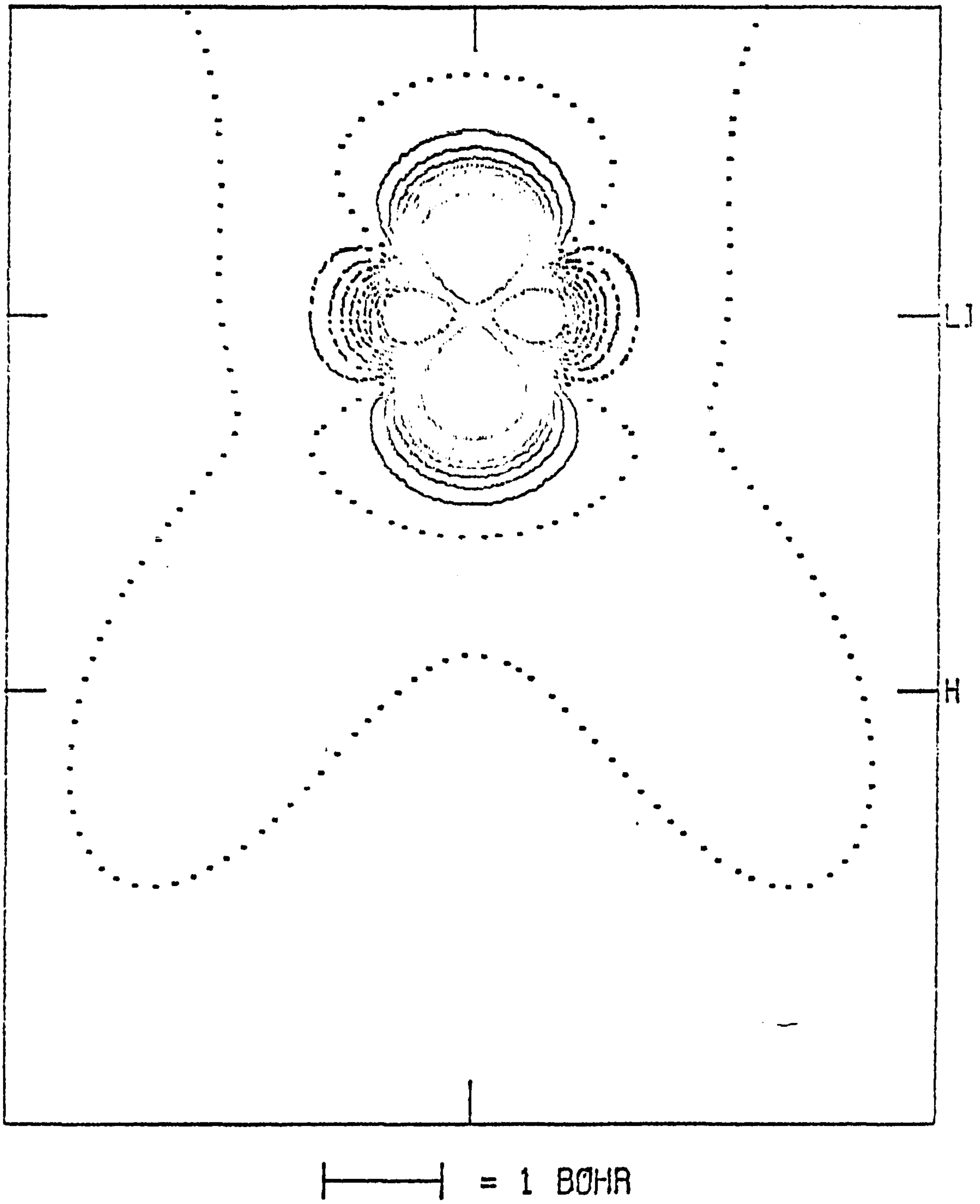
NATURAL ORBITAL CONTOUR MAP 5.
LIH K SHELL 5 PI 2 (OC=-.00388)



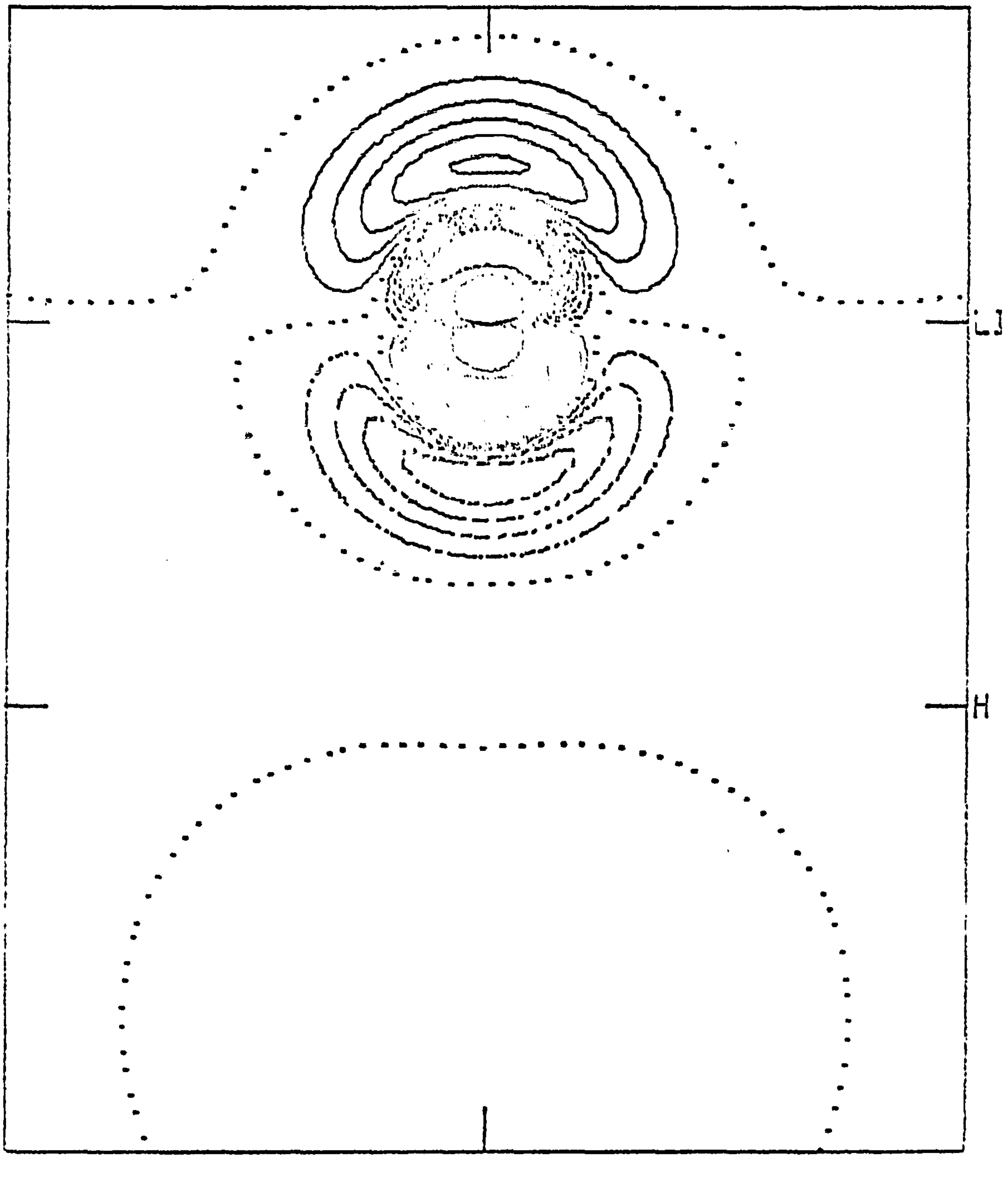
NATURAL ORBITAL CONTOUR MAP 6.
LIH K SHELL 6 PI 3 (OC=-.00385)



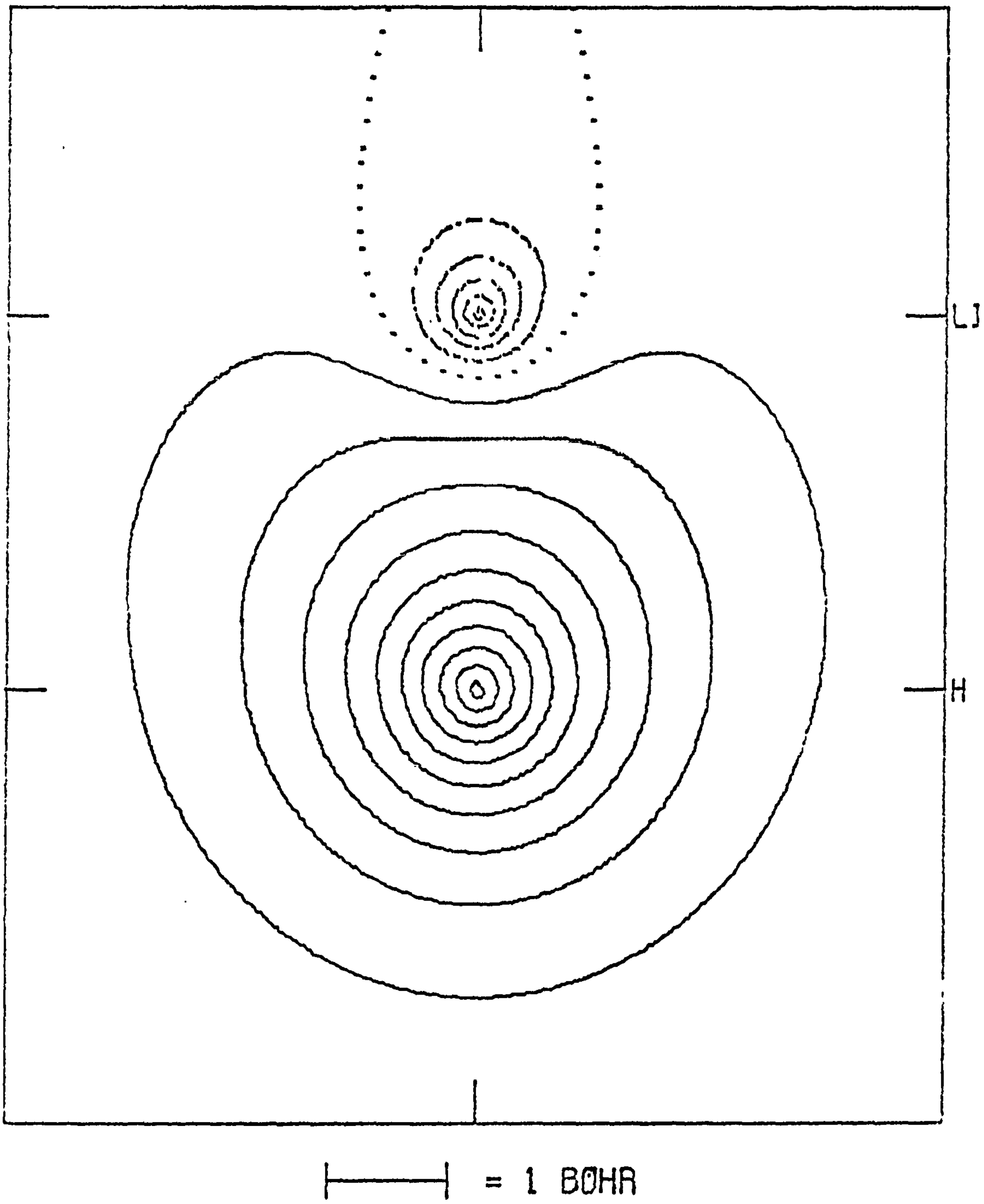
NATURAL ORBITAL CONTOUR MAP 7.
LIH K SHELL 7 DELTA 1 (OC=-.00384)



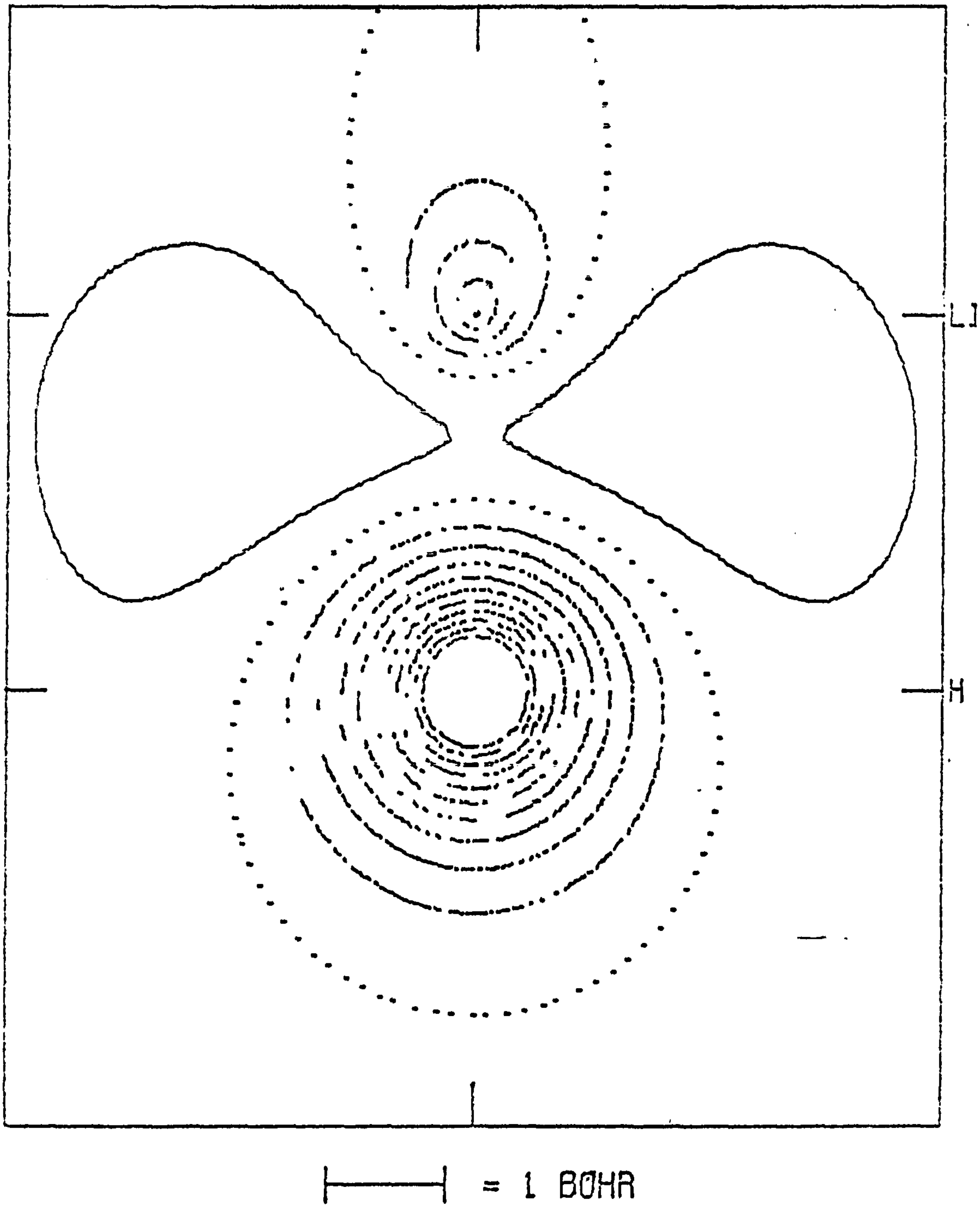
NATURAL ORBITAL CONTOUR MAP 8.
LIH K SHELL 8 SIGMA 4 (OC=-.00383)



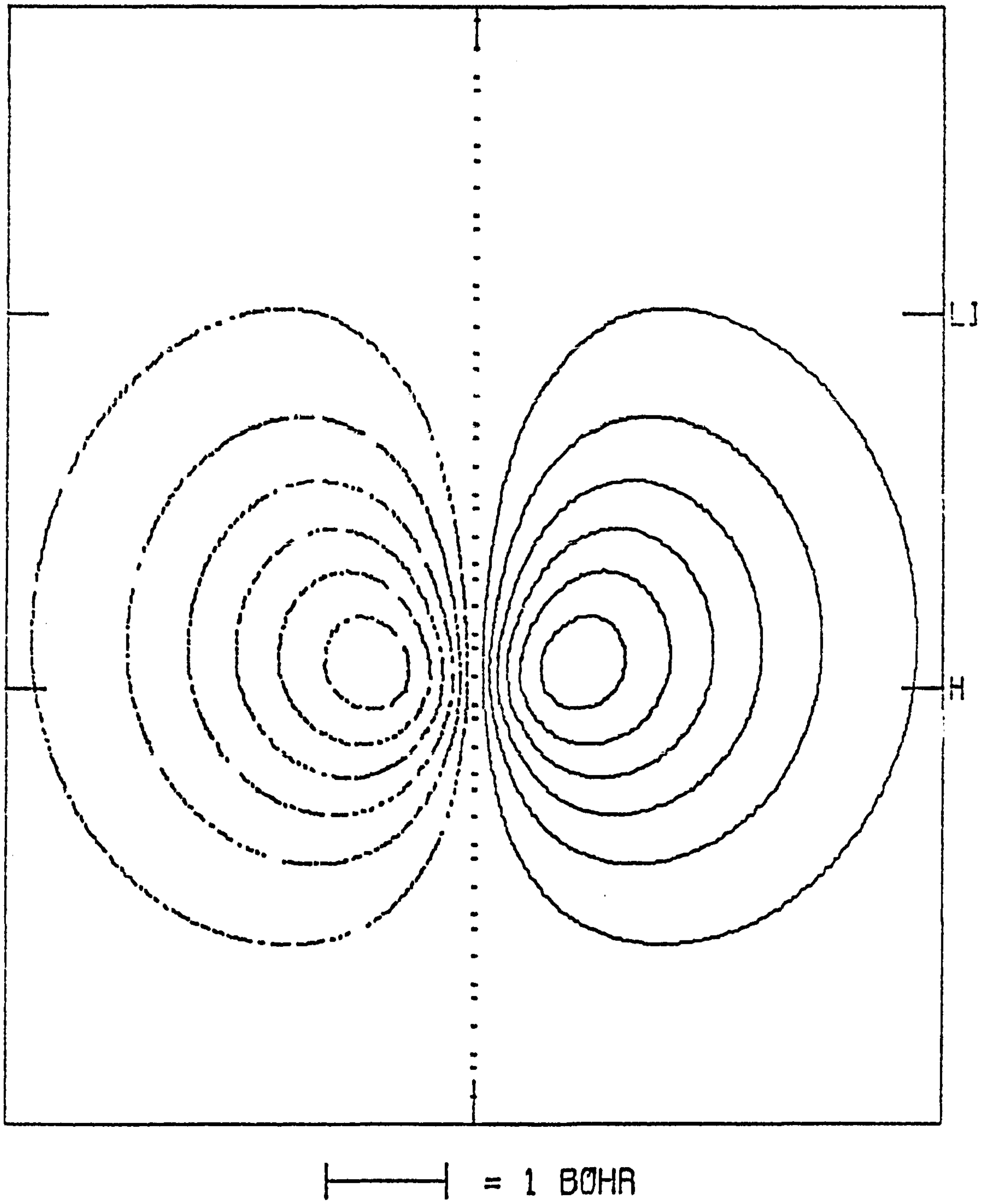
NATURAL ORBITAL CONTOUR MAP 9.
LIH K SHELL 9 SIGMA 5 (OC=-.00142)



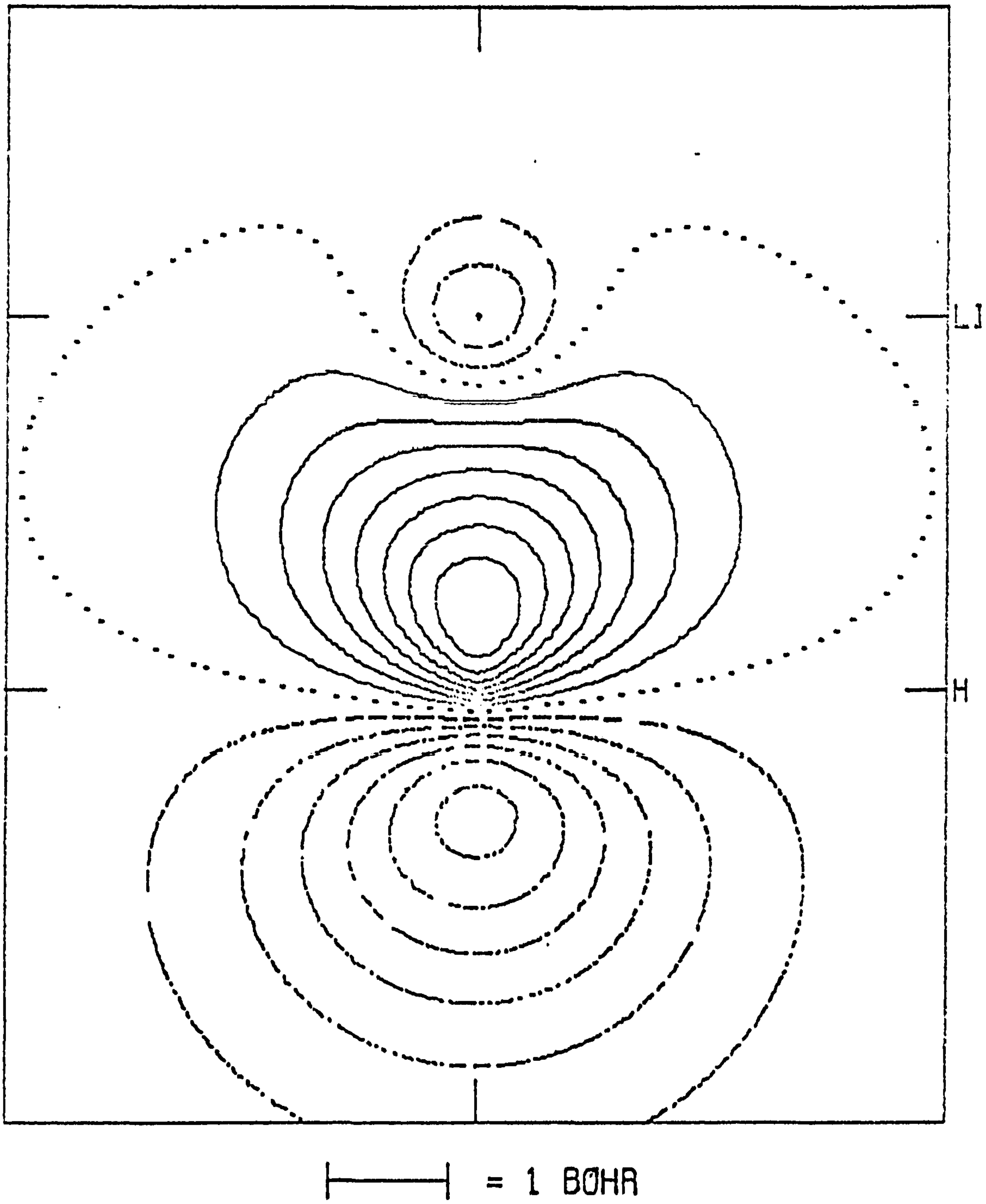
NATURAL ORBITAL CONTOUR MAP 10.
LIH BONDING 1 SIGMA 1 (OC= .96548)



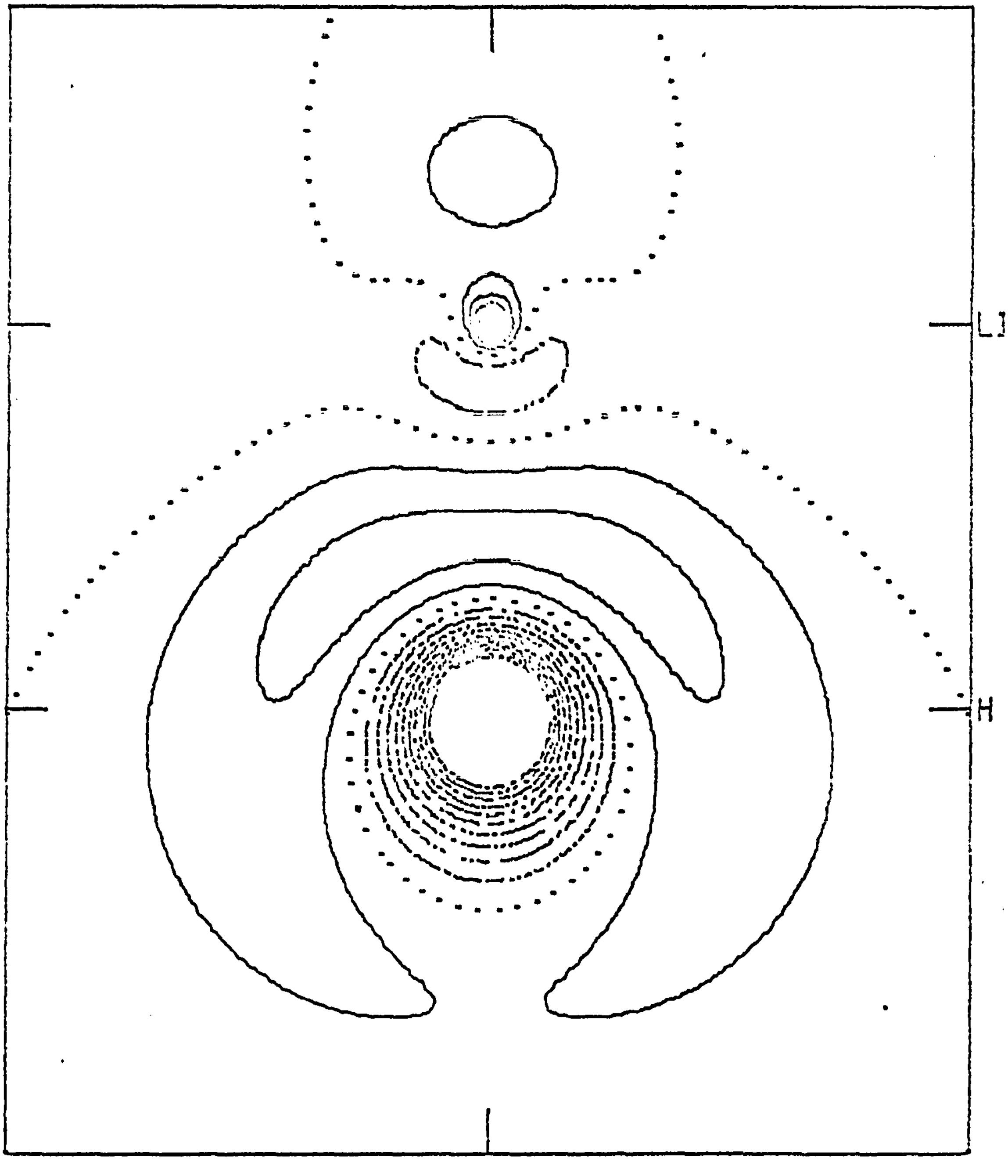
NATURAL ORBITAL CONTOUR MAP 11.
LIH BONDING 2 SIGMA 2 (OC=-.12321)



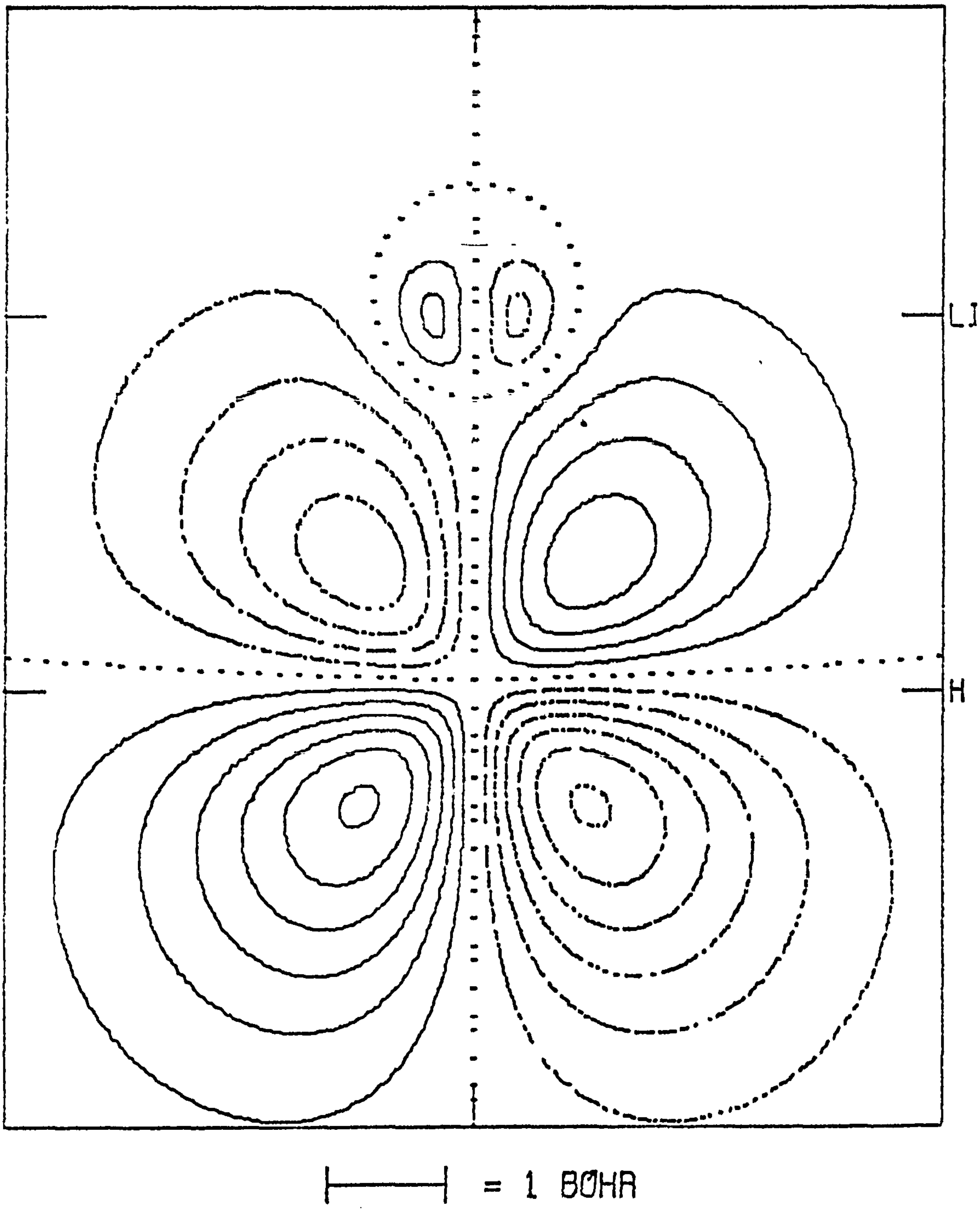
NATURAL ORBITAL CONTOUR MAP 12.
LIH BONDING 3 PI 1 (OC=-.07080)



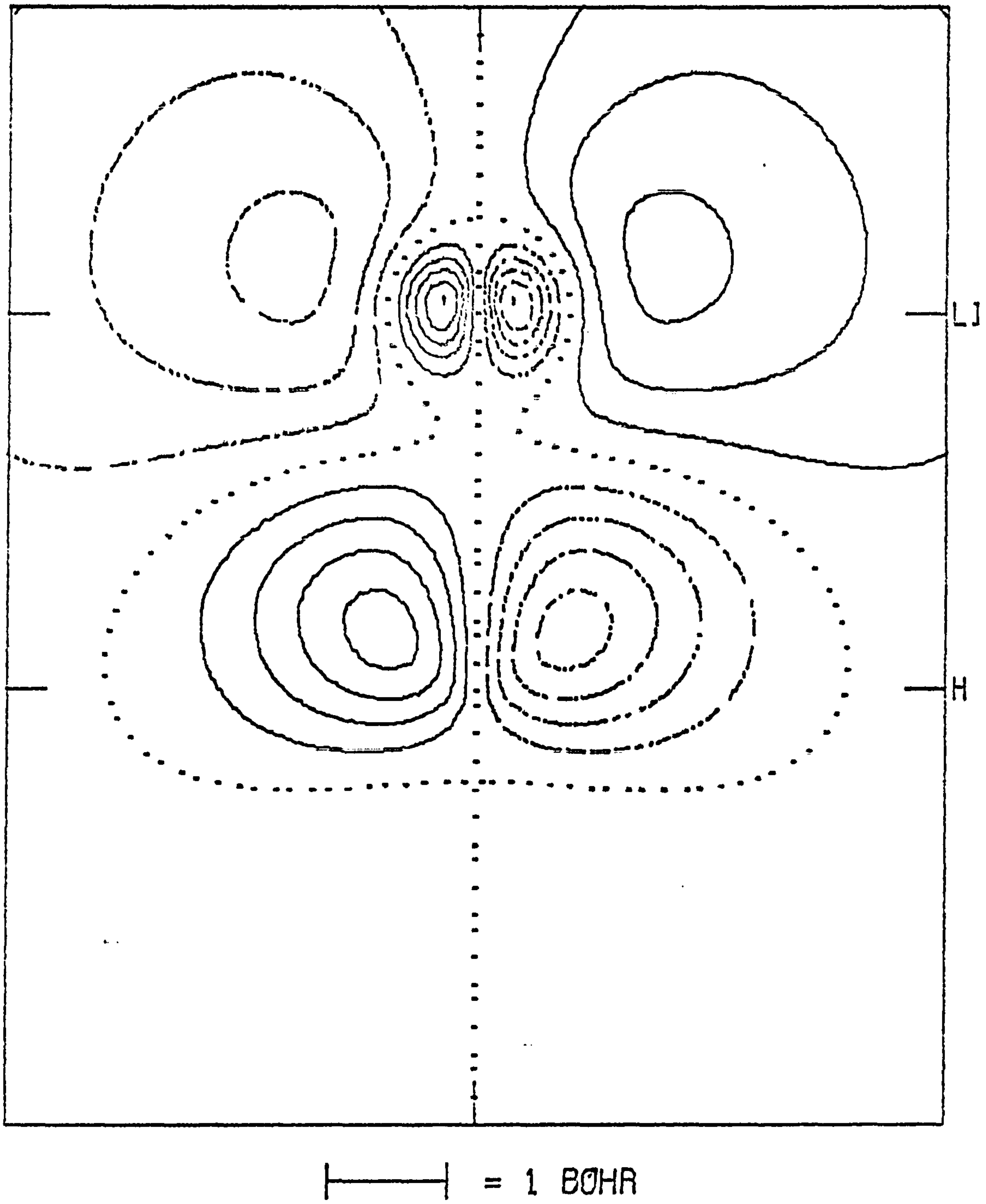
NATURAL ORBITAL CONTOUR MAP 13.
LIH BONDING 4 SIGMA 3 (OC=-.05696)



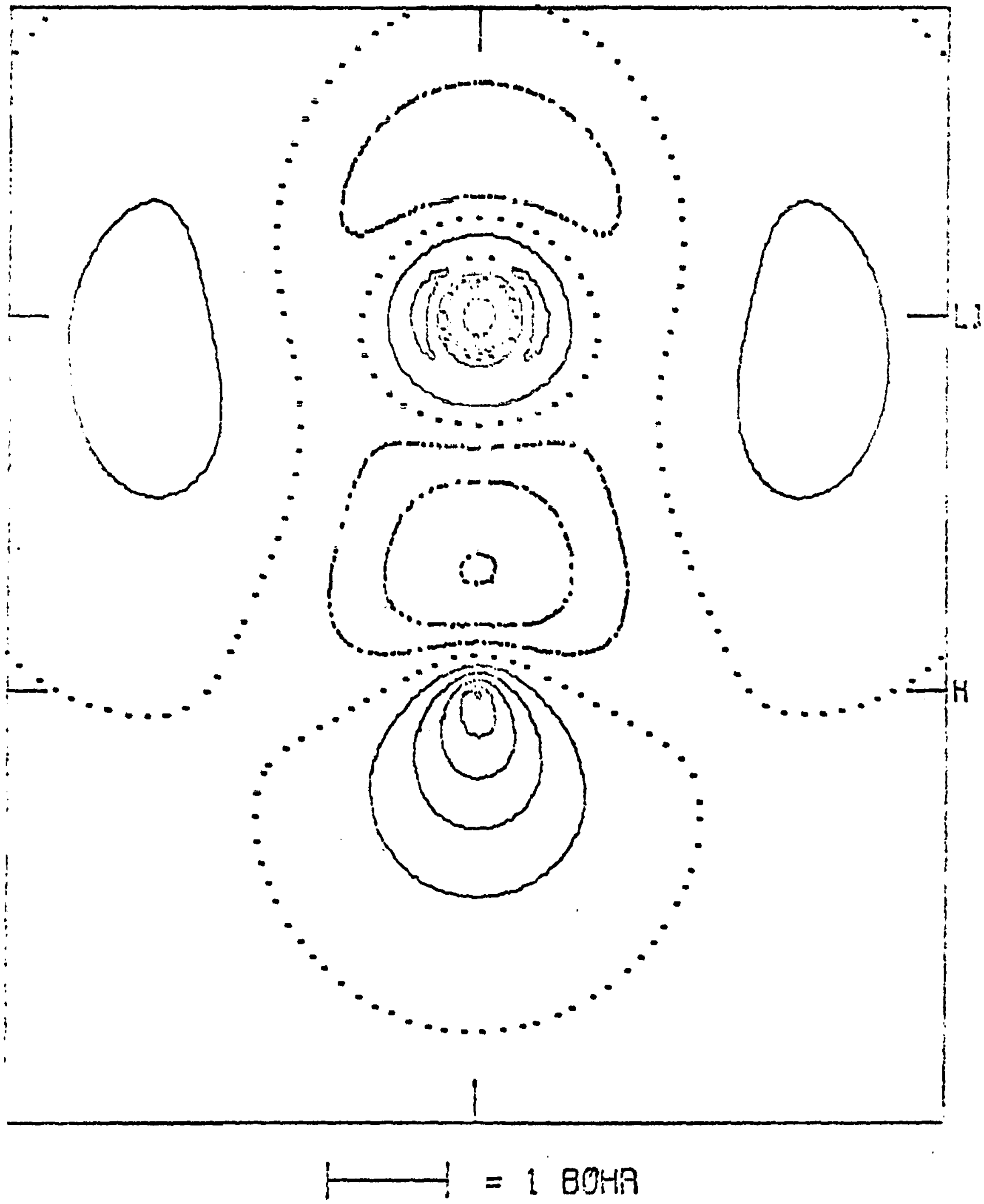
NATURAL ORBITAL CONTOUR MAP 14.
LIH BONDING 5 SIGMA 4 (OC=-.01232)



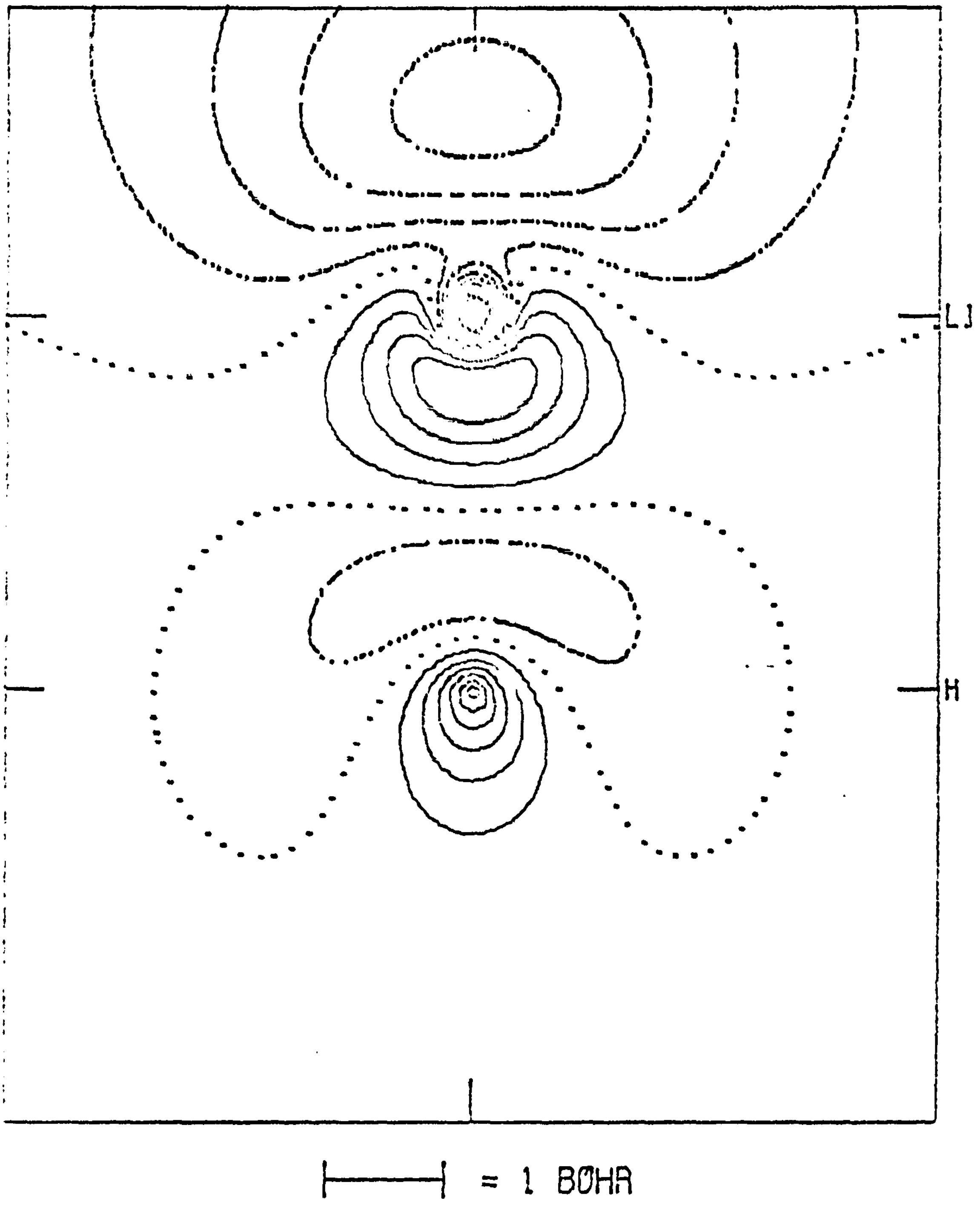
NATURAL ØRBITAL CØNTØUR MAP 15.
LIH BØNDING 6 PI 2 (ØC=-.00945)



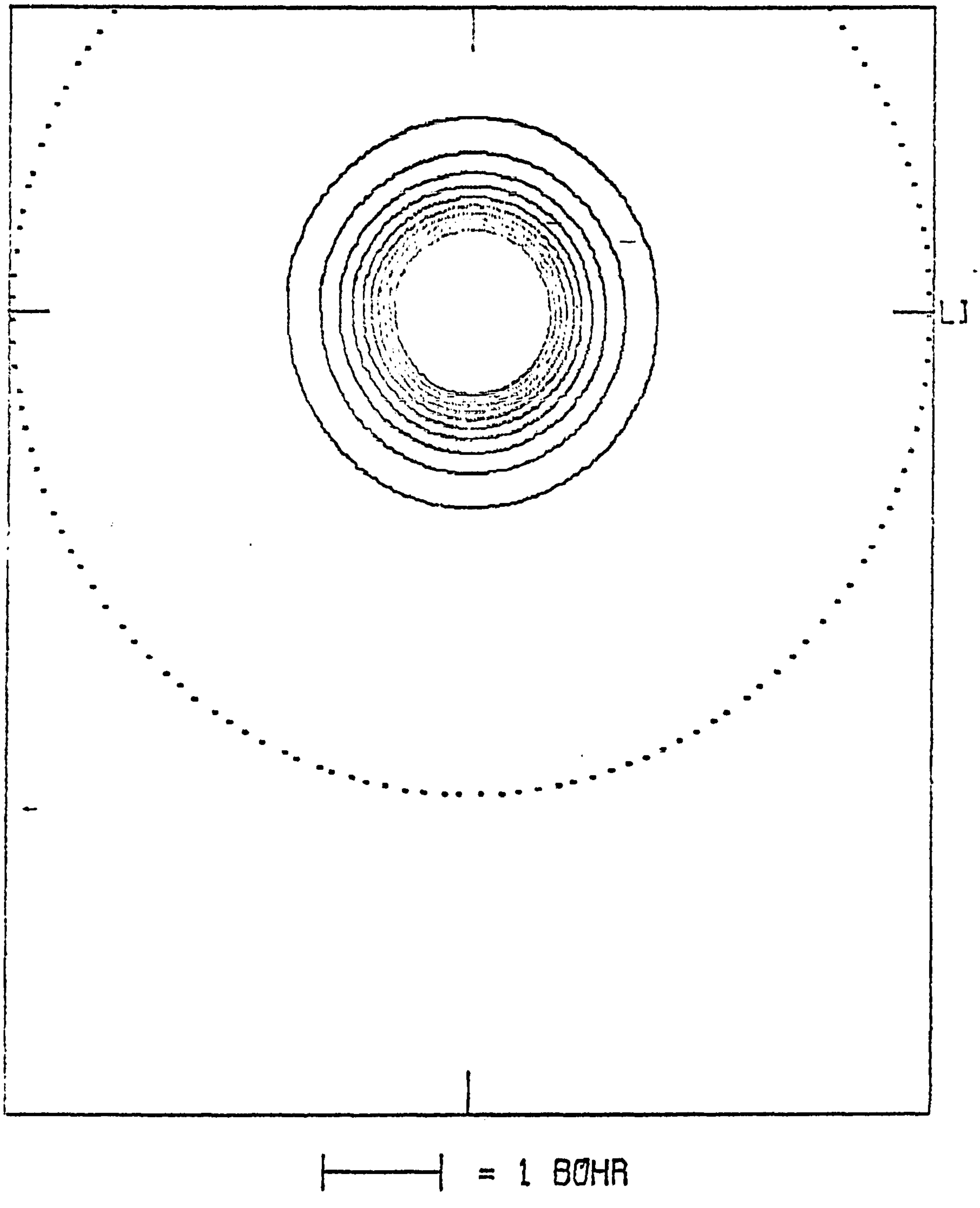
NATURAL ØRBITAL CØNTØUR MAP 16.
LIH BØNDING 7 PI 3 (ØC=-.00493)



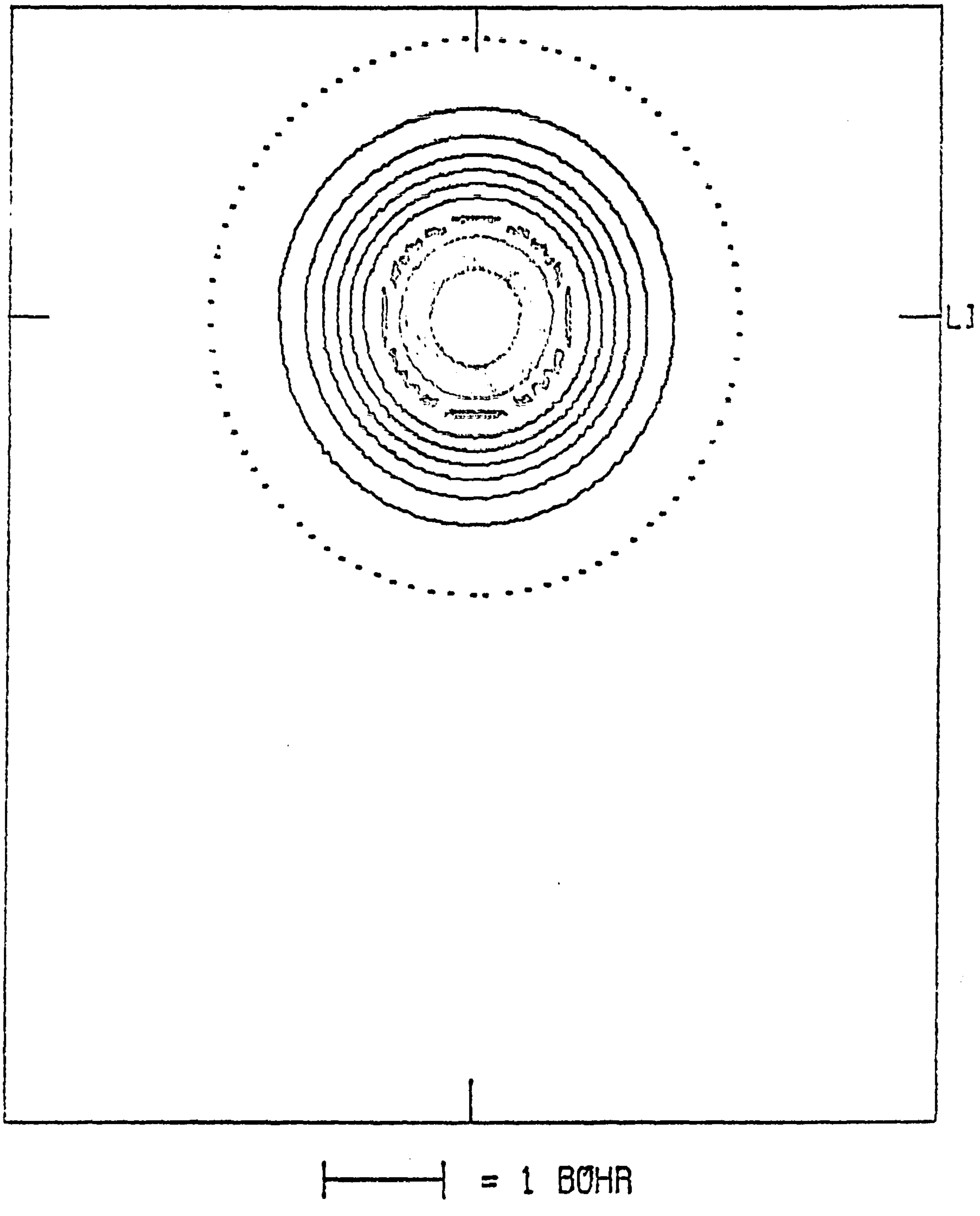
NATURAL ORBITAL CONTOUR MAP 17.
LIH BONDING 8 SIGMA 5 (OC=-.00198)



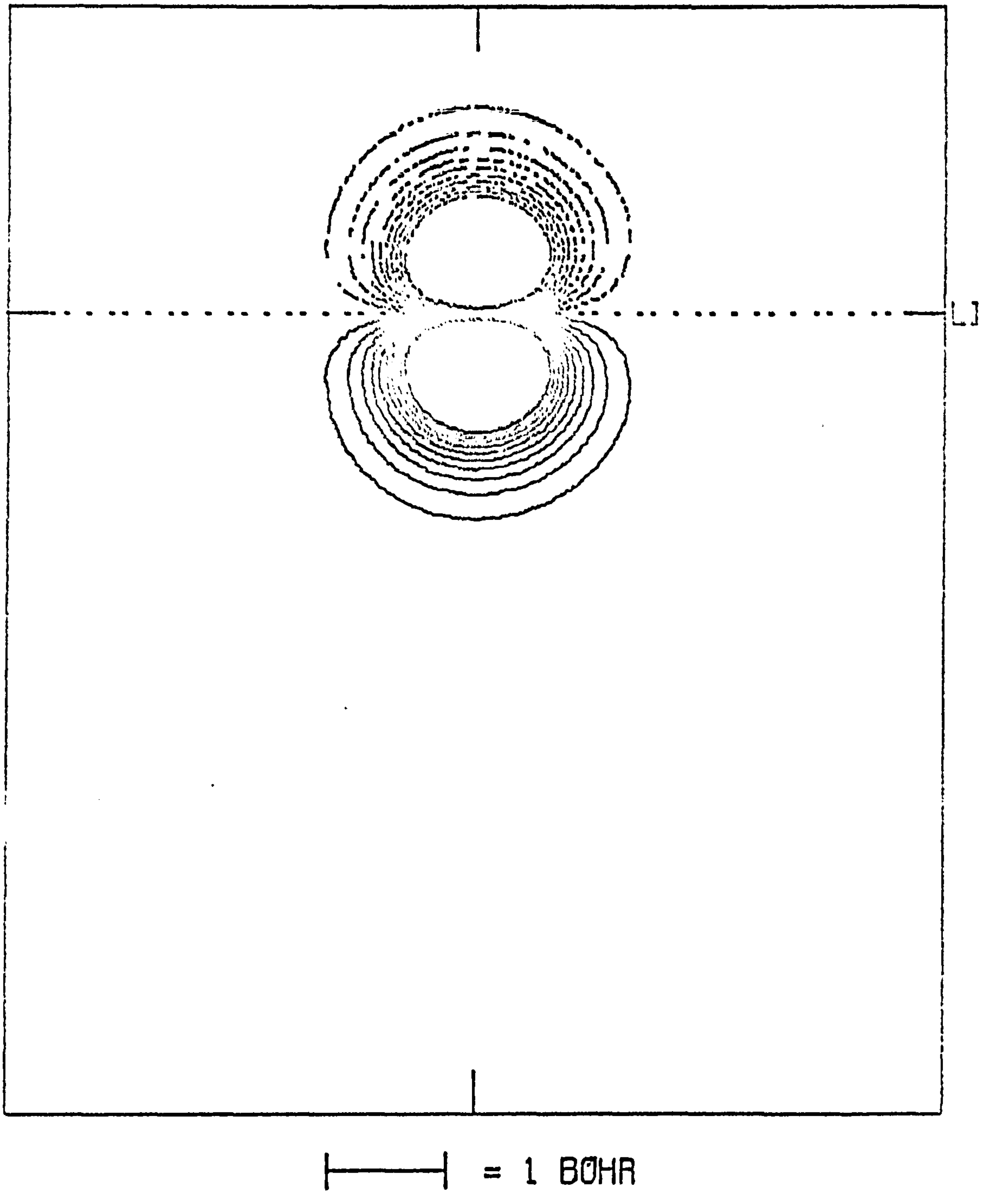
NATURAL ORBITAL CONTOUR MAP 18.
LIH BONDING 9 SIGMA 6 (OC=-.00094)



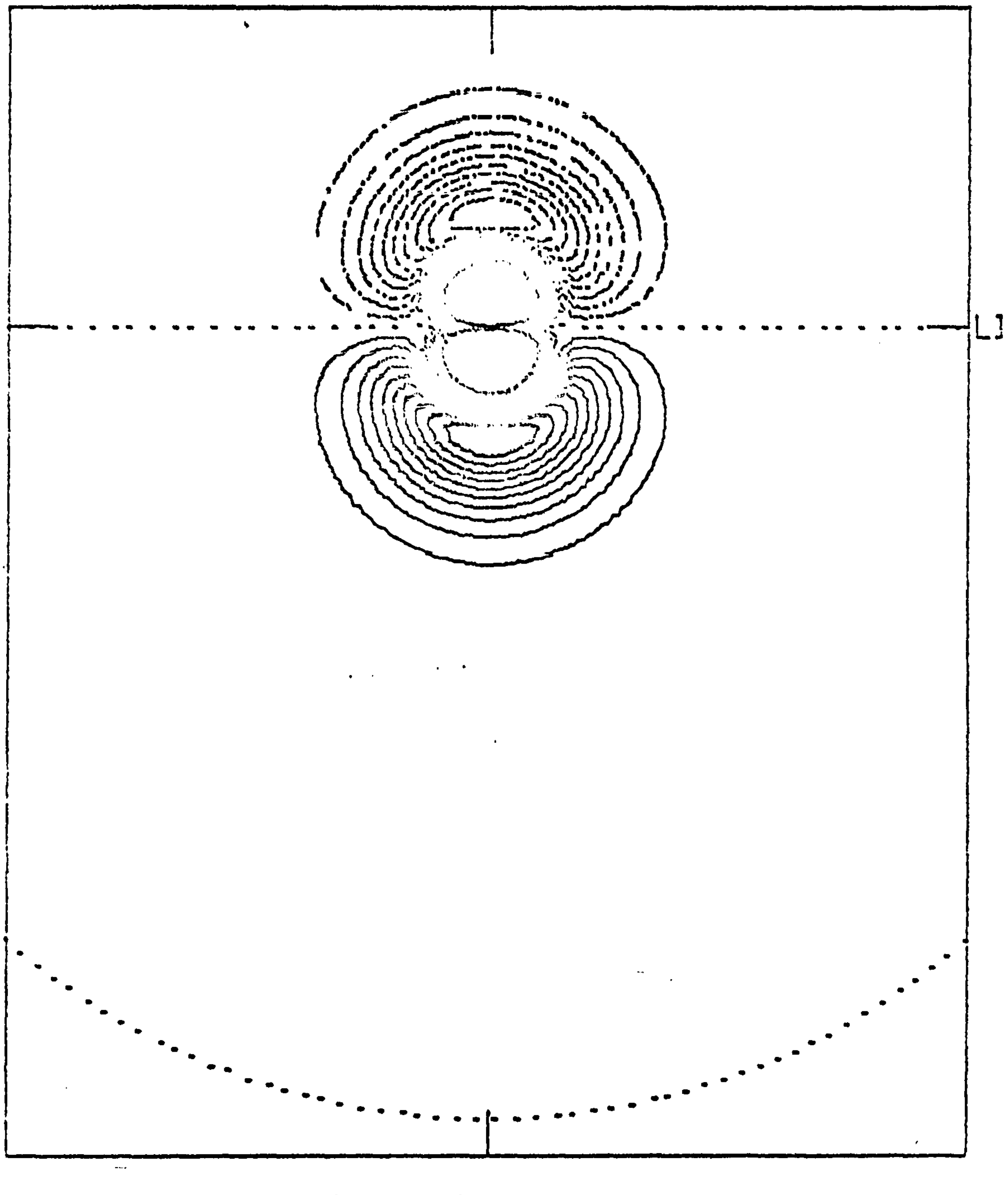
NATURAL ORBITAL CONTOUR MAP 19.
LI K SHELL 1 S 1 (OC= .99871)



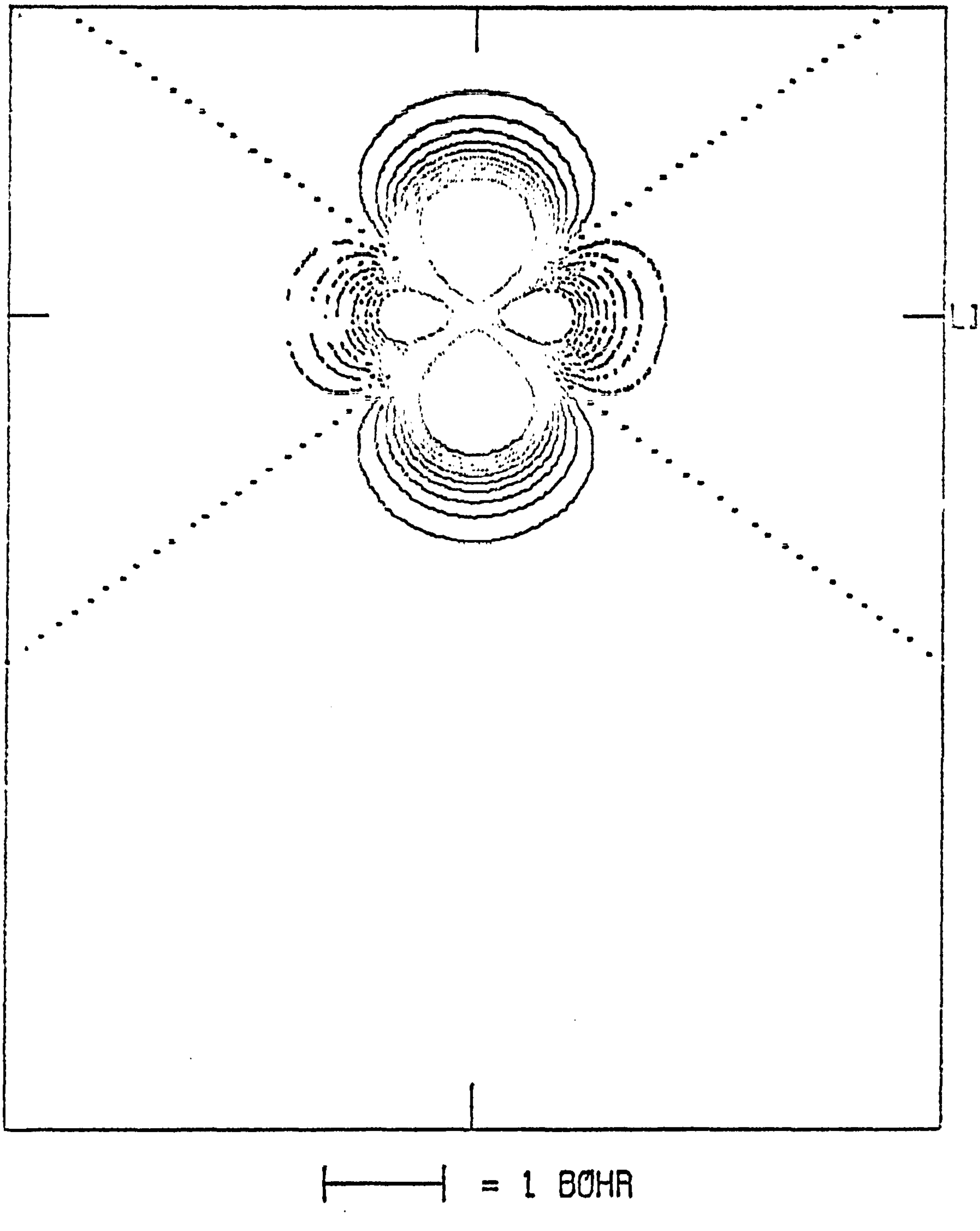
NATURAL ORBITAL CONTOUR MAP 20.
LI K SHELL 2 S 2 (OC=-.02650)



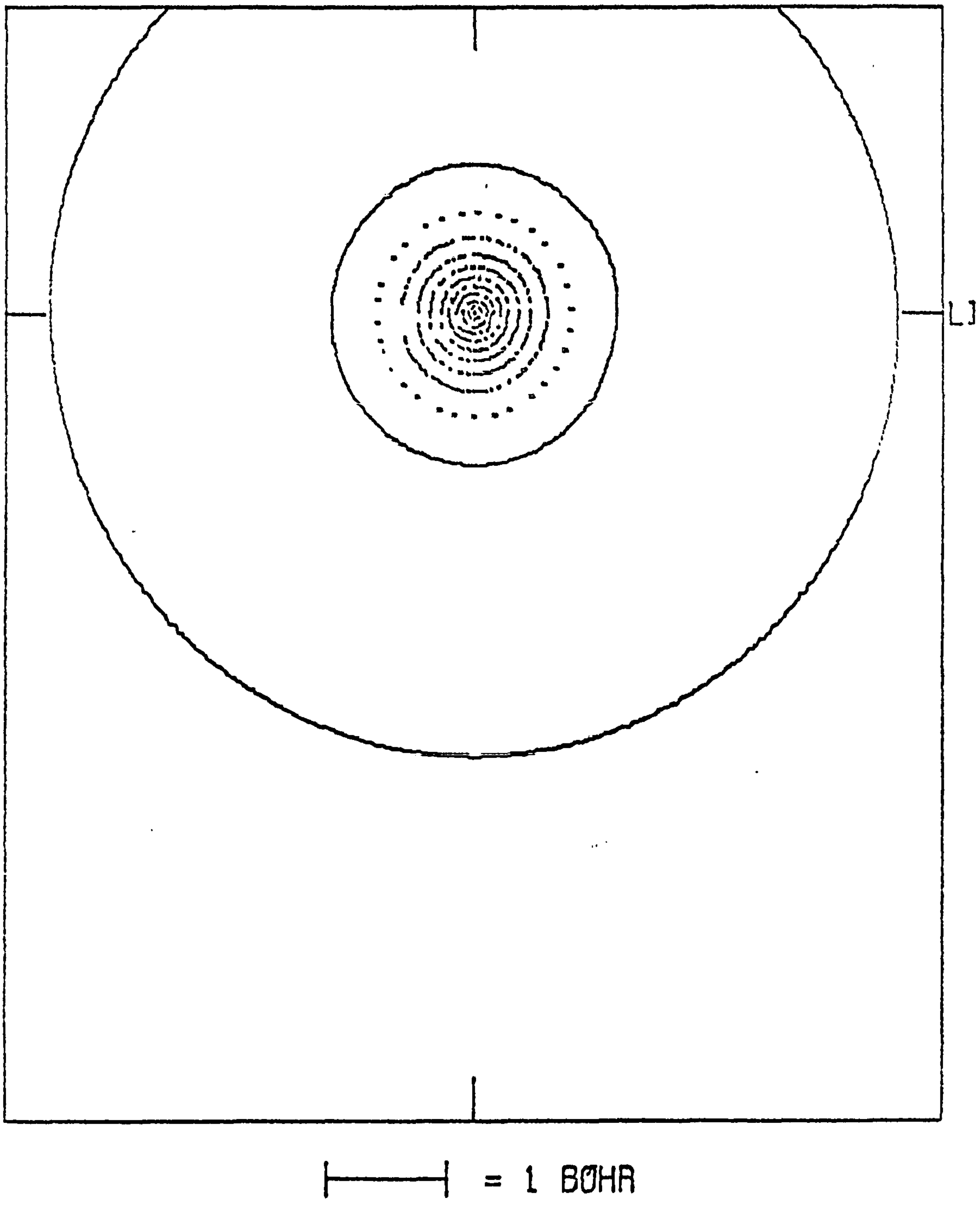
NATURAL ORBITAL CONTOUR MAP 21.
LI K SHELL 3 P 1 (OC=-.02420)



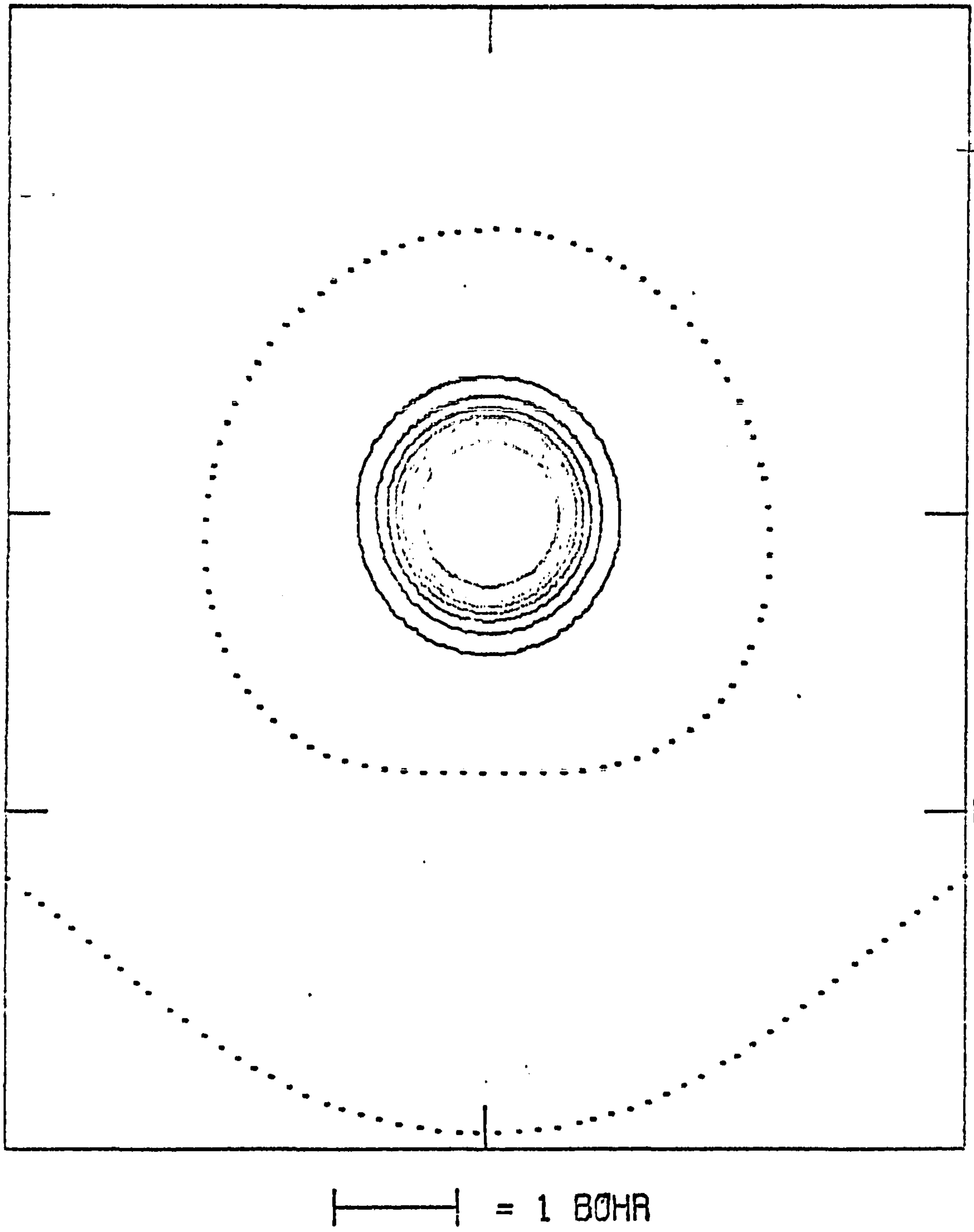
NATURAL ORBITAL CONTOUR MAP 22.
LI K SHELL 4 P 2 (OC=-.00405)



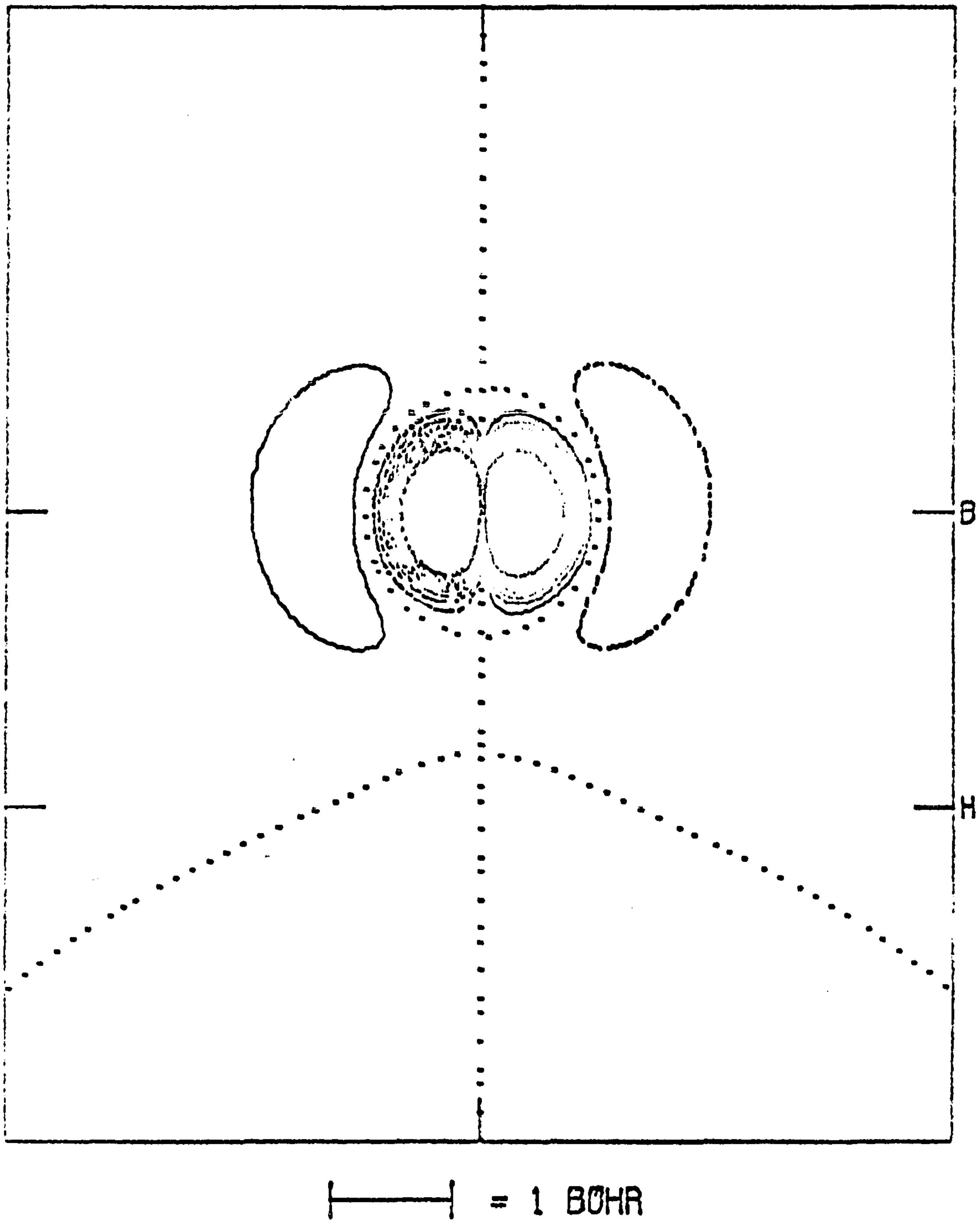
NATURAL ORBITAL CONTOUR MAP 23.
LI K SHELL 5 D 1 (OC=-.00381)



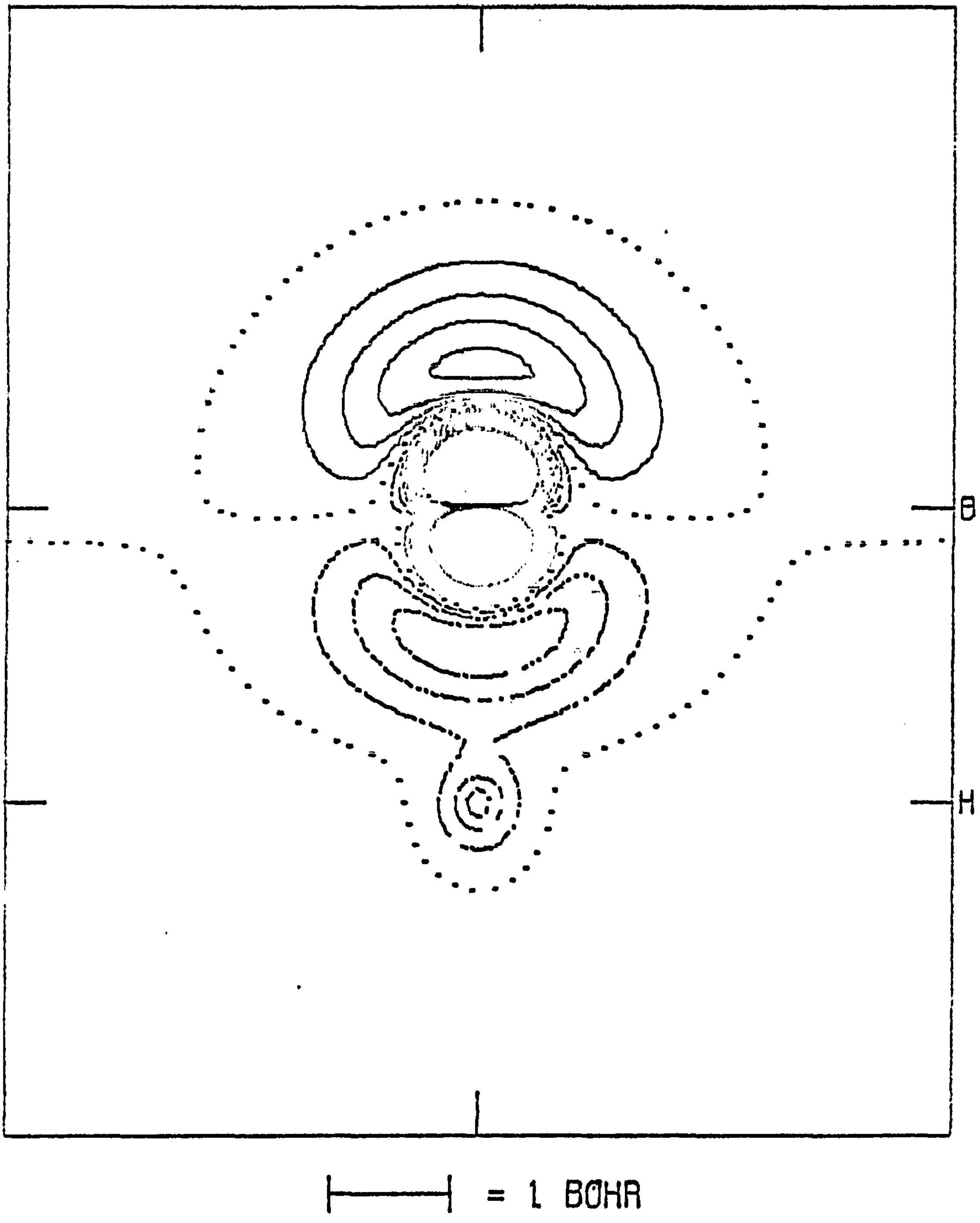
NATURAL ORBITAL CONTOUR MAP 24.
LI L SHELL 1 S 1 (OC= 1.00000)



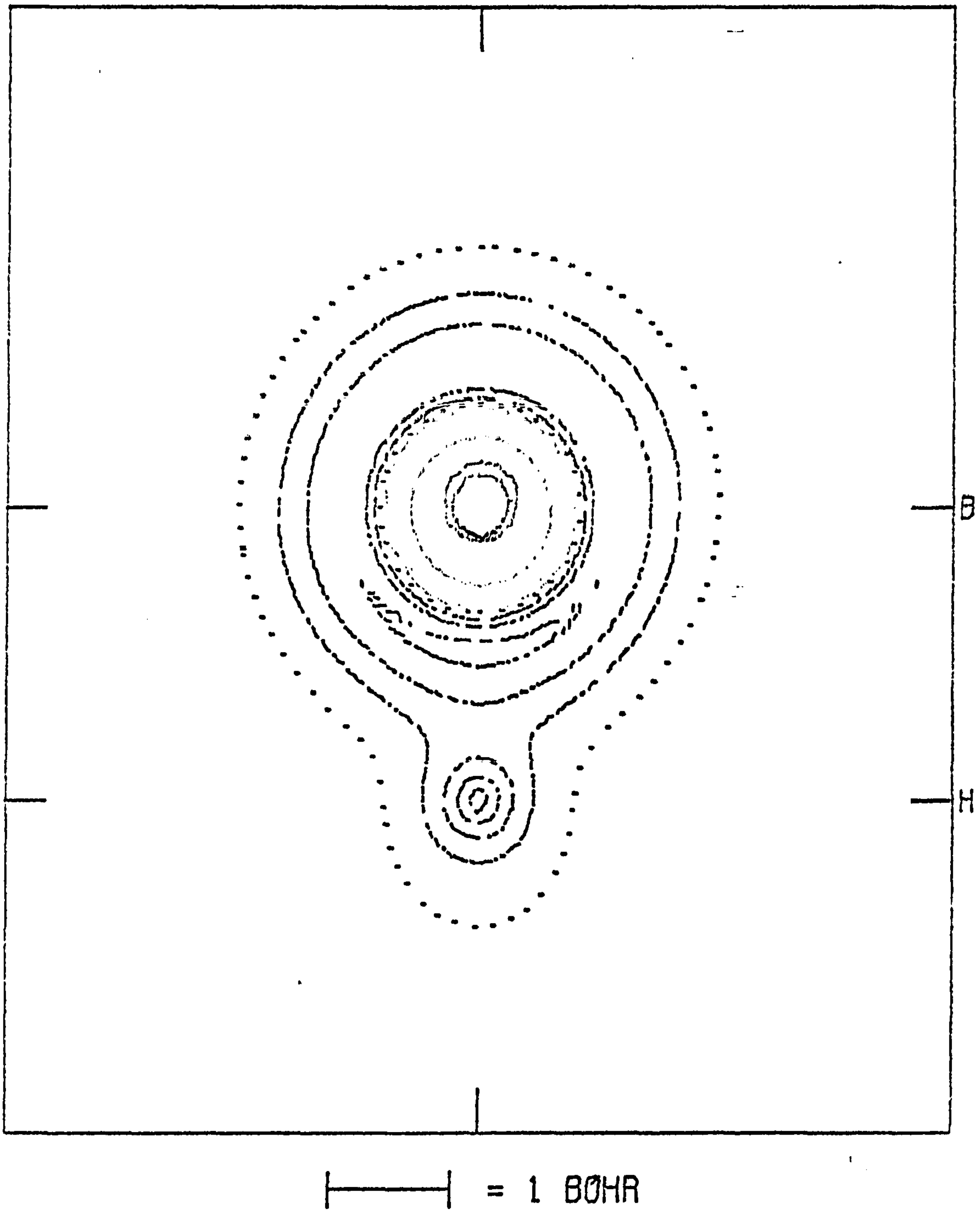
NATURAL ORBITAL CONTOUR MAP 25.
BH K SHELL 1 SIGMA 1 (OC= .99969)



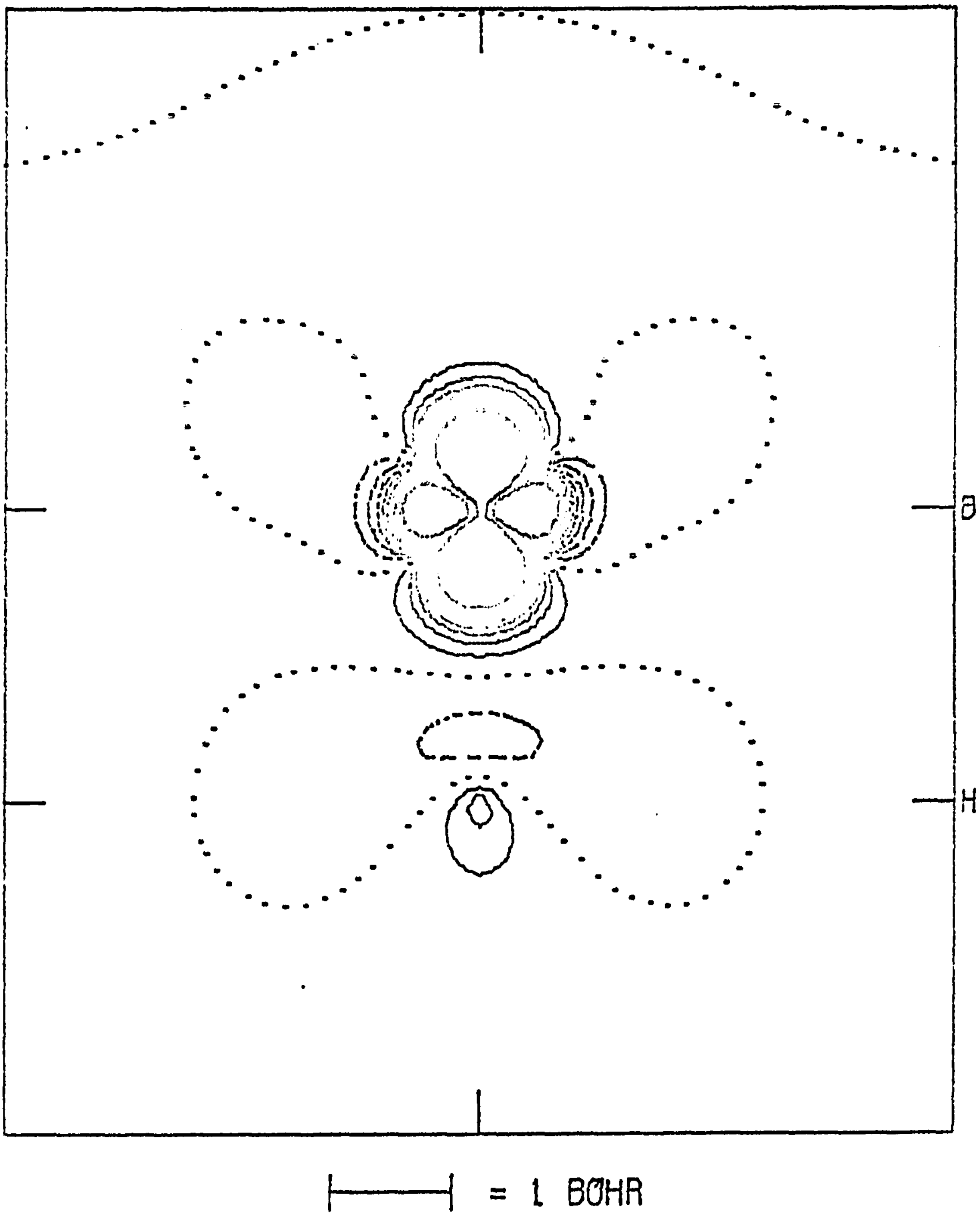
NATURAL ORBITAL CONTOUR MAP 26.
BH KSHELL 2 PI 1 (OC=-.01364)



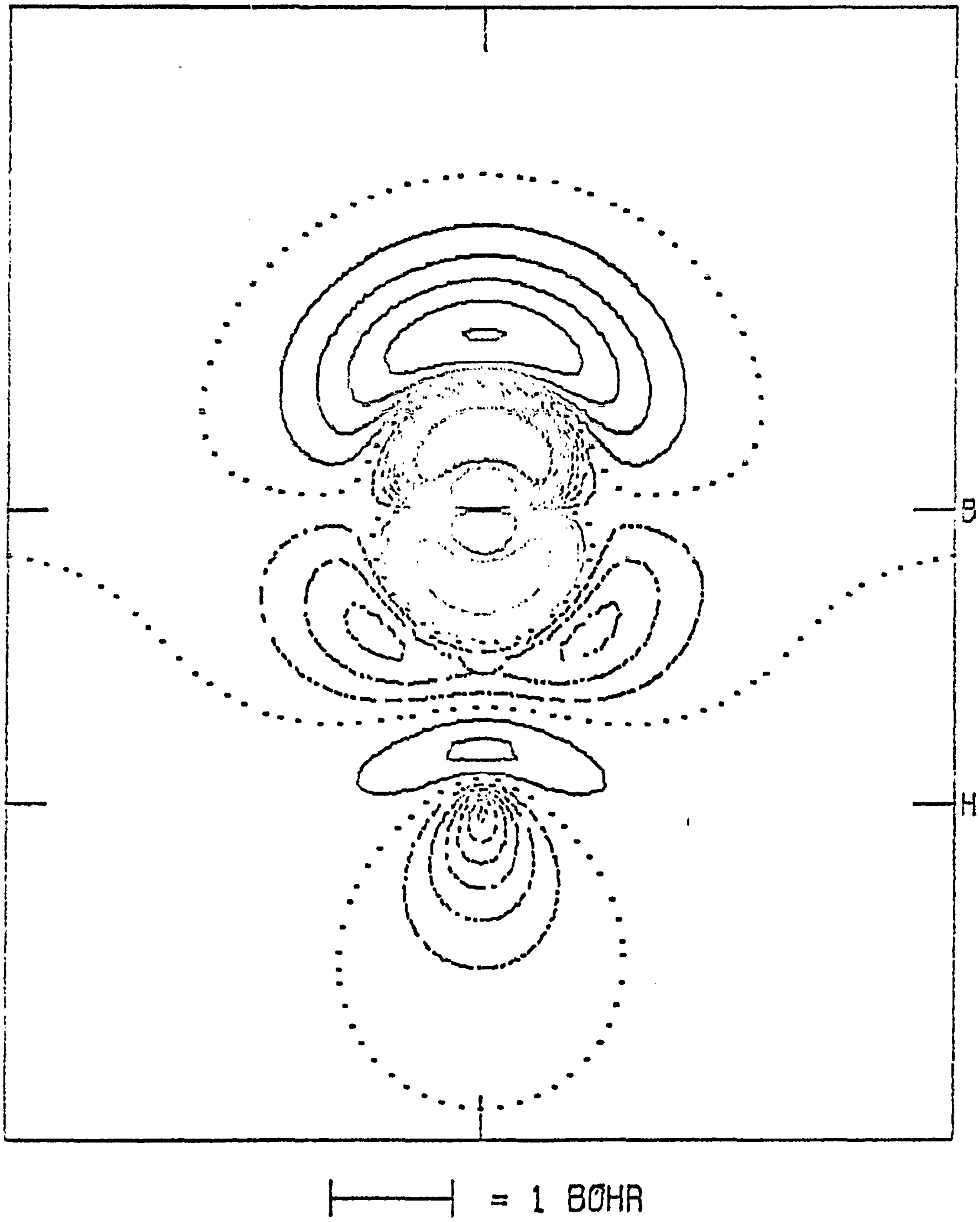
NATURAL ORBITAL CONTOUR MAP 27.
BH K SHELL 3 SIGMA 2 (OC=-.01181)



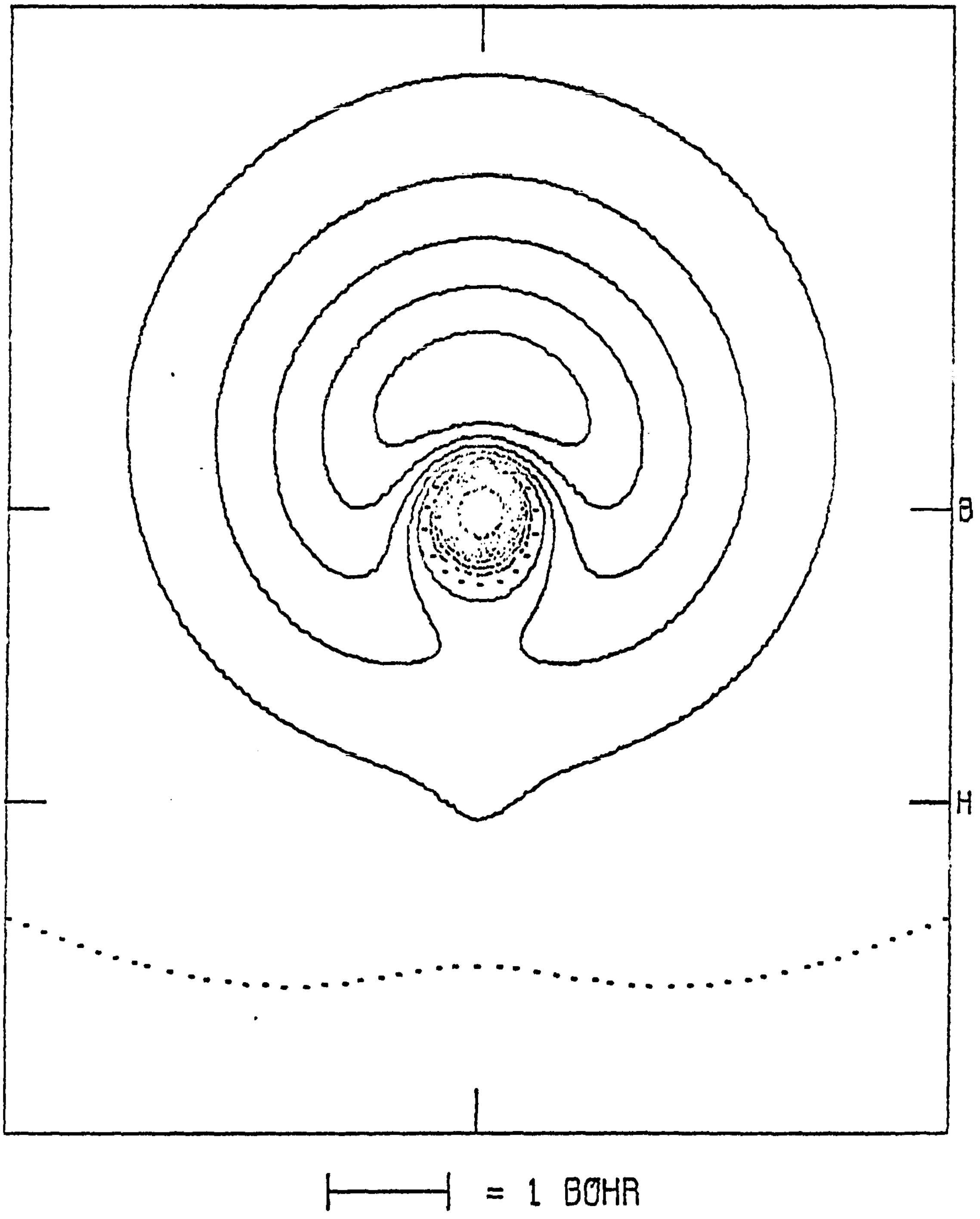
NATURAL ORBITAL CONTOUR MAP 28.
BH K SHELL 4 SIGMA 3 (0C=-.00970)



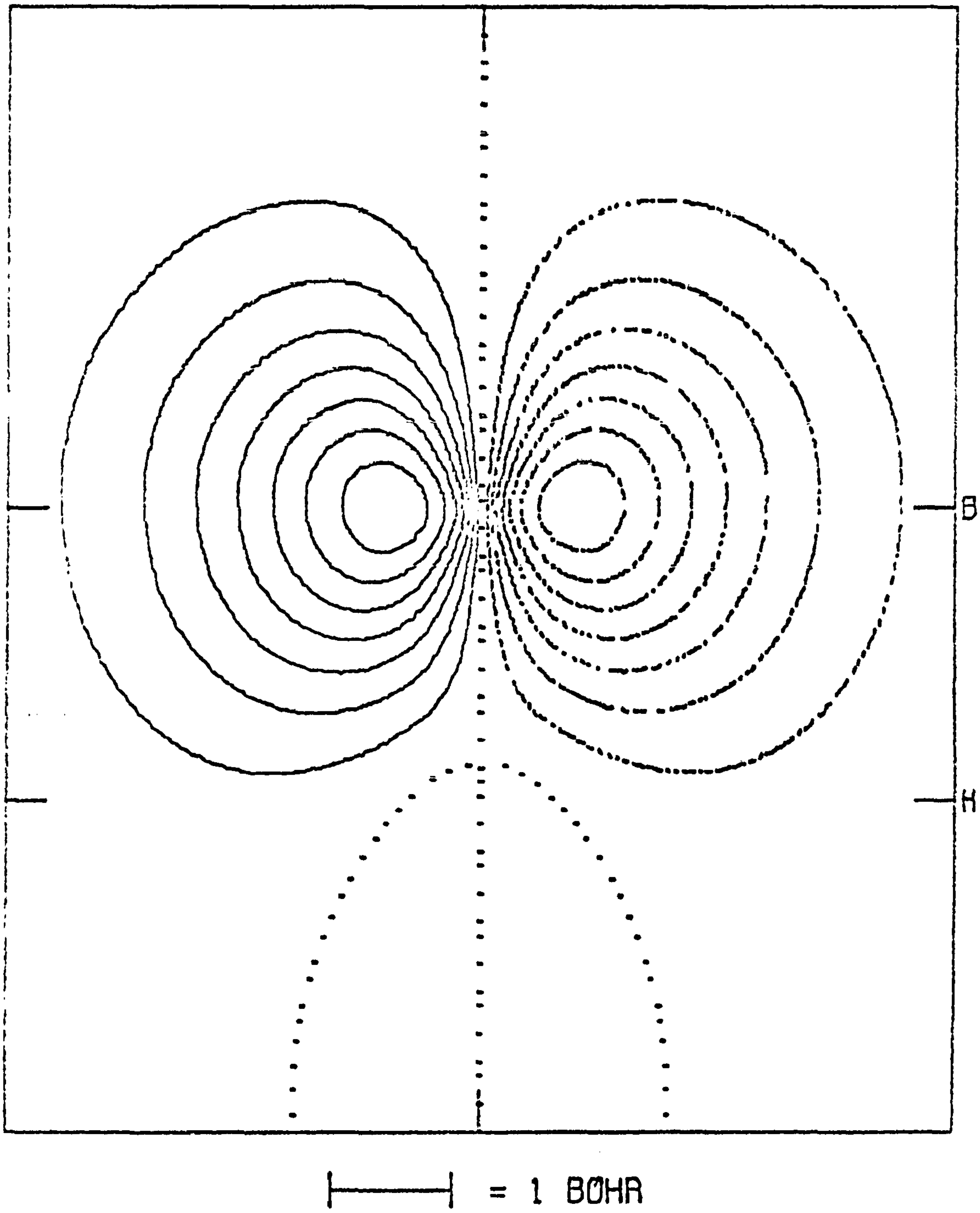
NATURAL ORBITAL CONTOUR MAP 29.
BH K SHELL 5 SIGMA 4 (OC=-.00271)



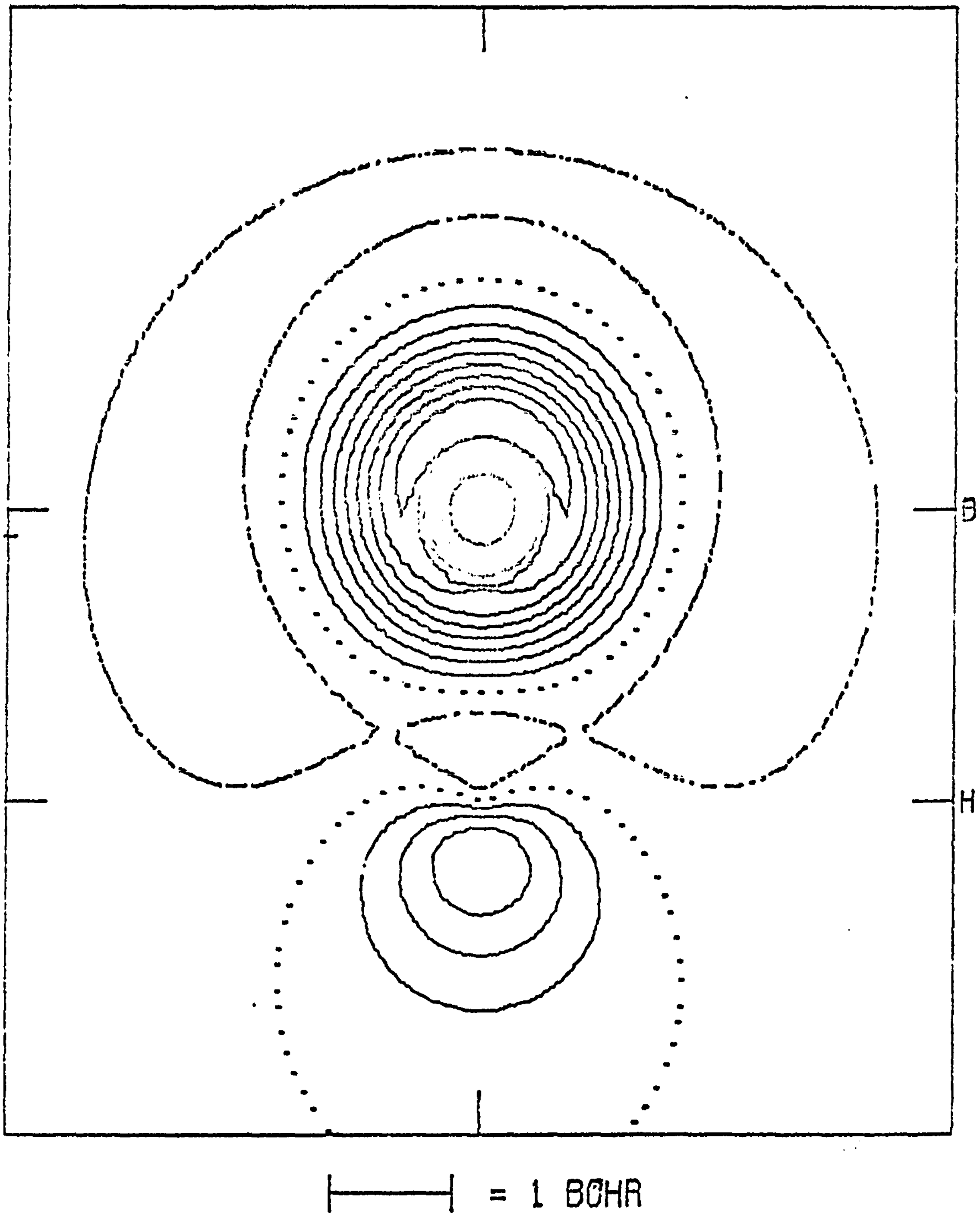
NATURAL ORBITAL CONTOUR MAP 30.
BH K SHELL 6 SIGMA 5 (OC=-.00264)



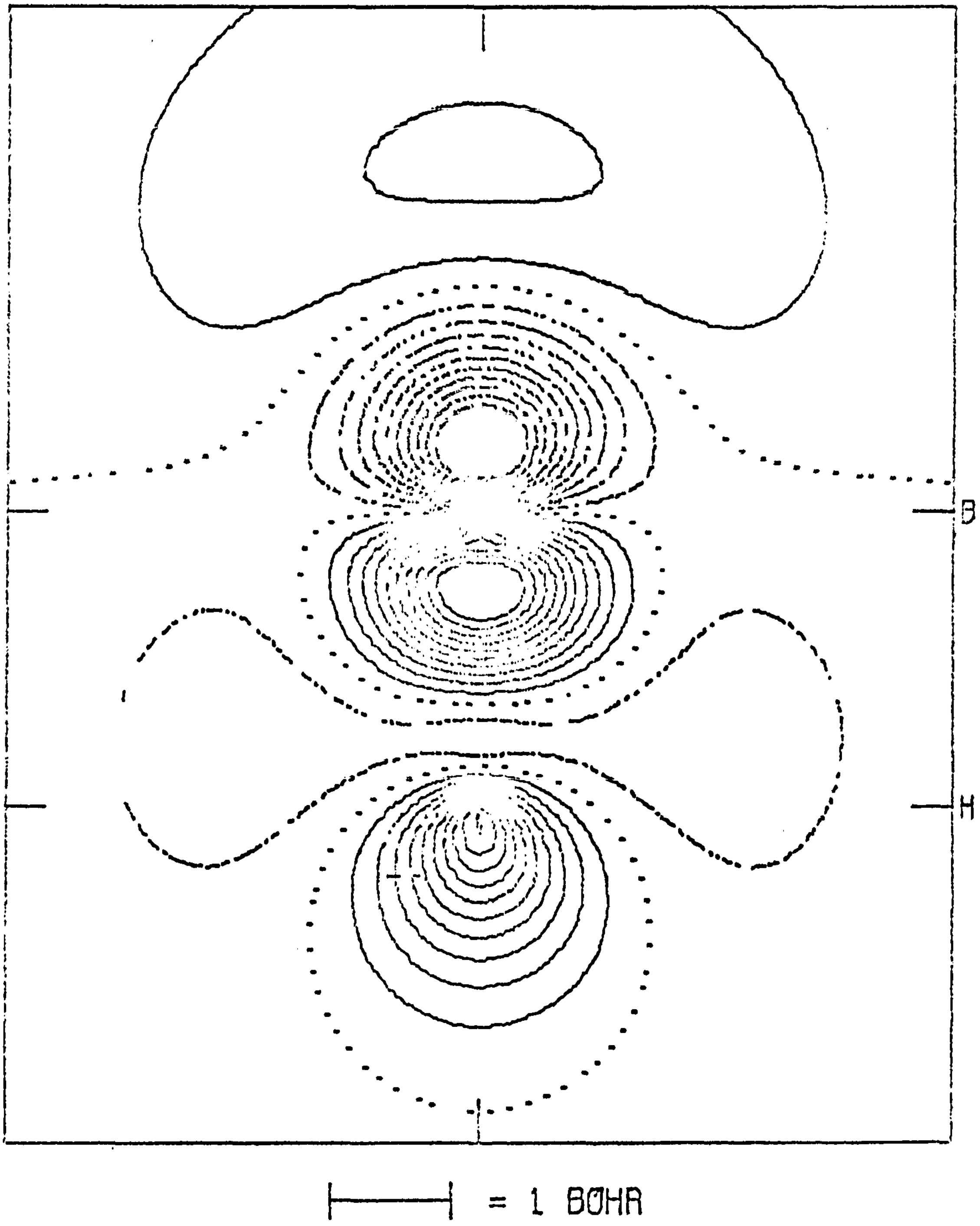
NATURAL ORBITAL CONTOUR MAP 31.
BH LONE PAIR 1 SIGMA 1 (OC= .97387)



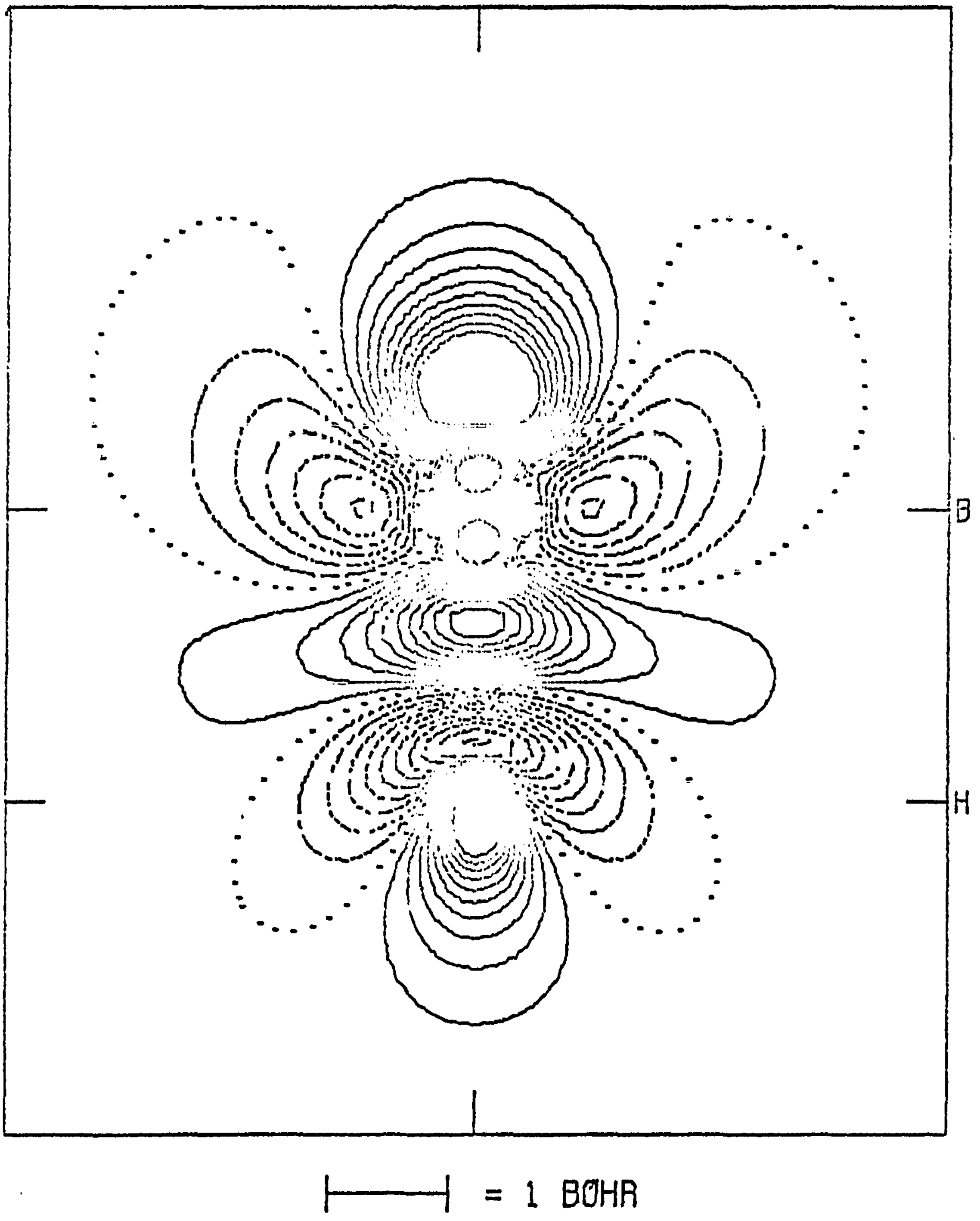
NATURAL ORBITAL CONTOUR MAP 32.
BH LONE PAIR 2 PI 1 (OC=-.16004)



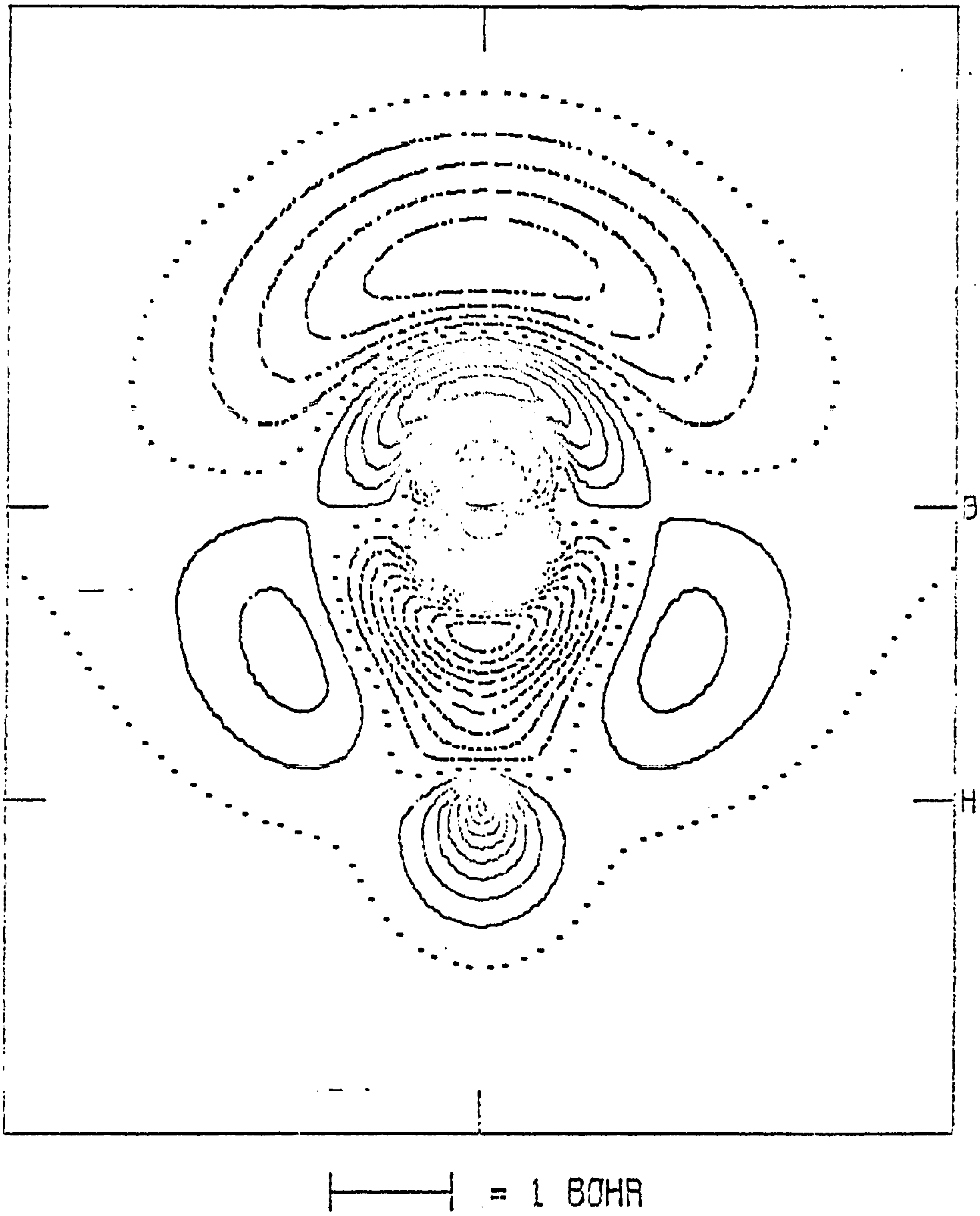
NATURAL ORBITAL CONTOUR MAP 33.
BH LONE PAIR 3 SIGMA 2 (OC=-.01600)



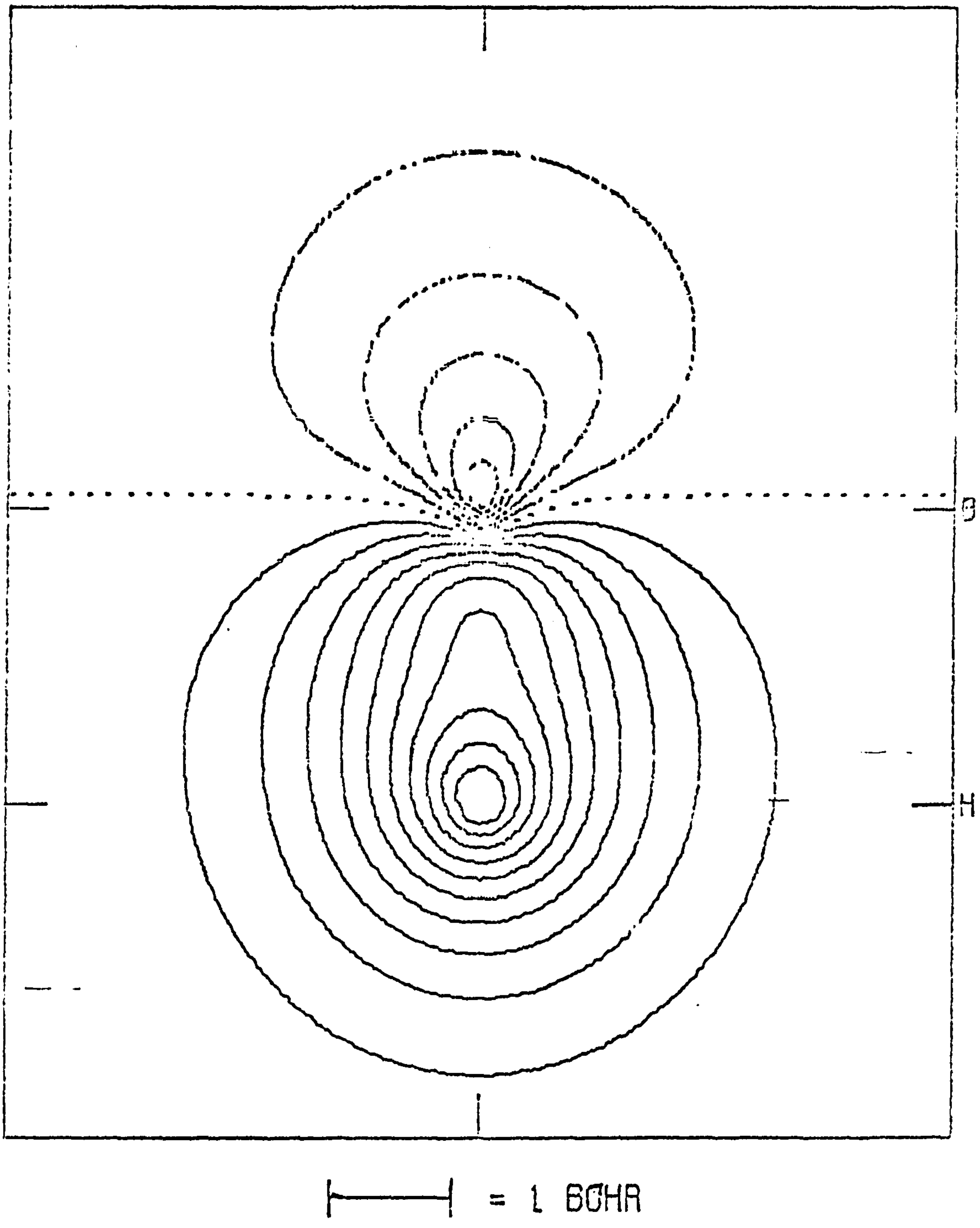
NATURAL ORBITAL CONTOUR MAP 34.
BH LONE PAIR 4 SIGMA 3 (OC=-.01018)



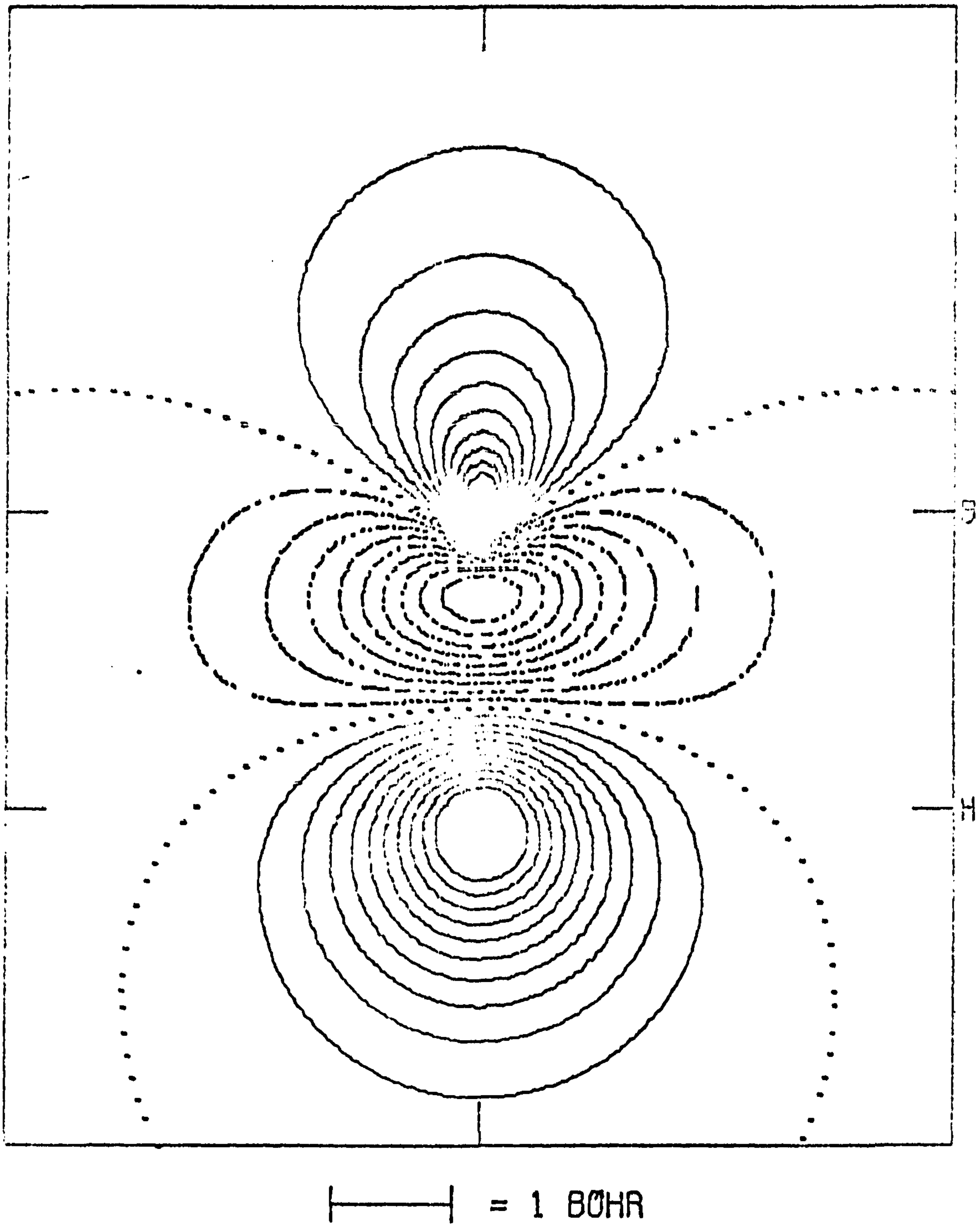
NATURAL ØRBITAL CØNTØUR MAP 35.
BH LØNE PAIR 5 SIGMA 4 (ØC=-.00235)



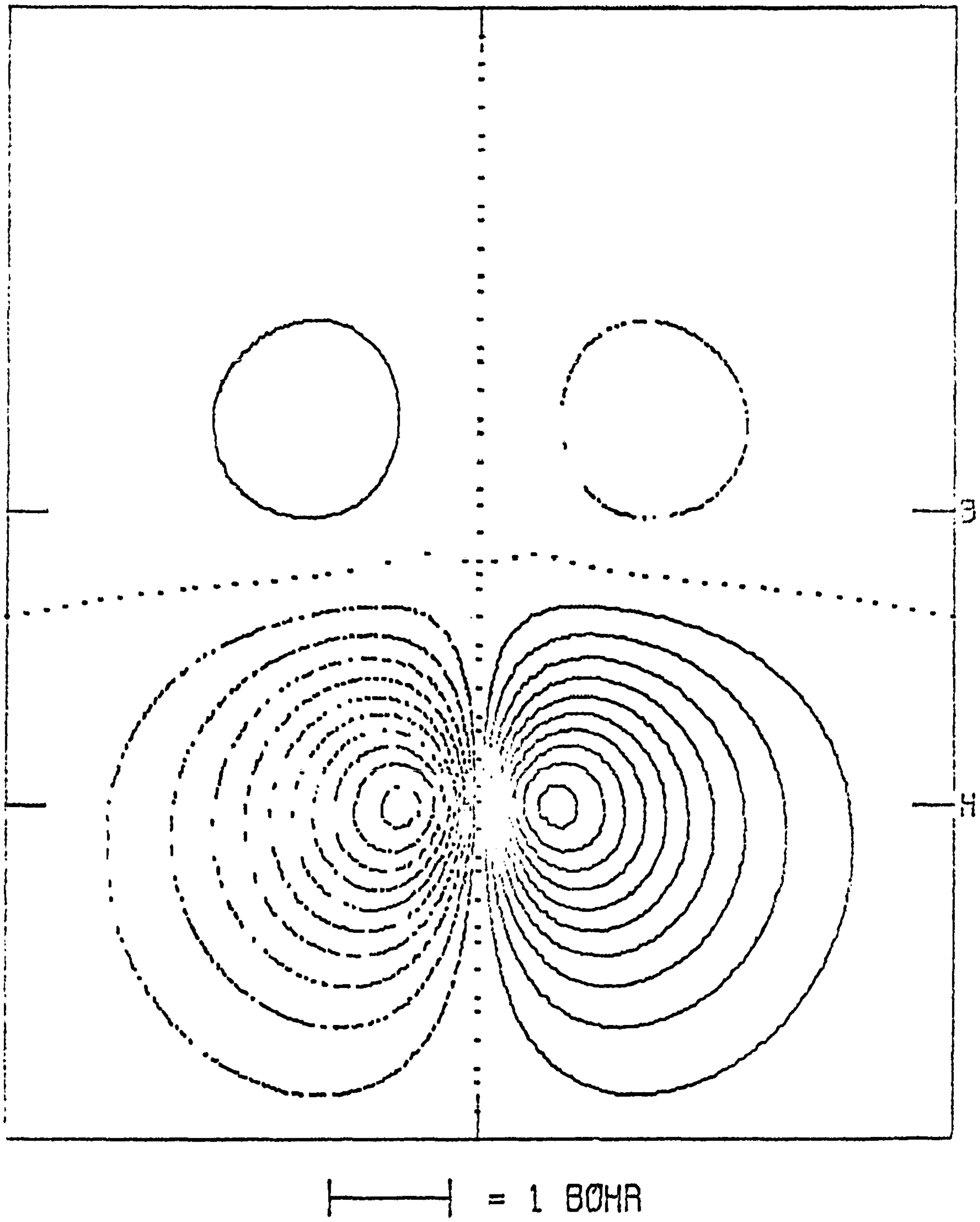
NATURAL ORBITAL CONTOUR MAP 36.
BH LONE PAIR 6 SIGMA 5 (OC=-.00086)



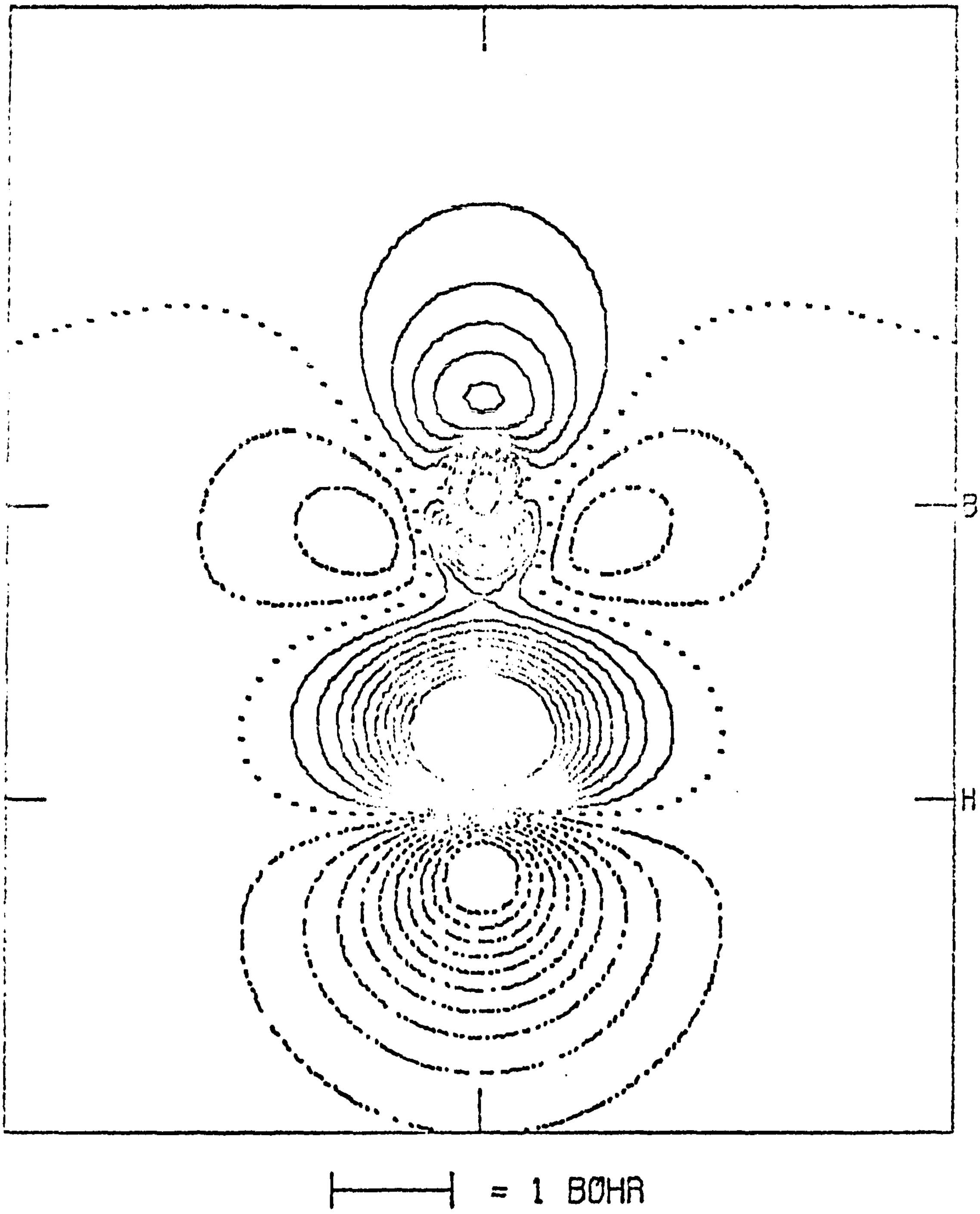
NATURAL ØRBITAL CØNTOUR MAP 37.
BH BØNDING 1 SIGMA 1 (ØC= .99377)



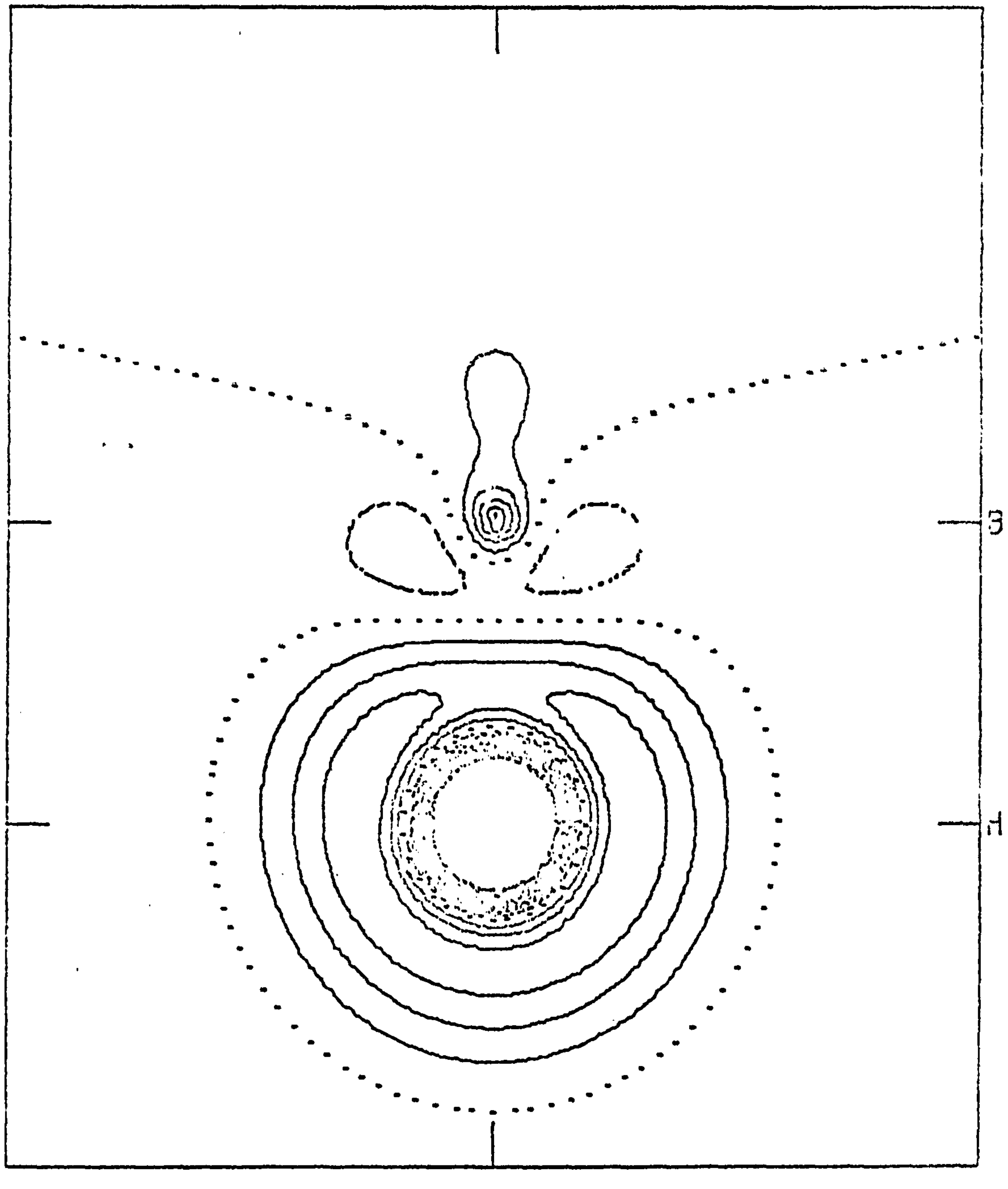
NATURAL ORBITAL CONTOUR MAP 38.
SH BONDING 2 SIGMA 2 (OC=-.09615)



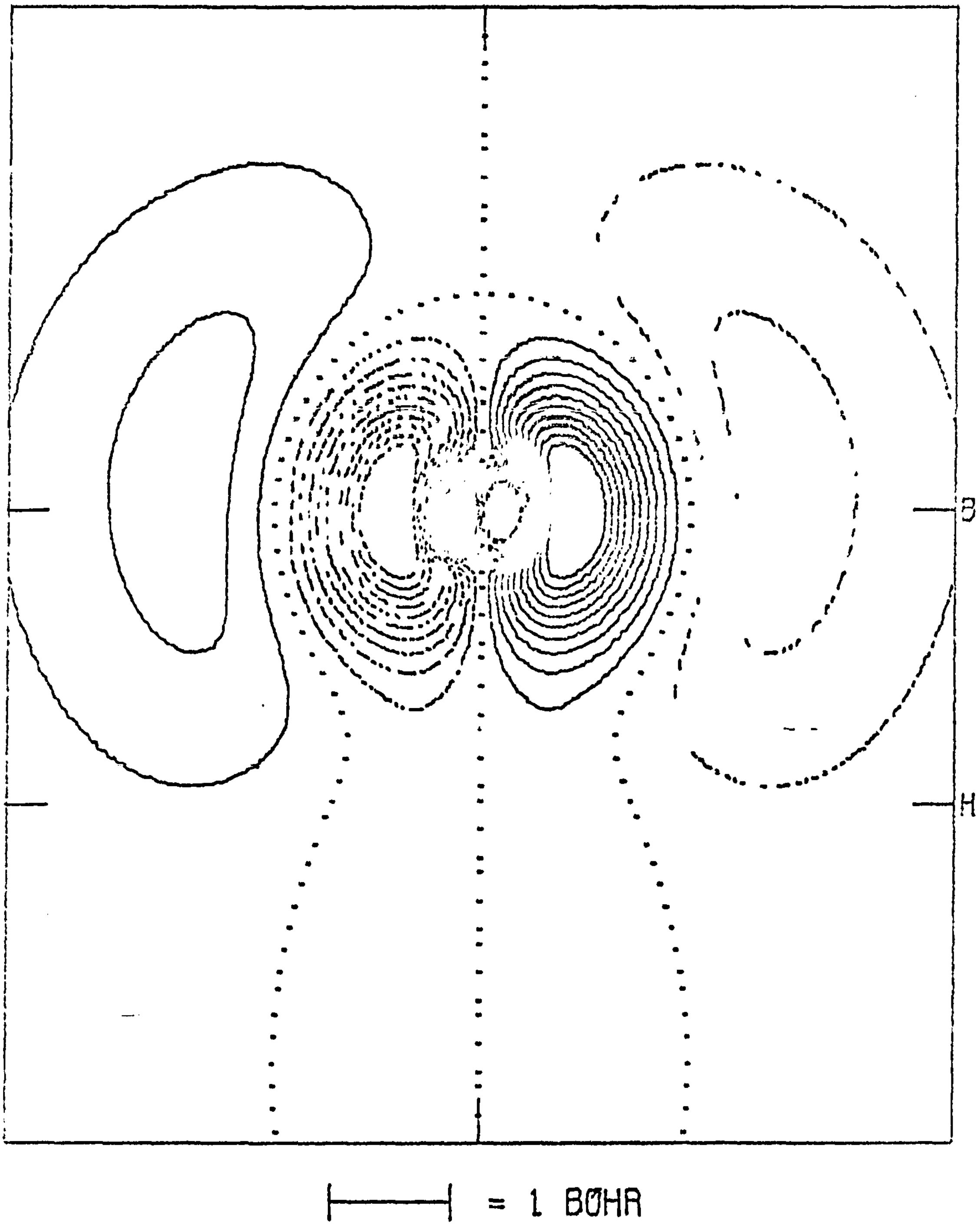
NATURAL ORBITAL CONTOUR MAP 39.
BH BONDING 3 PI 1 [OC=-.03694]



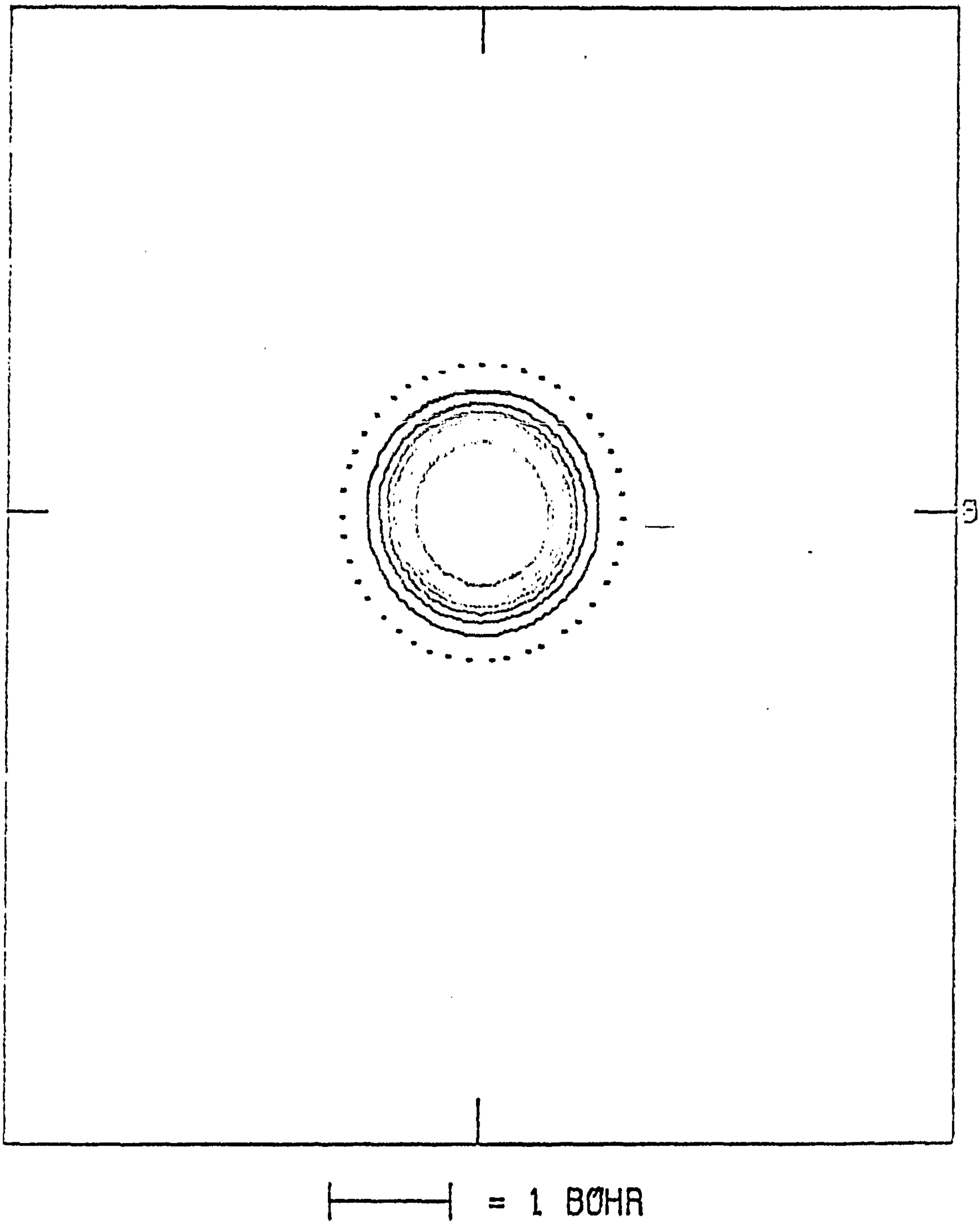
NATURAL ORBITAL CONTOUR MAP 40.
BH BONDING 4 SIGMA 3 (OC=-.02066)



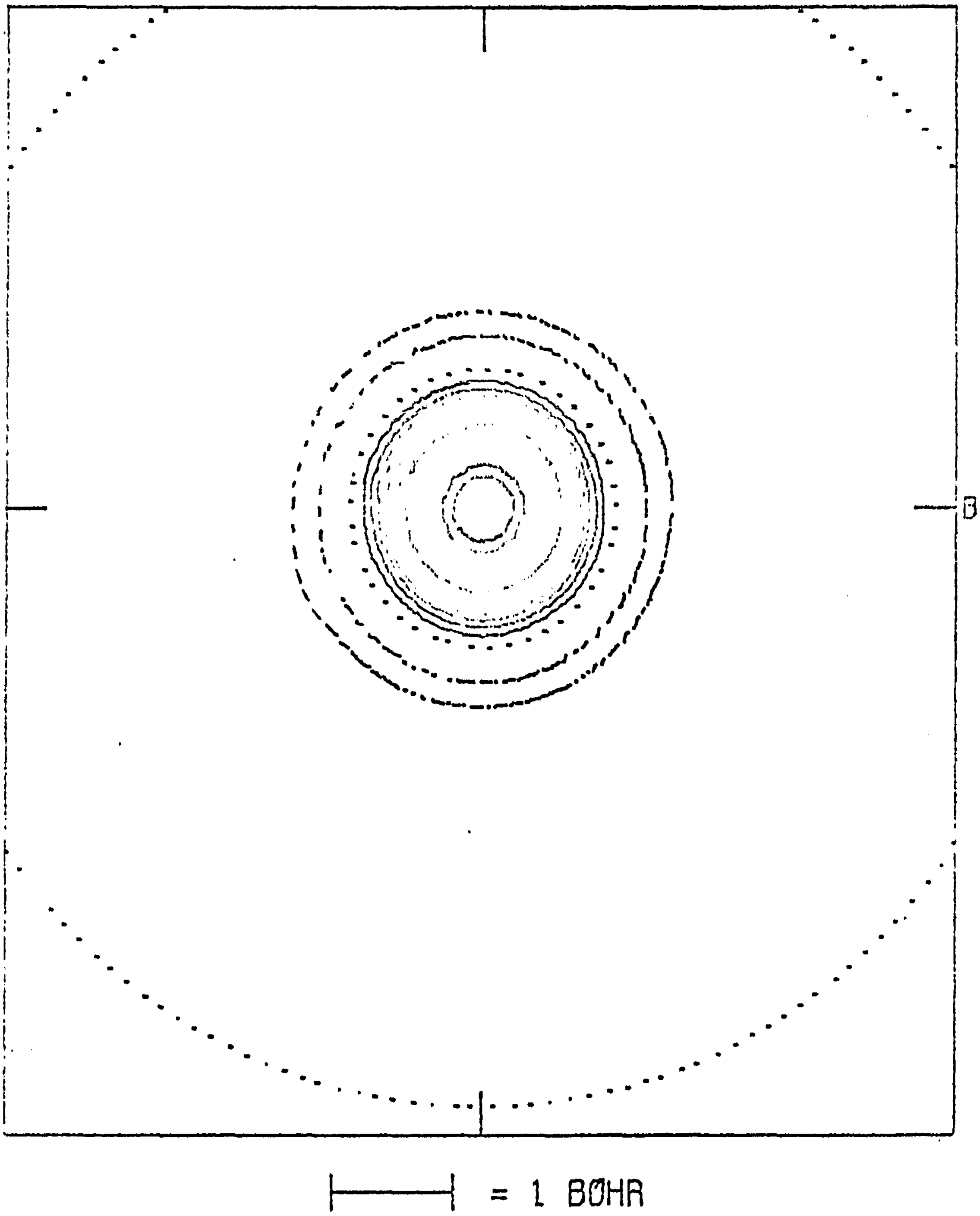
NATURAL ORBITAL CONTOUR MAP 41.
BH BONDING 5 SIGMA 4 (OC=-.00492)



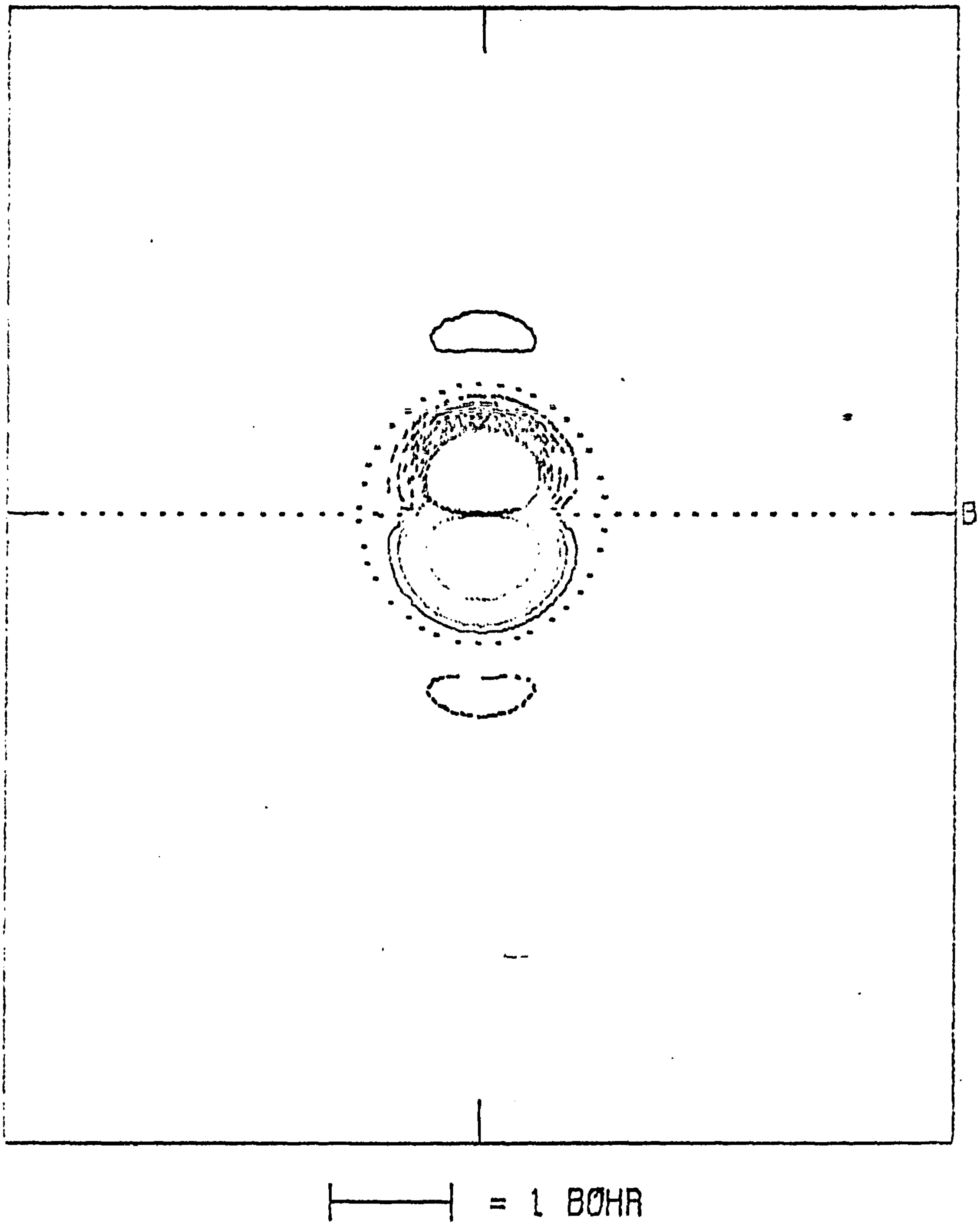
NATURAL ORBITAL CONTOUR MAP 42.
BH BONDING 6 PI 2 (OC=-.00067)



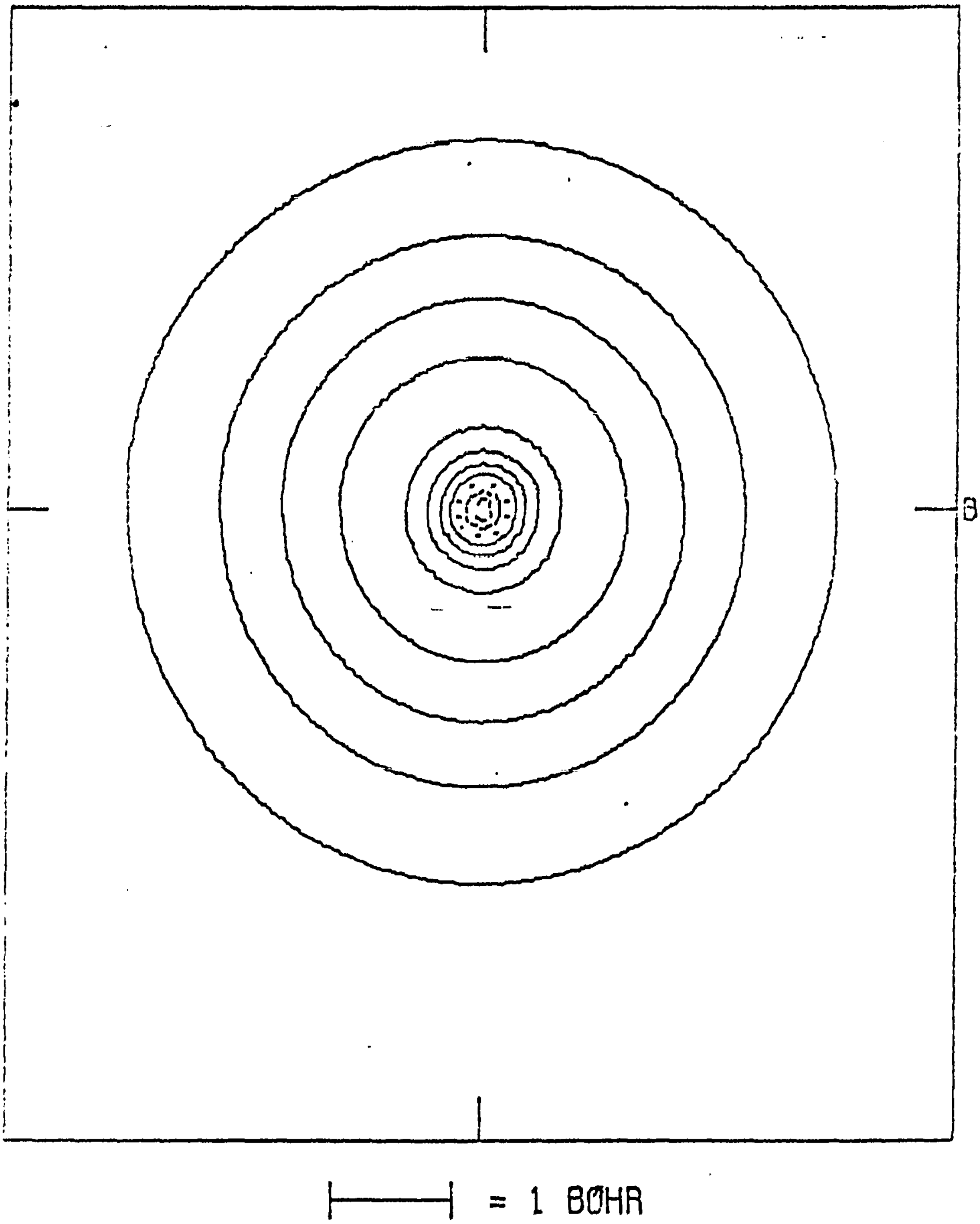
NATURAL ORBITAL CONTOUR MAP 43.
B K SHELL 1 S 1 (OC= .99959)



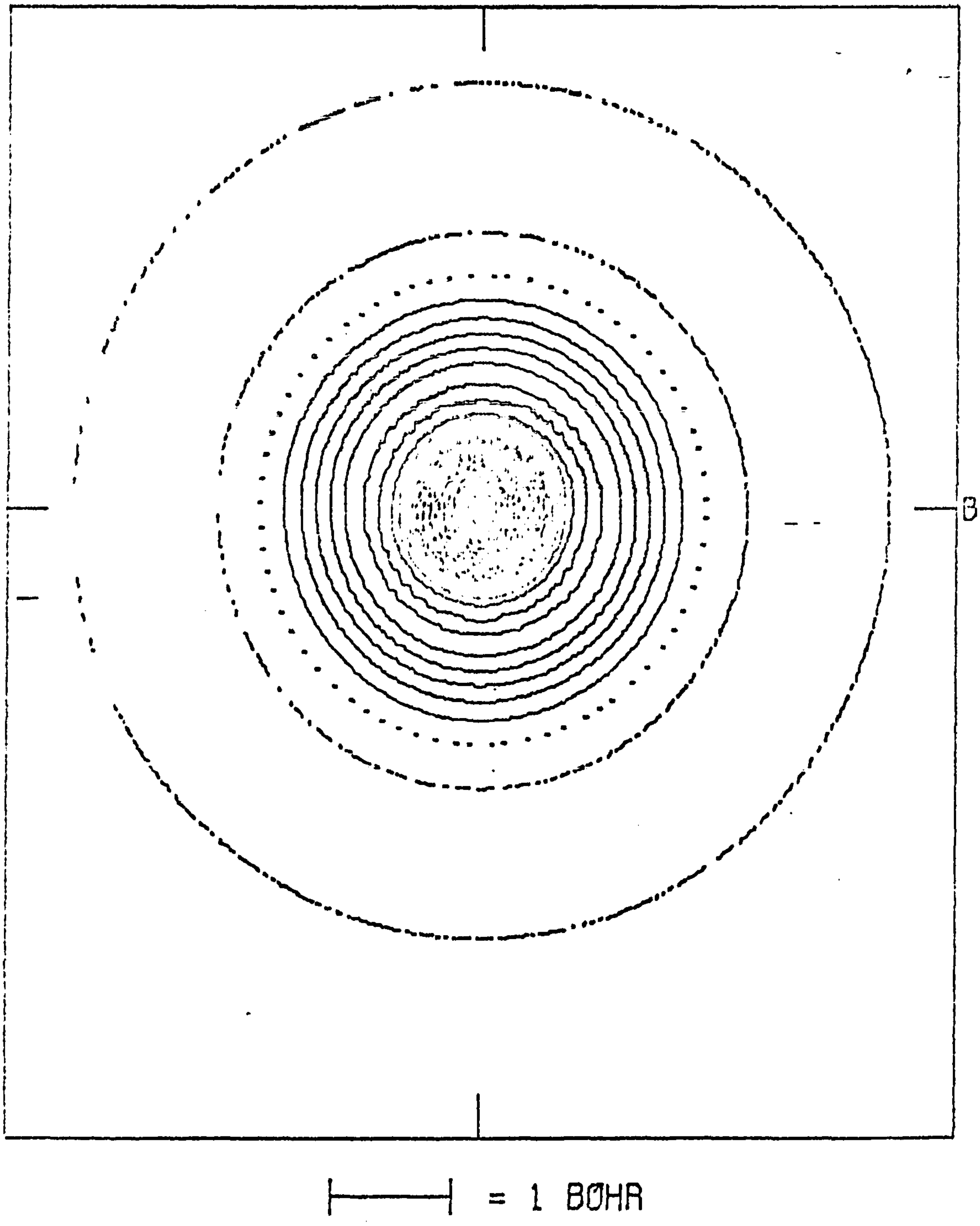
NATURAL ØRBITAL CØNTØUR MAP 44.
B K SHELL 2 S 2 (ØC=-.01680)



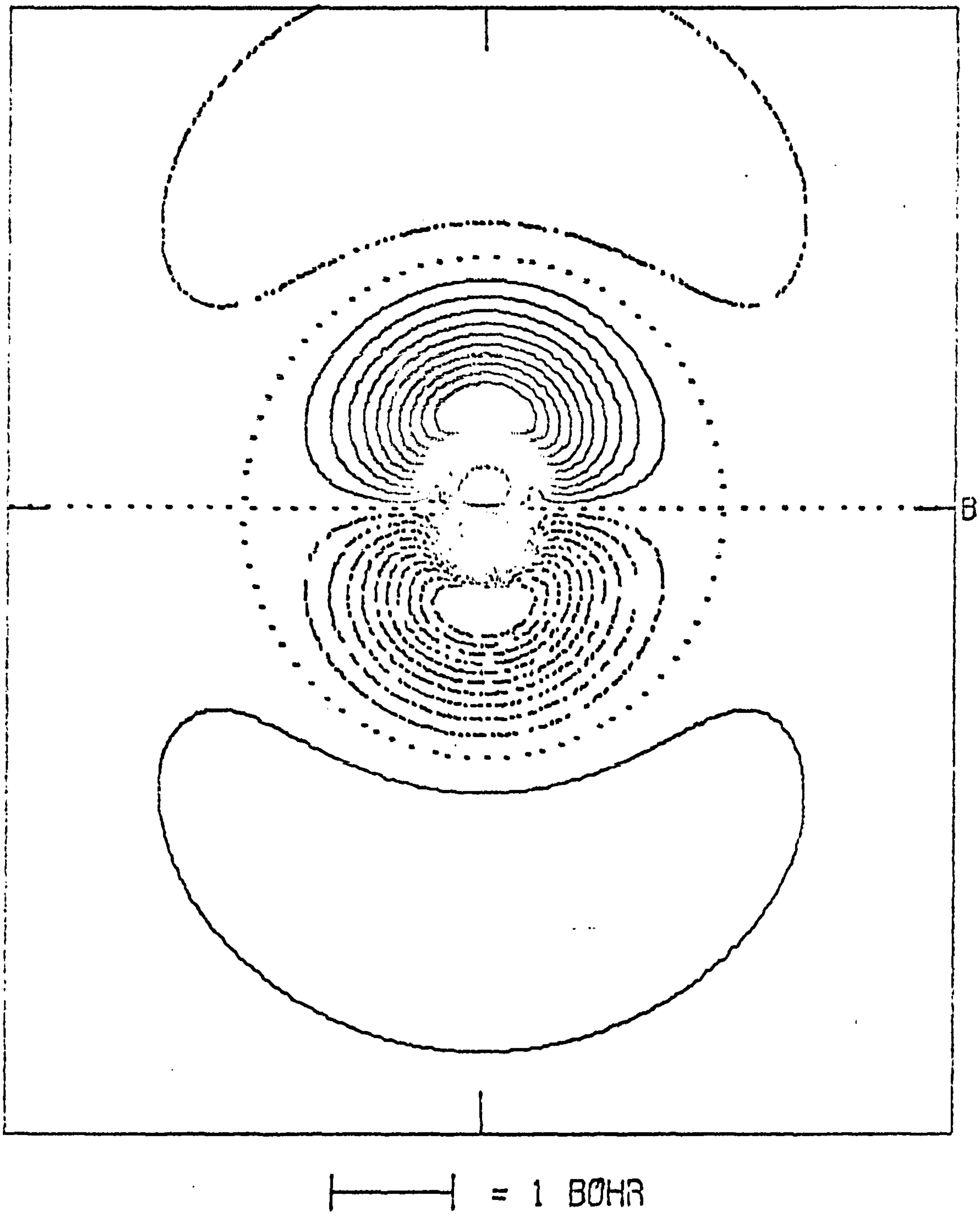
NATURAL ORBITAL CONTOUR MAP 45.
3 K SHELL 3 P 1 (OC=-.01344)



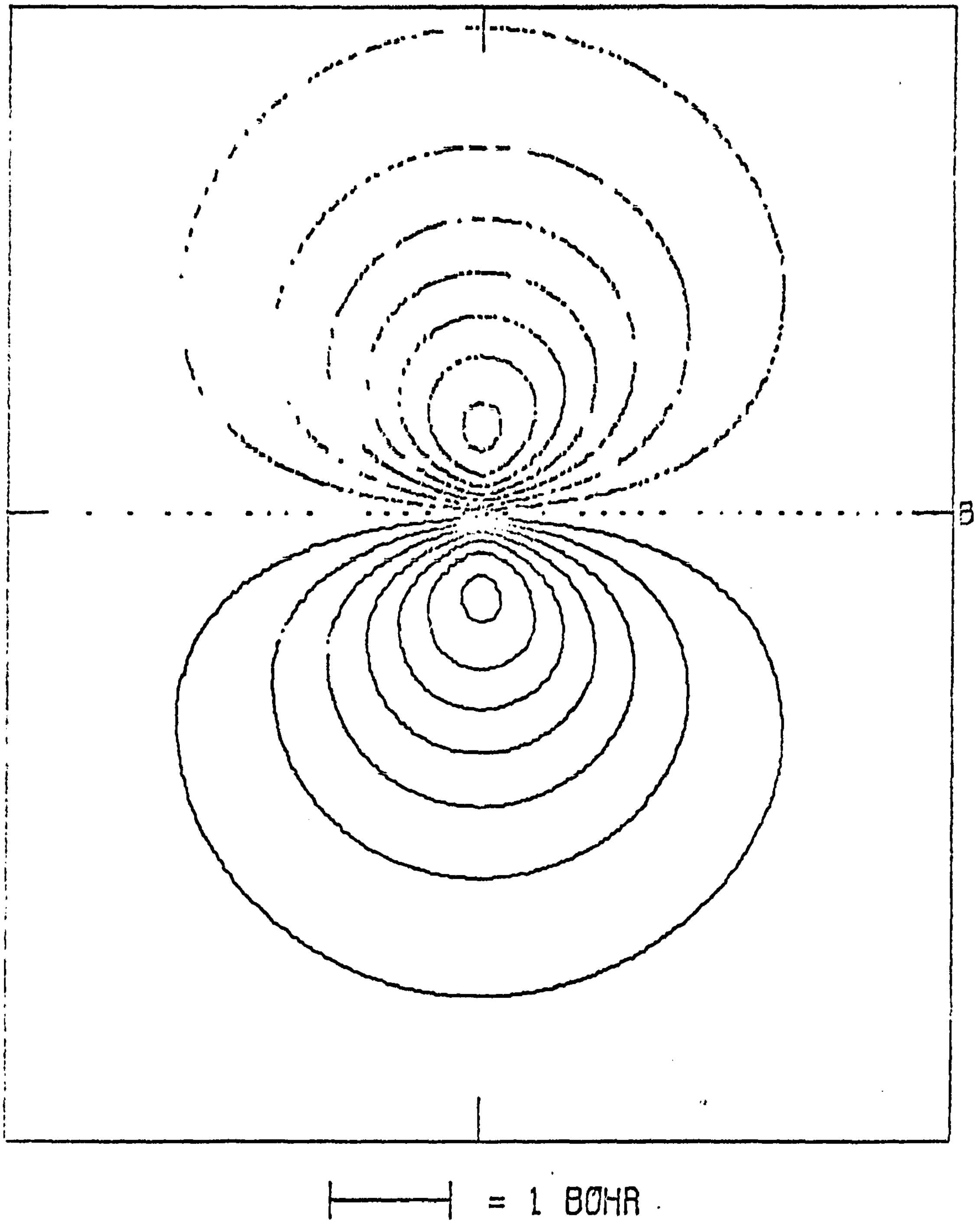
NATURAL ORBITAL CONTOUR MAP 46.
B LONE PAIR 1 S 1 (OC= .99995)



NATURAL ORBITAL CONTOUR MAP 47.
B LONE PAIR 2 S 2 (OC=-.00499)



NATURAL ORBITAL CONTOUR MAP 48.
B LONE PAIR 3 P 1 (OC=-.00497)



NATURAL ORBITAL CONTOUR MAP 49.
B LONE ELECTRON 1 P 1 (OC= .57335)