THE MINIMUM KINETIC ENERGY ORBITAL
AND
THE BAND STRUCTURE OF SODIUM

Thesis by

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ABSTRACT

For calculations on molecules and solids it has proven useful to replace the various core electrons with a pseudopotential. The most common method for doing this, that of Phillips andKleinman, suffers from the disadvantage that the pseudopotential obtained is not unique. It has previously been shown, however, th t the non-uniqueness problem can be resolved by the use of ab-initio GI orbitals as the basis for the potential. Such potentials have proven quite satisfactory in replacing the core electrons in molecular and solid-state calculations. Unfortunately, systems of ten or more electrons are not accessible to GI, so that the approach cannot be used for sodium, for example.

We have examined the GI orbitals and effective potentials for Li, Be+, B++ and compared these orbitals and potentials with those obtained from the usual Hartree-Fock formalism, but employing an extra condition on the orbitals to ensure uniqueness. It was found that a condition suggested (but apparently never tried) by Cohen and Heine, that the Hartree-Fock core orbitals be allowed to mix with the valence orbital in such a way as to minimize the kinetic energy, produced orbitals and potentials nearly identical to those from the GI method.

We then employed this method to obtain local potentials for the ^2S, ^2P and ^2D states of sodium. These potentials were found to reproduce the spectrum of sodium quite well.

These potentials were then used to study the energy levels of sodium metal at the high symmetry points in the Brillouin zone, employing the GI band structure formalism.

I. INTRODUCTION

This paper reports research on the use of pseudopotentials in metals and on problems arising in the determination of such pseudopotentials. The introduction of the pseudopotential into the theory of metals has allowed for certain computational and conceptual simplifications which have been found to be quite useful.(1-5) Subsequently, it was shown that the pseudopotential could be determined from the orbitals obtained from the G1 method.(6) These pseudopotentials were then applied to the calculation of the band structure of Li metal.(7) The problem that will be presented here is what to do when the G1 wavefunction is not (and can at present not be) calculated. That is, some way must be found to obtain a G1-like wavefunction which can be calculated, say, from a Hartree-Fock wavefunction. We shall deal first with this problem, specifically with regard to Na and then deal with the application of the resulting potential to the band structure of Na metal.

II. THE MINIMUM KINETIC ENERGY ORBITAL

For the purposes of this discussion we will be concerned with the Phillips-Kleinman (1) type pseudopotential. Their development of the pseudopotential was a direct outgrowth of the orthogonalized-plane-wave (OPW) method. The basic idea of their work (as given by Cohen and Heine(5)) was to find the equation satisfied by the "smooth" part of the valence orbital. That is if the valence orbital ϕ satisfies an equation

$$H\phi = (T+V)\phi = E\phi$$

where $T=-\frac{1}{2}\nabla^2$ and V is in general some non-local operator, then the "smooth" part is ϕ^s which is an eigenfunction of some other Hamiltonian with the same eigenvalue,

$$H^s \phi^s = E \phi^s$$

Indeed, Cohen and Heine find that the Hamiltonian is of the form

$$H^s = H + V^R = T + V + V^R = T + V_{eff}$$

where V_R is a repulsive potential which cancels much of the attractive V in the core region thus leading to a smoother orbital. Thus the total effective potential, Veff, is much weaker than V. This has two important consequences: (i) the Fourier transforms would be expected to be more rapidly convergent, and (ii) the potential could be used as a perturbation to describe electron-phonon interactions. Consequently, the "smooth" wave function could easily be approximated by a few simple functions such as a few plane waves. There are some problems, however, with Veff. It is a non-local operator (5) (integral operator),

it is not Hermitian (8) and it is not unique.(5) It has been pointed out (6) the ϕ^3 cannot be interpreted as a one particle eigenstate of an electron moving in the averaged field of all of the other electrons.

As was pointed out by Goddard (6), the way out of this dilemna may be found by using a different basis for the determination of the pseudopotential. That is, one begins with the ab initio atomic solution using the G1 wavefunction. The equations thus obtained are of the form

$$H_i \phi_i = \epsilon_i \phi_i \qquad i = 1, \cdots, N \qquad N = \#\text{ electrons}$$

where ϕ_i are the optimum orbitals and H_i is of the form

$$H_i = T + V_{nucl} + U_i^{G1}$$

V_{nucl} = nuclear potential, U_i^{G1} = averaged potential due to other N-1 electrons.

In this case H_i is Hermitian and non-local and the ϕ_i are not orthogonal. The G1 valence orbital for an atom is a smooth, nodeless orbital. This method, then, should form a good basis for the determination of a pseudopotential. (Note that the total G1 energy is lower than the total Hartree-Fock energy.) What we wish to do is find a local potential U^P which satisfies the equation

$$\left(-\tfrac{1}{2}\nabla^2 - \frac{Z_{nuc}}{r} + U^P\right)\phi_i = \epsilon_i \phi_i$$

where U^P is a function only of r. If ϕ_i is nodeless, as the G1 valence orbital is, this equation may be simply inverted to obtain

$$U^P(r) = \epsilon_i + \frac{Z_{nuc}}{r} + \frac{\frac{1}{2}\nabla^2\phi_i}{\phi_i}$$

Furthermore, if one uses $\frac{\Theta(r)}{r} = \phi(r)$, then the equation reduces to

$$U^P(r) = \epsilon_i + \frac{Z_{nuc}}{r} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2\Theta}\frac{d^2\Theta}{dr^2}$$

The total effective potential, Veff, thus becomes

$$V_{eff}(r) = U^{p}(r) - \frac{Z_{nuc}}{r}$$

As was pointed out by Goddard, the potential and thus the Hamiltonian have none of the previous difficulties (i.e. it is Hermitian, local, and unique). Such pseudopotentials have been now used for molecular calculations with very good results (9); as well as for band structures (7).

The problem of finding the pseudopotential is then reduced to the problem of performing the atomic G1 calculation. Things are not quite that simple. At present only atoms through Ne may be calculated with existing G1 programs. Therefore, to attack problems of physical interest one must find an alternate route to the pseudopotential. One would hope to be able to retain the advantageous features of the G1 pseudopotential, so that one might try to find a "pseudo-G1" wavefunction to use in the foregoing formalism. We shall now look at this aspect.

Cohen and Heine (5) suggested several methods for choosing ϕ^s so that it is unique. That is, since ϕ^s is not unique, it is possible to introduce an extra constraint on ϕ^s to make it unique. One way suggested (although apparently never tried) was to choose ϕ^s to be the "smoothest" possible function; i.e. to minimize the quantity

$$\frac{\int |\nabla \phi^s|^2 \, d\tau}{\int \phi_s^* \phi_s \, d\tau}$$

This is equivalent to minimizing the Kinetic energy of ϕ^s, that is, to finding the ϕ^s for which

$$\frac{\langle \phi^s | T | \phi^s \rangle}{\langle \phi^s | \phi^s \rangle} \quad , \quad T = -\tfrac{1}{2}\nabla^2$$

is a minimum. Thus the "smoothest" orbital for use in a

pseudopotential determination is the minmum kinetic energy orbital. However, the G1 orbital is also a smooth nodeless orbital. Is there a connection? More specifically, we wish to investigate the connection between the G1 valence orbital and the minimum kinetic energy (referred to hereafter as MKE) valence orbital for an atom.

First of all, for Hartree-Fock wavefunctions it is possible to mix an arbitrary amount of an orbital for a closed shell with an open shell orbital to form a new open shell orbital. Consider the case of Li. Here we have the Hartree-Fock wavefunction Ψ which may be written

$$\Psi = \mathcal{A}\,(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}\alpha)$$

where $\mathcal{A}$ is the antisymmetrizer. If we construct a new 2s orbital ϕ_{2s}' such that

$$\phi_{2s}' = c_1\phi_{1s} + c_2\phi_{2s}$$

and then evaluate the energy, we find that

$$E' = \frac{\langle \mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)|\,H\,|\mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)\rangle}{\langle \mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)\,|\,\mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)\rangle}$$

$$= \frac{\langle \phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha\,|H\,|\mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)\rangle}{\langle \phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha\quad|\,\mathcal{A}(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha)\rangle}$$

But we have,

$$\mathcal{A}\,(\phi_{1s}\alpha\,\phi_{1s}\beta\,(c_1\phi_{1s}+c_2\phi_{2s})\alpha) = c_2\,\mathcal{A}\,(\phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}\alpha)$$
$$= c_2\,\Psi$$

Thus we have

$$E' = \frac{\langle \phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha\,|H|\,c_2\,\Psi\rangle}{\langle \phi_{1s}\alpha\,\phi_{1s}\beta\,\phi_{2s}'\alpha\,|\,c_2\,\Psi\rangle}$$

$$= E\frac{\langle \phi_{1s}\alpha\,\phi_{1s}\beta(c_1\phi_{1s}+c_2\phi_{2s})\alpha\,|\,c_2\,\Psi\rangle}{\langle \phi_{1s}\alpha\,\phi_{1s}\beta\,(c_1\phi_{1s}+c_2\phi_{2s})\alpha\,|\,c_2\,\Psi\rangle} = E$$

where $H\Psi = E\Psi$ originally. So we see that the energy of the system is left invariant under this transformation. However C_1 and C_2 were arbitrary in this development. In particular, we wish to choose C_1 and C_2 in such a way that $\frac{\langle \phi_{2s'} | \nabla^2 | \phi_{2s'} \rangle}{\langle \phi_{2s'} | \phi_{2s'} \rangle}$ be a minimum. We find that this is equivalent to diagonalizing the kinetic energy matrix, $\underset{\sim}{T}$ and choosing the eigenvector corresponding to the lowest eigenvalue. Note that $\underset{\sim}{T}$ will be block diagonal in symmetry types so that for Na, for example, the new orbital ϕ'_{3s} will be of pure S symmetry. We will further require this new MKE orbital to be normalized. From the foregoing discussion, this is obviously no restriction.

Now we will compare the G1 and MKE orbitals.(10) First consider Li, Be^{+}, B^{++}, all of which have the configuration $(1S)^2$ (2S). In Figure 1 we compare the MKE and G1 orbitals for Li; for a more detailed comparison, a plot of the difference between the two functions is given in Figure 2. Note that the two orbitals are indeed very similar. Figures 3-6 give similar plots for Be^{+} and B^{++}, where we find similar close comparison between the MKE and G1 orbitals. In all cases the differences in the wavefunctions are small, with the largest differences in the core region. (It should be noted in passing that the Hartree- Fock energy in the G1 basis is lower than that of Clementi (11) for a basis set optimized for Hartree-Fock.)

In Table 1 the MKE, G1, and experimental orbital energies of the nS states are compared. The good agreement of the MKE and G1 further verifies the validity of the method.

Figure 1

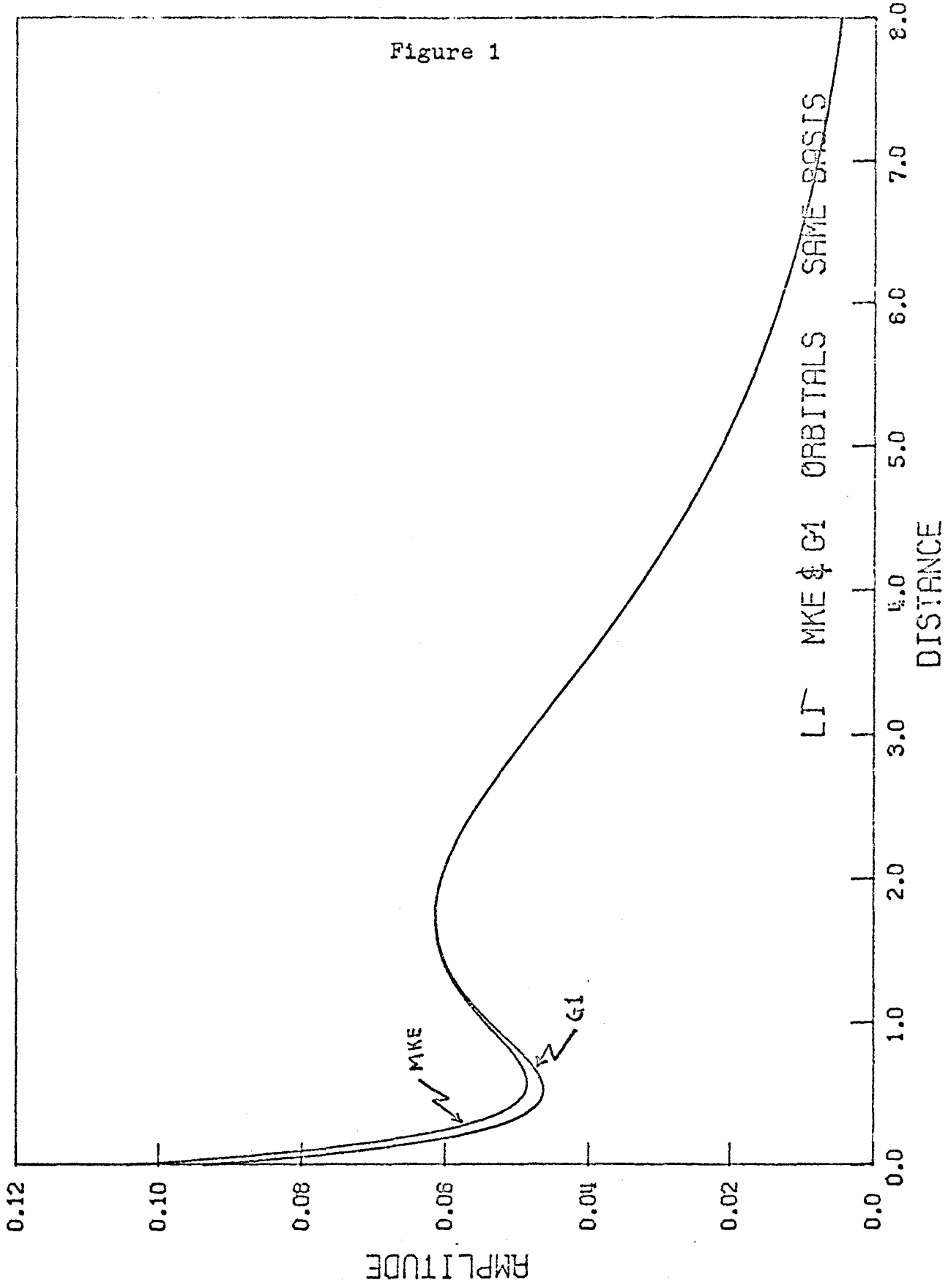

LI MKE & G1 ORBITALS SAME BASIS
AMPLITUDE
DISTANCE
0.0
0.02
0.04
0.06
0.08
0.10
0.12
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
MKE
G1

Figure 3

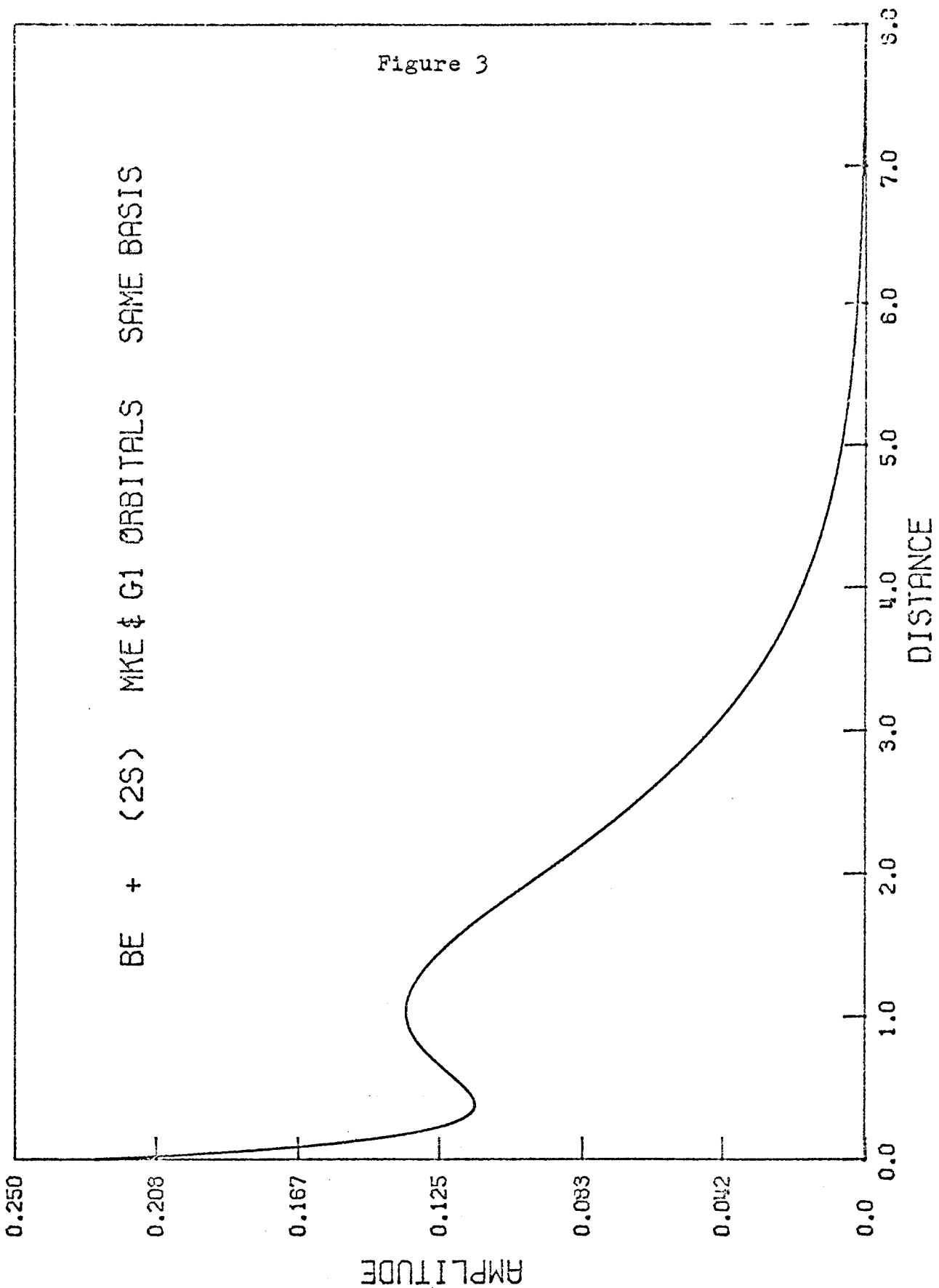

BE + (2S) MKE$ G1 ORBITALS SAME BASIS
AMPLITUDE
0.250
0.208
0.167
0.125
0.083
0.042
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Figure 4

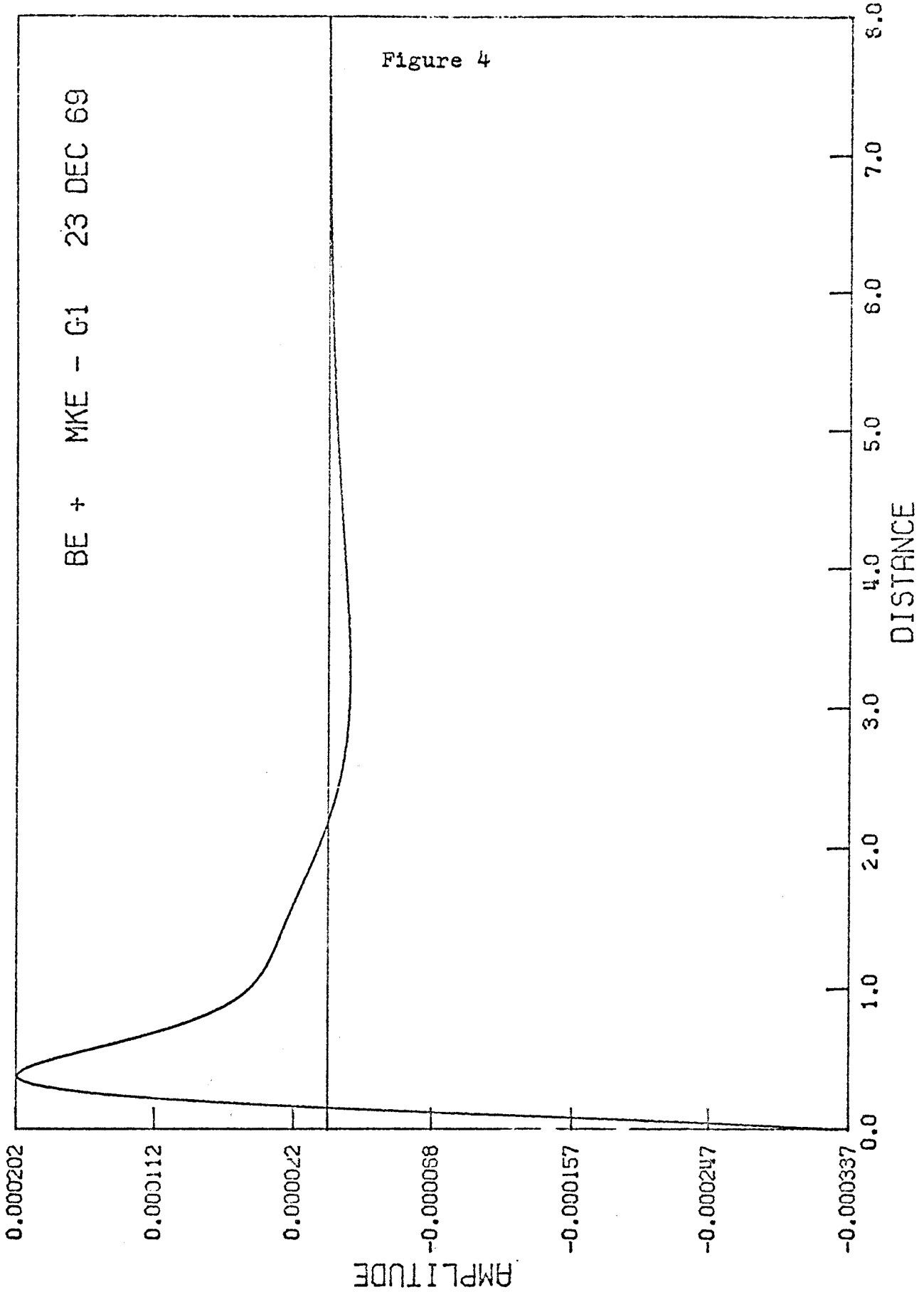

BE + MKE - G1 23 DEC 69
AMPLITUDE
0.000202
0.000112
0.000022
-0.000068
-0.000157
-0.000247
-0.000337
DISTANCE
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 5

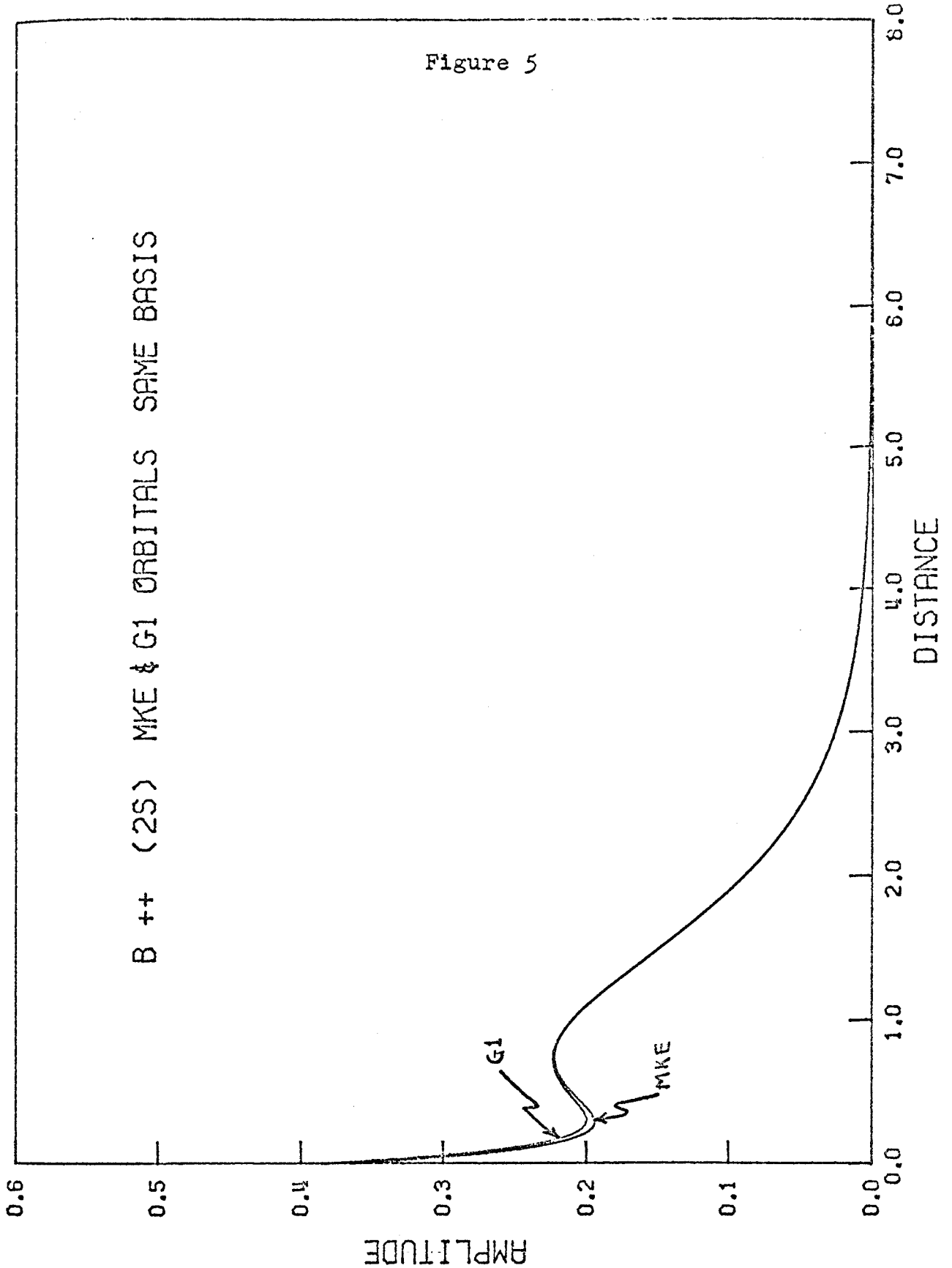

B ++ (2S) MKE & G1 ORBITALS SAME BASIS
AMPLITUDE
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE
G1
MKE

Figure 6

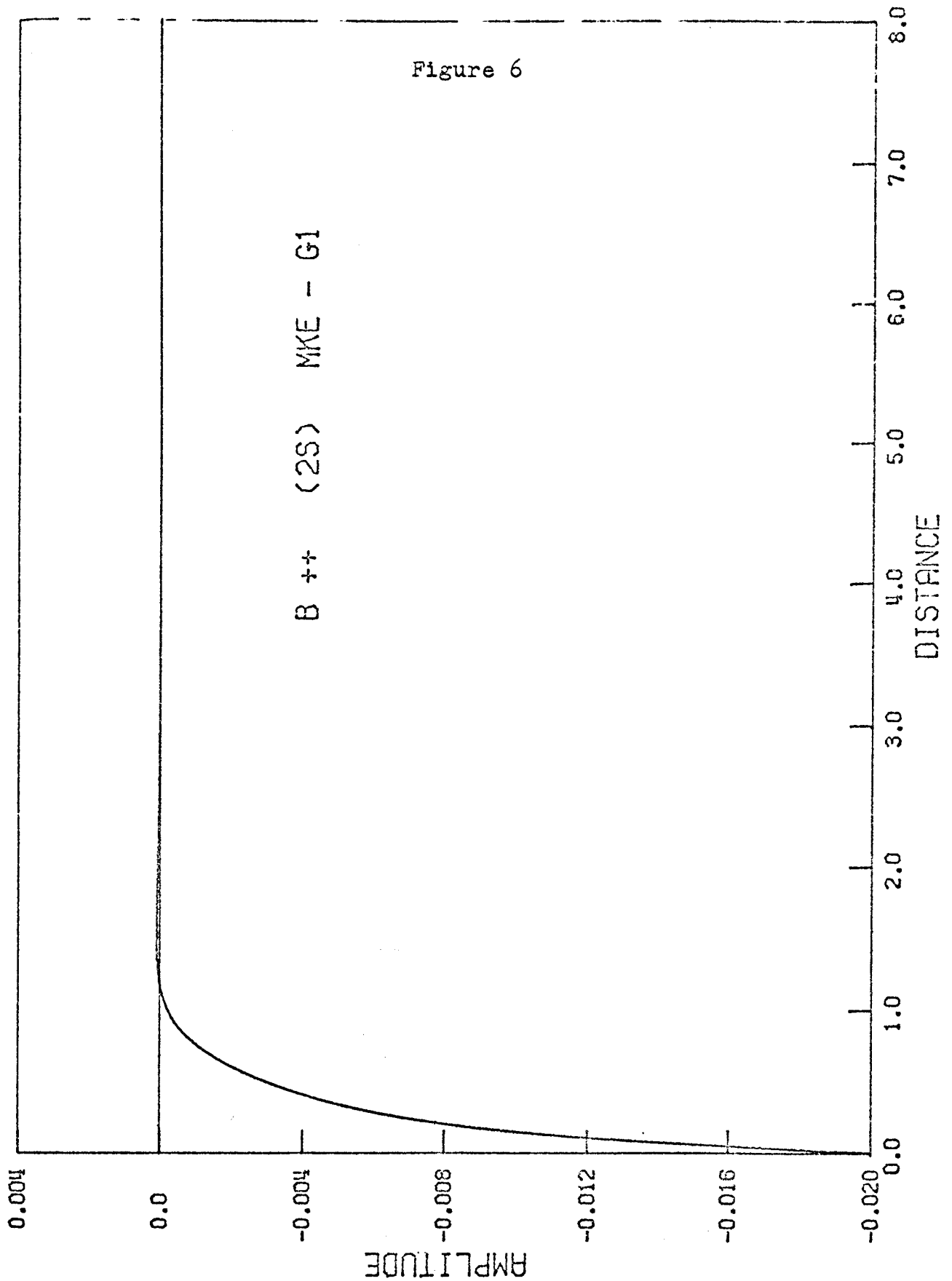

B ++ (2S) MKE - G1
AMPLITUDE
0.004
0.0
-0.004
-0.008
-0.012
-0.016
-0.020
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Table 1

Comparison of MKE and G1 Orbital Energies

State	Experimental	G1	MKE
Li			
2^2S	-0.19814222	-0.19618189	-0.19625758
3^2S	-0.07418201	-0.07422112	-0.07483115
4^2S	-0.03861553	-0.03899702	-0.03896831
5^2S	-0.02363685	-0.02383899	-0.01605556
6^2S	-0.01594512	-0.01606078	-0.01605556
Be+			
2^2S	-0.66924203	-0.66595082	-0.66621943
3^2S	-0.26723135	-0.26776916	-0.27308570
4^2S	-0.14314411	-0.10237338	-0.14623585
5^2S	-0.08905631	-0.00718589	-0.09070003
6^2S	-0.06070223	+0.05133327	-0.06167763
B++			
2^2S	-1.39392474	-1.38966450	-1.39001274
3^2S	-0.57286487	-0.58360070	-0.58338610
4^2S	-0.31090428	-0.25879529	-0.25876554
5^2S	-0.19489679	-0.07190142	-0.07199464

MKE and G1 values obtained by numerical integration to 100 au using 500 grid points.

So far we have compared MKE with G1 wavefunctions. The G1 wavefunction of Li has the core orbitals coupled in a singlet pair and the valence electron in such a way as to obtain a doublet state. There is another way to couple these three orbitals into a doublet. In addition, there is a method for optimizing the spin-coupling and the orbitals, the Spin-Coupling Optimized GI (SOGI) method (12). For these systems the SOGI wavefunction is almost identical with the G1 wavefunction. Figures 7-12 compare the MKE and SOGI orbitals for Li, Be^{+} and B^{++} (13). Here we see that in the core region the SOGI orbital is somewhat lower than the MKE orbital.

The conclusion is that MKE will provide a "pseudo-G1" orbital for use in pseudopotential calculations. The MKE orbital is not in general a "pseudo-SOGI" orbital, the agreement of MKE and SOGI being best when SOGI approaches G1.

It should be noted that other operators were tested as possible candidates for use in the minimization criteria. That is, wavefunctions ψ for which

$$\frac{\langle \psi | \hat{O} | \psi \rangle}{\langle \psi | \psi \rangle}$$

was a minimum for various operators $\hat{O}$ were also investigated. Operators tried were 2J-K, J, K, T+V+2J, T+V+4J, T+V+4J-2K, where

T = Kinetic Energy
V = Nuclear Potential Energy
J = Coulomb Operator
K = Exchange Operator.

Figure 7

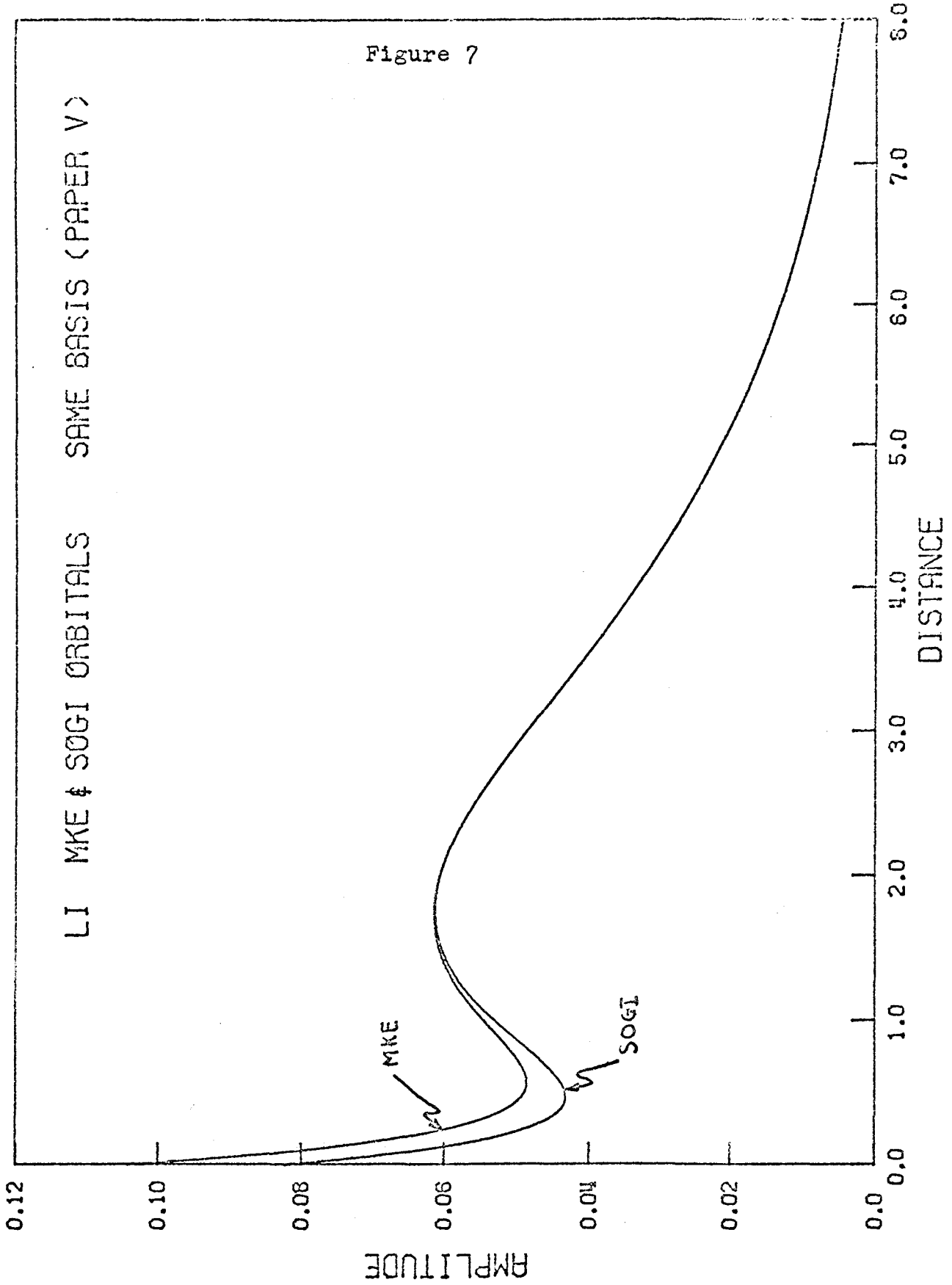

LI MKE & SOGI ORBITALS SAME BASIS (PAPER V)
MKE
SOGI
AMPLITUDE
DISTANCE
0.12
0.10
0.08
0.06
0.04
0.02
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 8

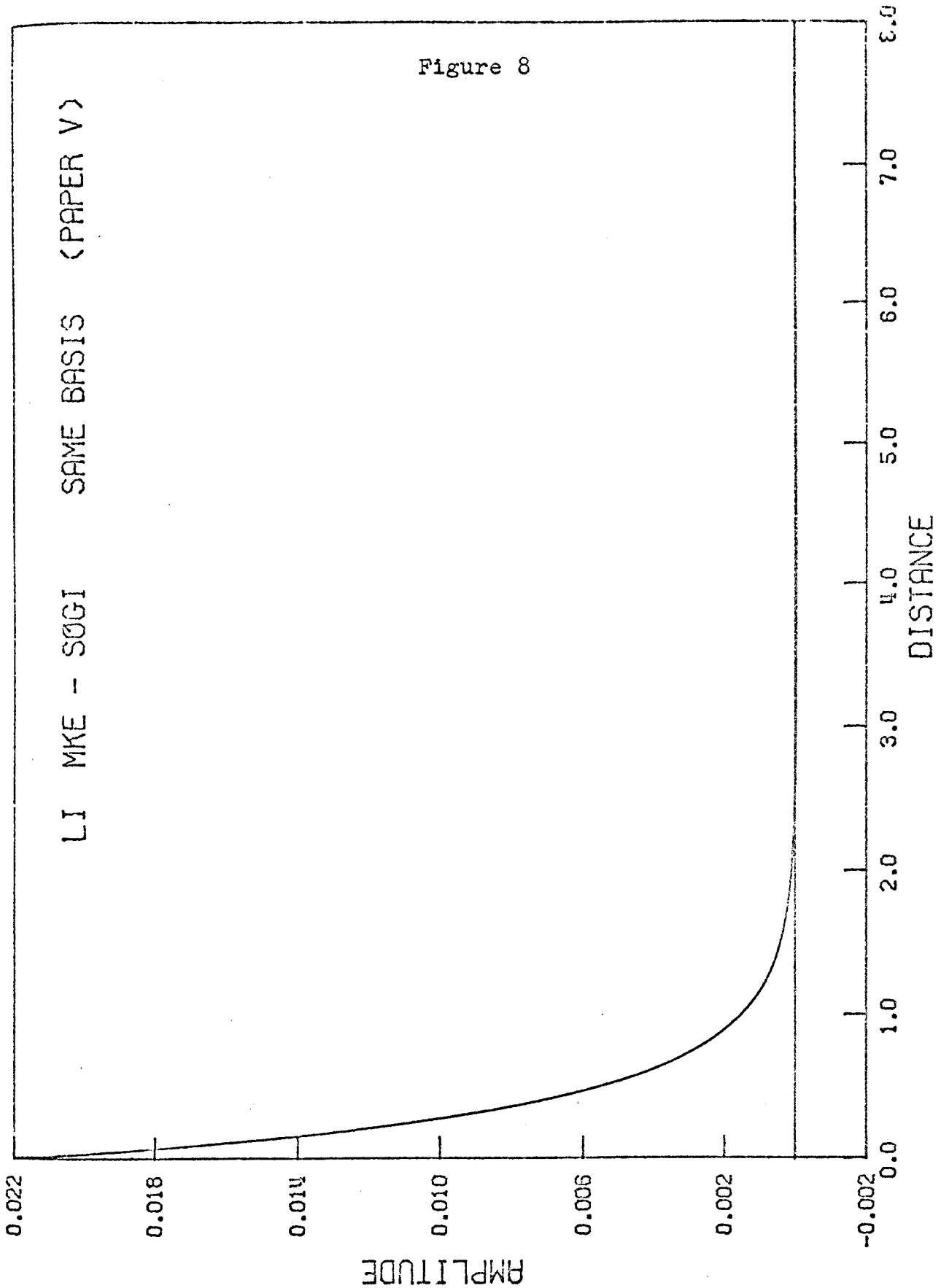

LI MKE - SØGI SAME BASIS (PAPER V)
AMPLITUDE
0.022
0.018
0.014
0.010
0.006
0.002
-0.002
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Figure 9

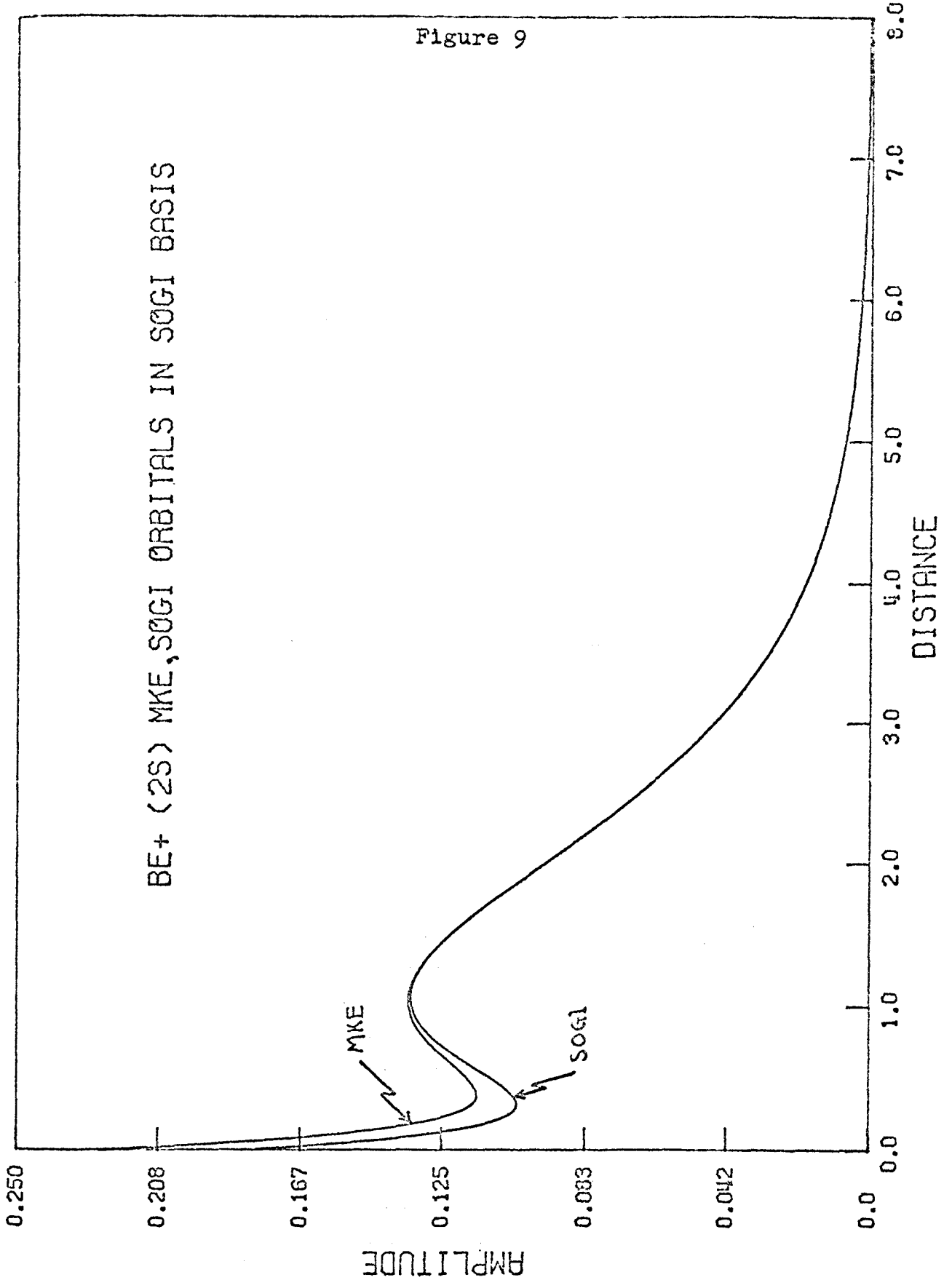
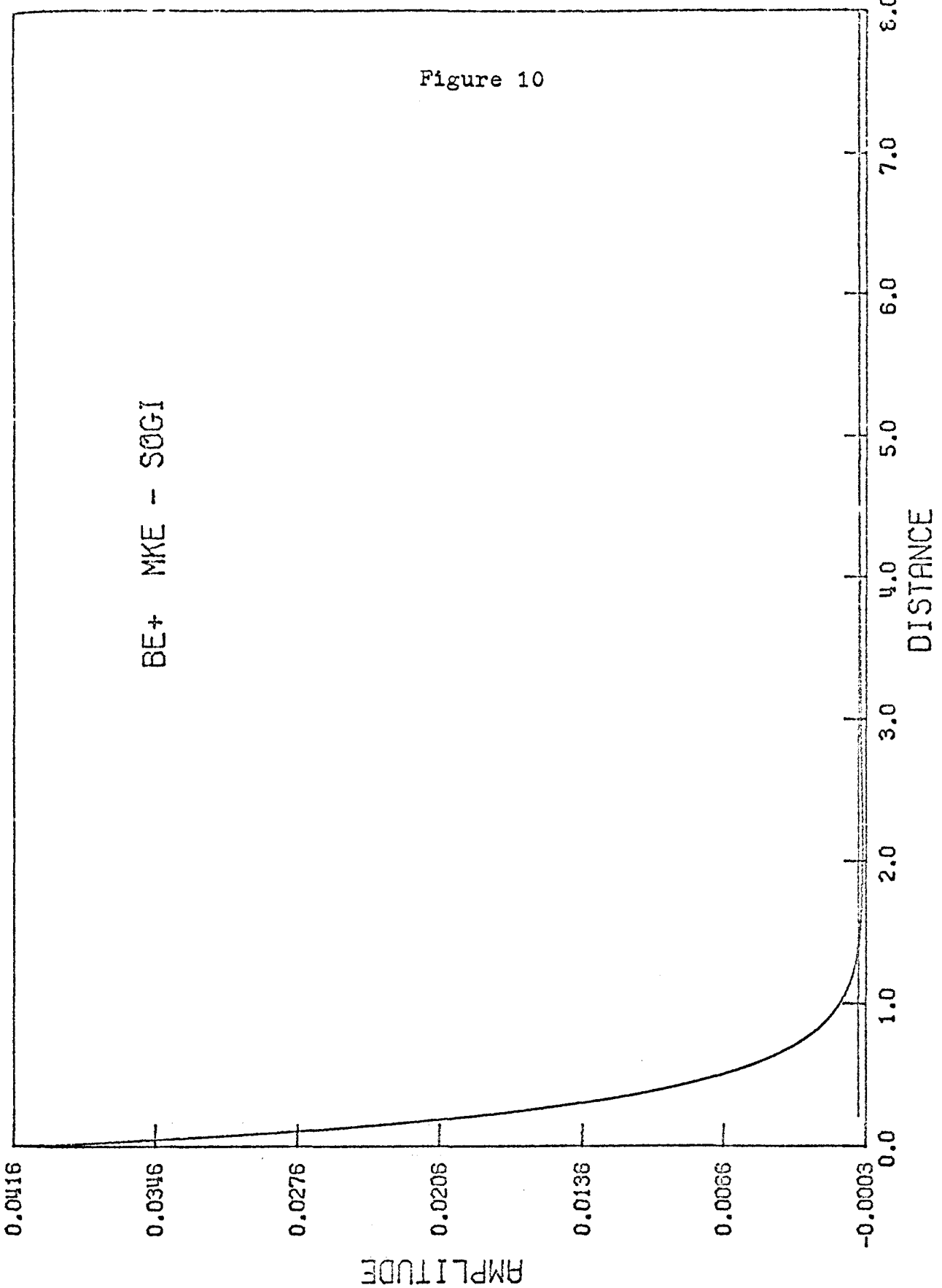

BE+ (2S) MKE,SOGI ORBITALS IN SOGI BASIS
MKE
SOGI
AMPLITUDE
0.250
0.208
0.167
0.125
0.083
0.042
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Figure 10


BE+ MKE - S0G1
AMPLITUDE
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0.0346
0.0276
0.0206
0.0136
0.0066
-0.0003
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Figure 11

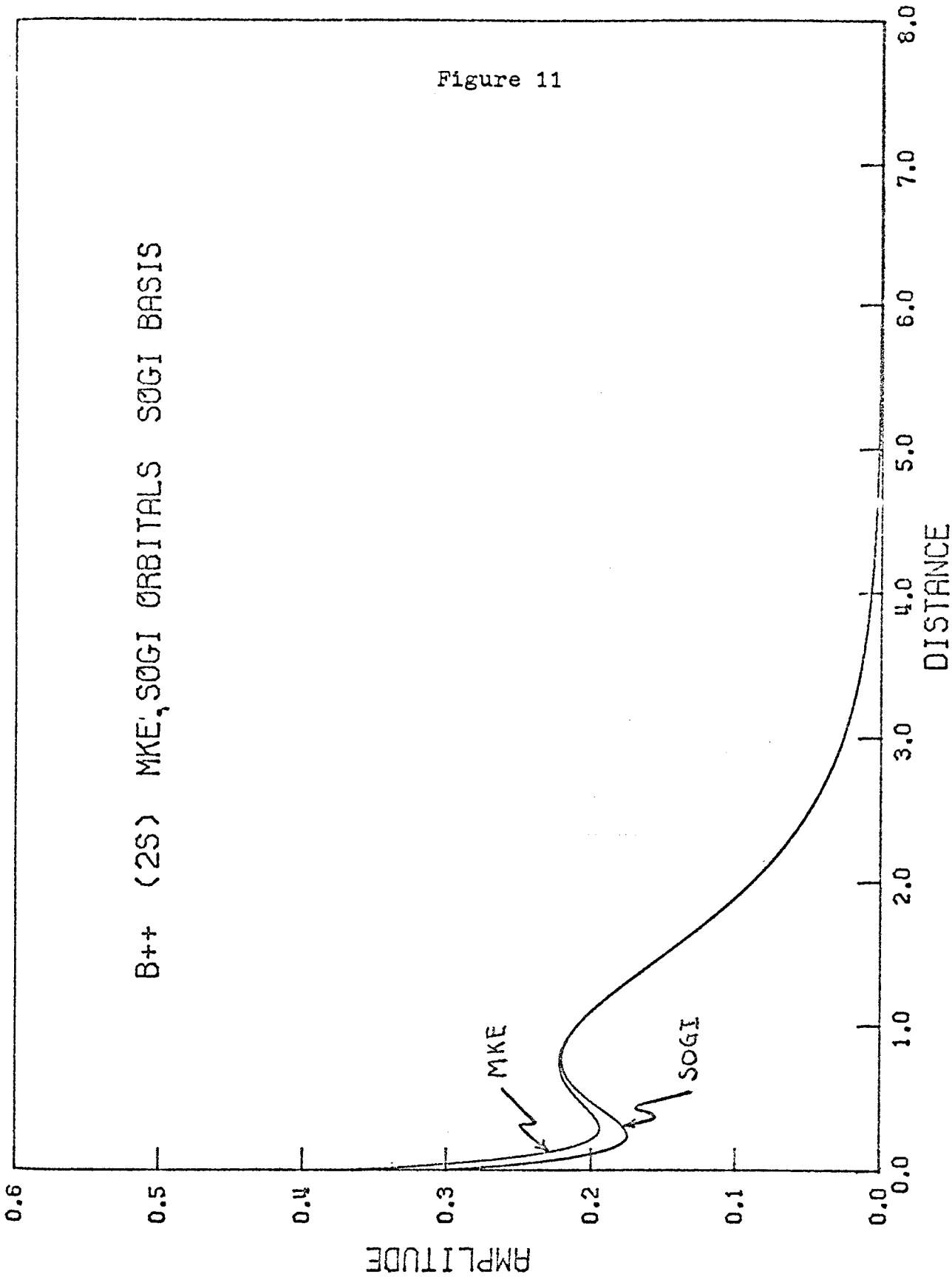
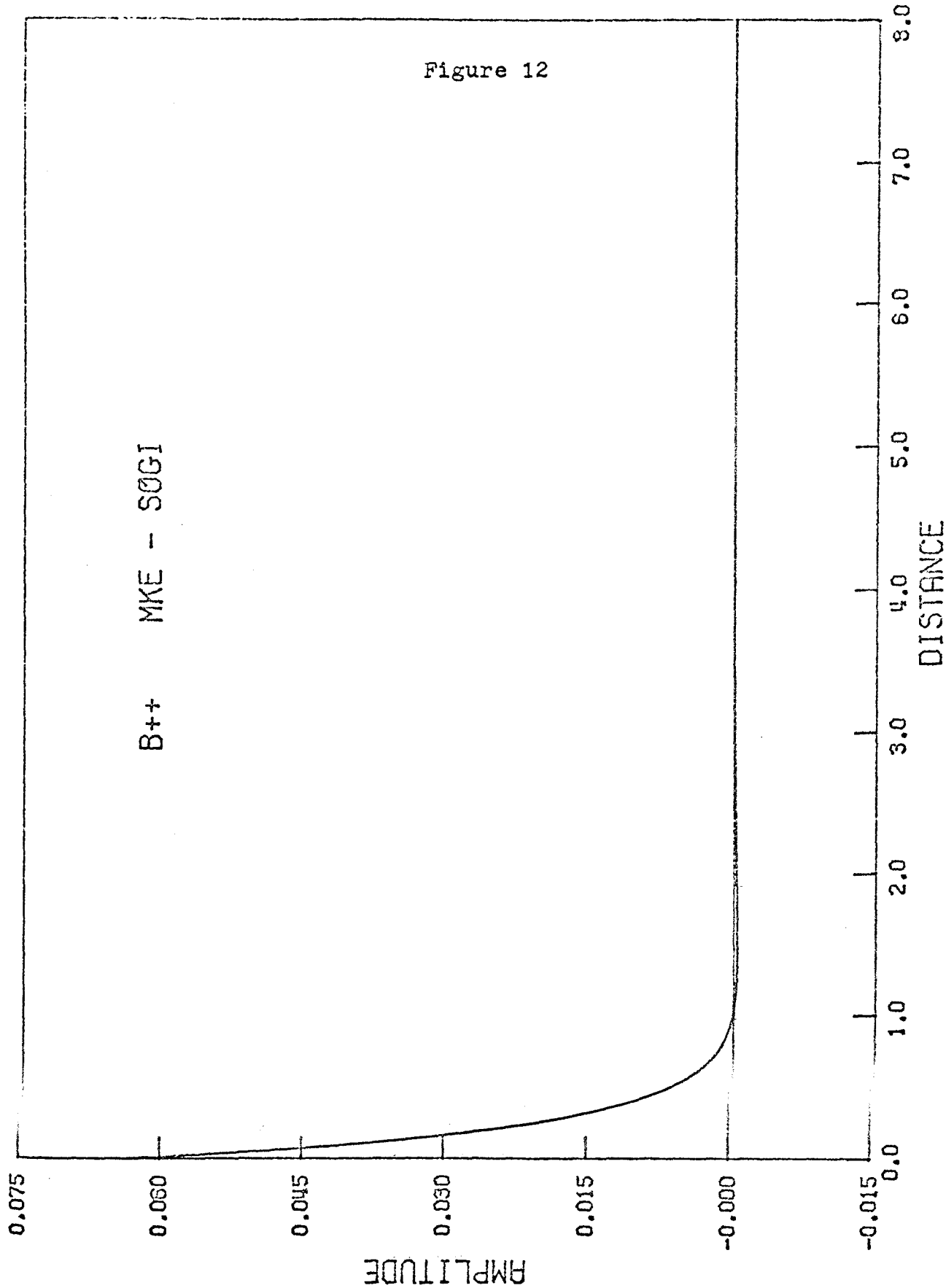

B++ (2S) MKE,SØGI ØRBITALS SØGI BASIS
MKE
SOGI
AMPLITUDE
DISTANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 12


B++ MKE - SØGI
AMPLITUDE
0.075
0.060
0.045
0.030
0.015
-0.000
-0.015
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Using Li as a test case, none of these operators produced a suitable smooth wave function. On the basis of this evidence it was deciced to accept MKE as a workable method and to procede from there.

To perform the band structure calculation for Sodium it is necessary to have the wave functions for the ^2S, ^2P and ^2D states. We will want to expand the total potential in terms of angular momentum eigenstates as follows (5,9),

$$V = \sum_{\ell=0}^{\infty} V_\ell \, |\ell\rangle\langle\ell|$$

where V_ℓ is the pseudopotential for the angular momentum eigenstate $|\ell\rangle$, and where $|\ell\rangle\langle\ell|$ is the angular momentum projection operator. Here V_ℓ is a function only of the radial distance from the nucleas. It is expected that $V_\ell = V_2$ for $\ell \geq 2$ so that (a) can be written

$$V = (V_S - V_d)\,|S\rangle\langle S| + (V_P - V_d)\,|P\rangle\langle P| + V_d$$

First, however, it was necessary to solve the atomic Hartree-Fock problem for the ^2P and ^2D states of sodium. The results of these calculations are given in Tables 2 and 3. The minimum kinetic energy orbital for the various states was determined. These are given in Figures 13 to 15 . Note that for the sodium ^2D state there are no d-like core states and thus the 3d Hartree-Fock orbital is also the MKE orbital. However the 3d orbital is nodeless (except at r=0, which is no problem) so that there is no problem with the local potential. The pseudopotentials obtained from these orbitals are given in Figures 16 and 17. In Figure 16 U is plotted. In Figure 17 the quantity plotted is V=U-z/r. As a check, the first few nS, nP and nD eigenvalues for the potentials

Table 2

Sodium ^2P State

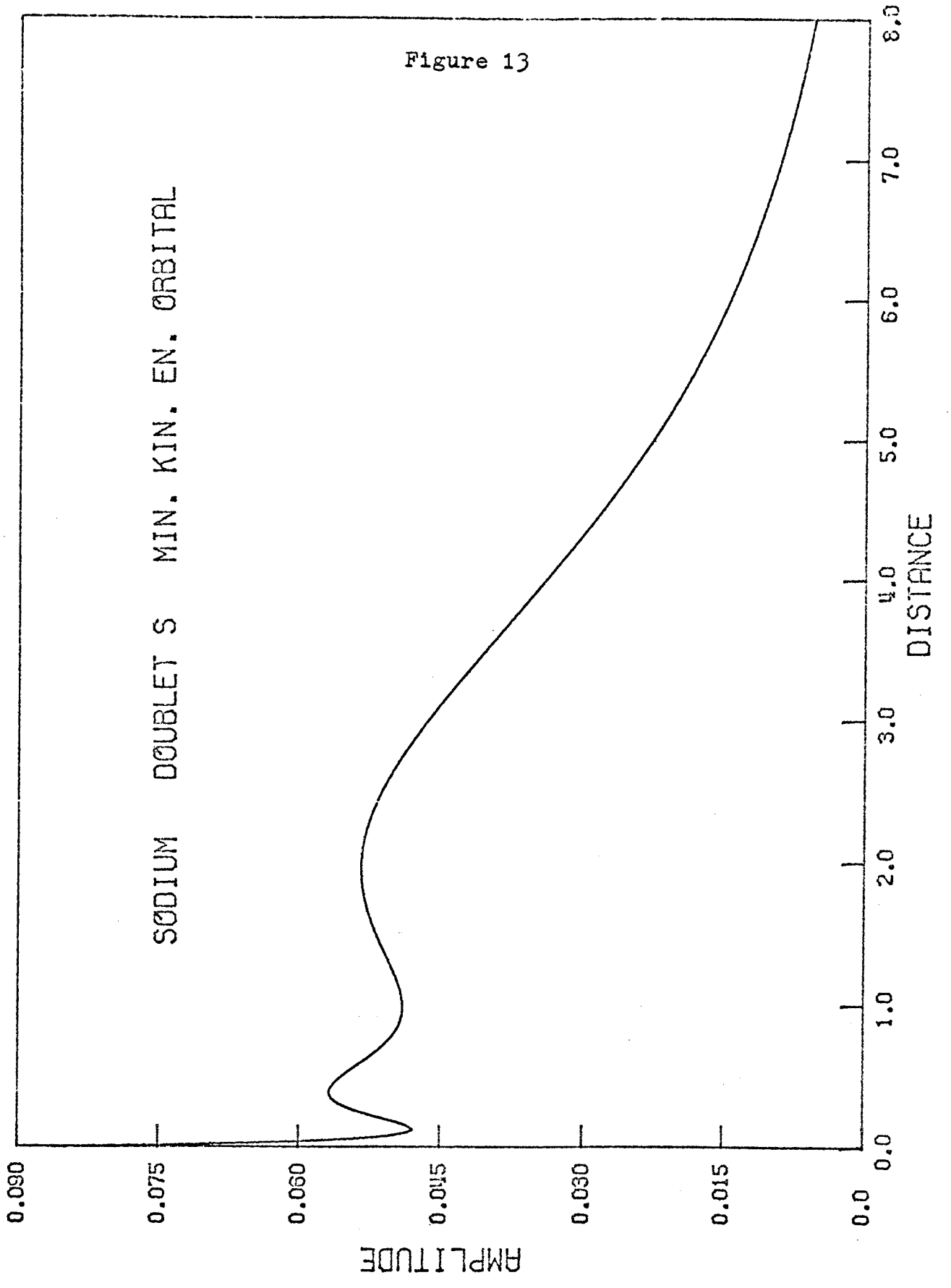
N	Orbital Exponent	Coefficients	
s orbitals		C_{1s}	C_{2s}
1	11.0	.96304403	-.23496820
3	12.3685	.04217993	-.00378323
3	8.0254	.01595266	.13153565
3	5.7059	-.00283717	.40097719
3	3.6310	.00160936	.52792173
3	2.1537	.00033420	04743699
31	1.1081	.00012320	-.00623188
Orbital Energy		-40.55828221	-2.87428246
p orbitals		C_{2p}	C_{3p}
2	5.50	.47415056	-.04703084
4	8.3937	.03542223	-.00356619
4	5.4206	.27881382	.02587554
4	3.5646	.32284042	-.02635041
4	2.2833	.07346077	.01709544
4	1.3241	-.00482152	.17730639
4	0.8249	.00274296	.46070896
4	0.5717	-.00145243	.43548163
4	0.3970	.00042350	.01043590
Orbital Energy		-1.59806892	-.10945443
Total Energy		-161.7863862	
Potential Energy		-323.5615637	
Kinetic Energy		161.7751775	
Virial Theorem		-2.0000693	

Table 3

Sodium ^2D State

N	orbital Exponent	Coefficients	
s orbitals		C_{1s}	C_{2s}
1	11.0	.96403848	-.23502350
3	12.3685	.04218093	-.00378141
3	8.0254	.01593954	.13160038
3	5.7059	-.00283232	.40112409
3	3.6310	.00160624	.52797880
3	2.1537	-.00033227	.04713876
3	1.1081	.00012386	-.00036803
3	0.7083	-.00004897	.00213789
Orbital Energy		-40.64807965	-2.96197971
p orbitals		C_{2p}	
2	5.50	.47435642	
4	8.3937	.03536698	
4	5.4206	.27918420	
4	3.5646	.32187251	
4	2.2833	.07689641	
4	1.7500	-.00664195	
Orbital Energy		-1.68549127	
d orbitals		C_{3d}	
3	3.6667	.00172943	
5	3.4893	.00447437	
5	1.7072	.03583736	
5	0.9032	.19590693	
5	0.5554	.48091369	
5	0.4007	.40096624	
5	0.2880	.01239445	
Orbital Energy		-0.05566411	
total energy		-161.7326046	
Potential Energy		-323.4540279	
Kinetic Energy		161.7214232	
Virial Theorem		-2.00006914	

Figure 13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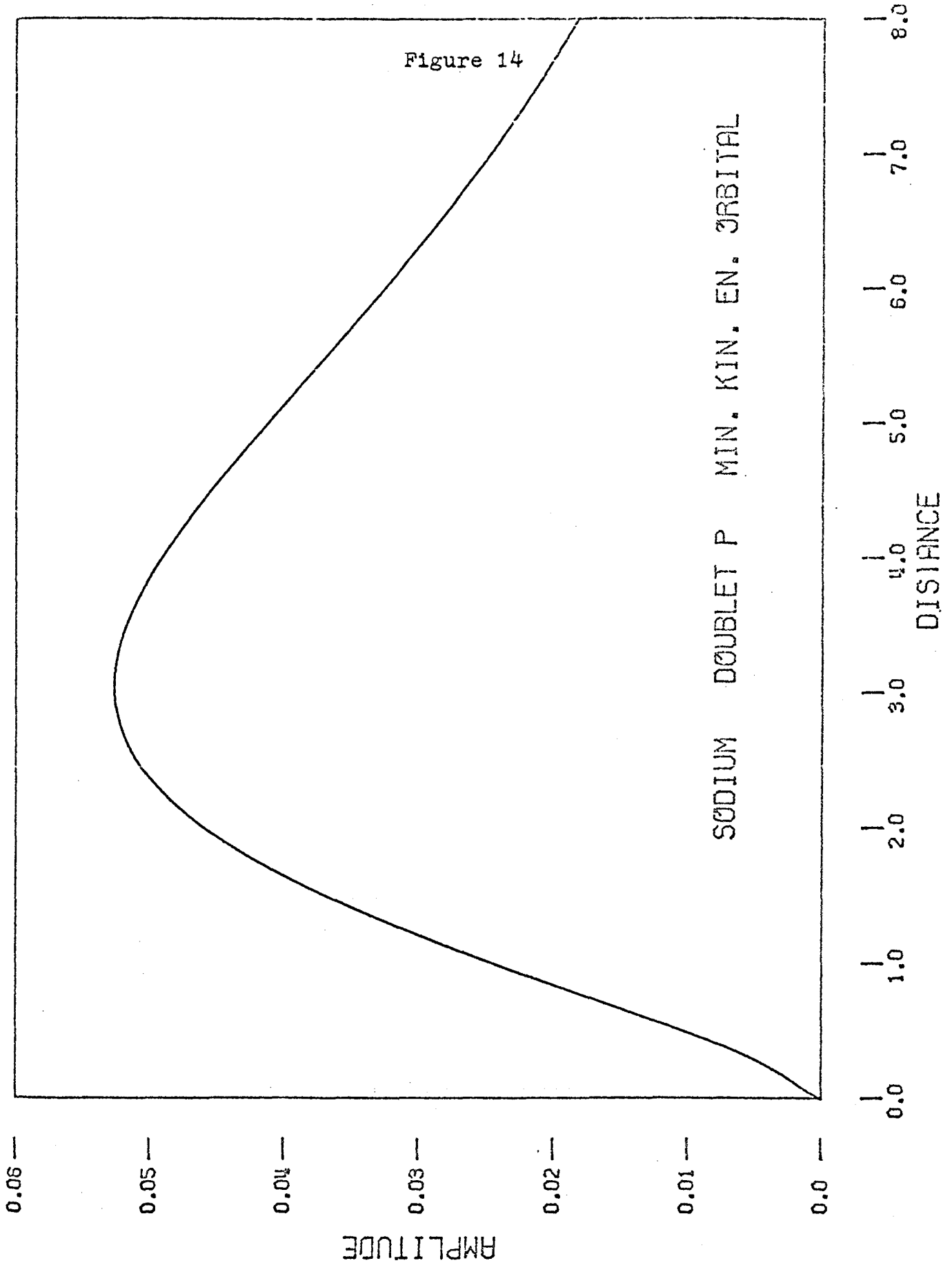
0.075
0.060
0.045
0.030
0.015
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DISTANCE

Figure 14


SODIUM DOUBLET P MIN. KIN. EN. ORBITAL
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0.02
0.03
0.04
0.05
0.06
DISTANCE
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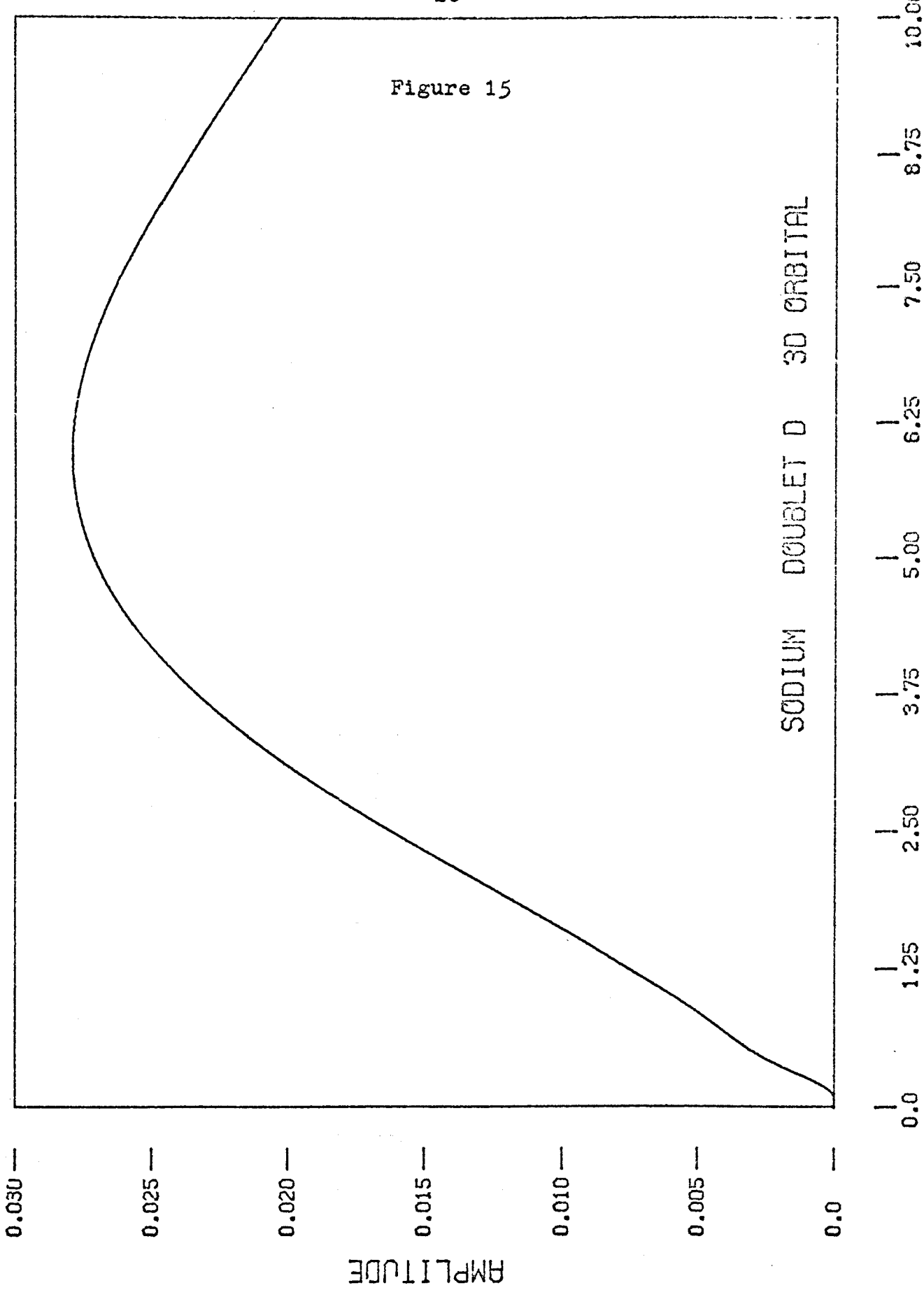
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

Figure 15


SODIUM DOUBLET D 3D ORBITAL
AMPLITUDE
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0.025
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0.015
0.010
0.005
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2.50
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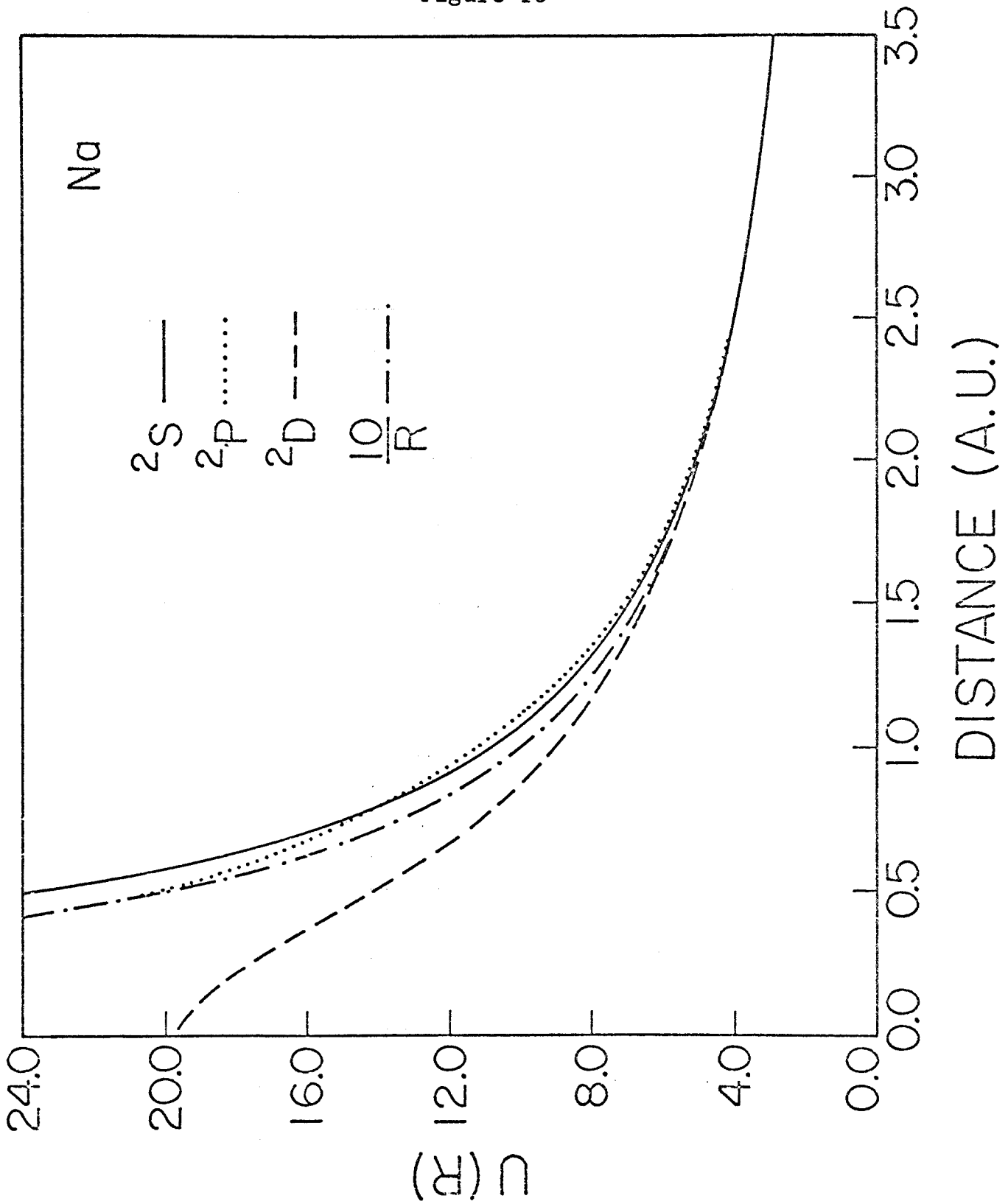
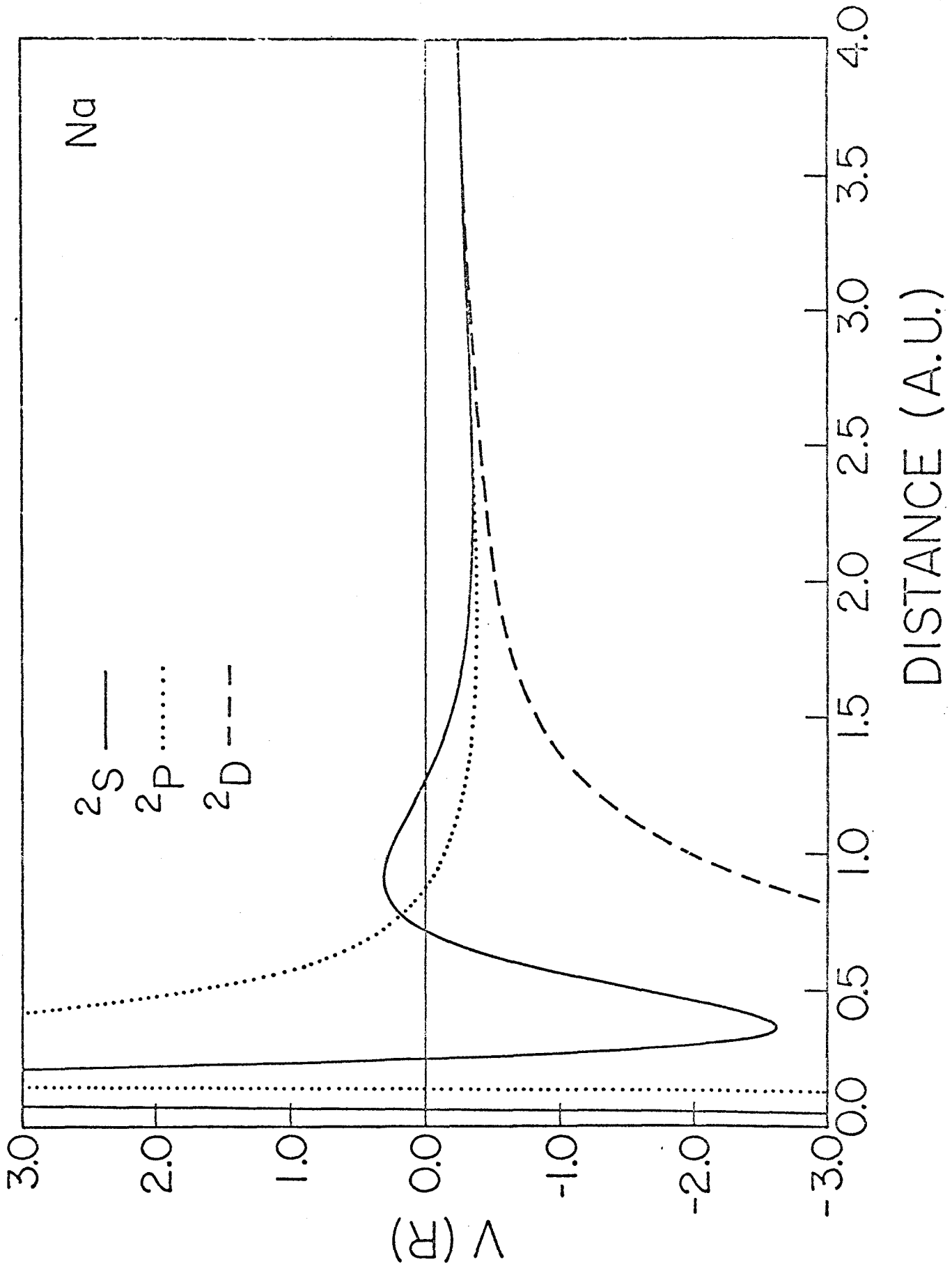
5.00
6.25
7.50
8.75
10.00
DISTANCE

Figure 16


Na
2S
2P
2D
10/R
U (R)
24.0
20.0
16.0
12.0
8.0
4.0
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
DISTANCE (A.U.)


Na
^2S
^2P
^2D
V (R)
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2.0
1.0
0.0
-1.0
-2.0
-3.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
DISTANCE (A.U.)

Figure 17

were calculated and compared to experiment. This is reported in Table 4. With this information, it is possible to move on to the consideration of the band structure.

Table 4

Comparison of Na S,P,D Pseudopotential Eigenvalues with Experiment

State	Pseudopotential Eigenvalue (a)	Experimental Orbital Energy (b)
$3\ ^2S$	-.18208873	-.18885851
$4\ ^2S$	-.07155570	-.07157907
$5\ ^2S$	-.03775222	-.03758500
$6\ ^2S$	-.02324997	-.02313253
$7\ ^2S$	-.01673595	-.01566172
$3\ ^2P$	-.10944050	-.11160045
$4\ ^2P$	-.05051122	-.05118027
$5\ ^2P$	-.02904466	-.02920329
$6\ ^2P$	-.01884940	-.01892309
$7\ ^2P$	-.01318114	-.01325214
$3\ ^2D$	-.05563463	-.05593719
$4\ ^2D$	-.03102171	-.03144279
$5\ ^2D$	-.02217508	-.02106511
$6\ ^2D$	-.01514680	-.01395315
$7\ ^2D$	-.01078597	-.01024700

a. Obtained by numerical integration to 100 au. Energies in hartree.

b. C. Moore, Atomic Energy Levels, Natl. Bur. Std.(U.S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D.C.,1949)

III. SODIUM BAND STRUCTURE CALCULATION

Recent work by O'Keefe and Goddard (7b) has been able to explain many of the anomalous properties of Li metal using a new approach to energy band calculations. This method is based on the GI method and makes explicit use of ab initio pseudopotentials of the type discussed in the first part of this paper. As has been pointed out, it is possible to extend the determination of the pseudopotentials to larger systems. From the application of these pseudopotentials to the band structure problem, one would hope to gain further insight into the nature of the alkali metals as well as further verification of the theoretical basis.

The usual context for considering band structure in solids is Hartree-Fock (14). In Hartree-Fock one has an antisymmetrized product of spin orbitals as the total wavefunction. The double occupancy requirement requires that the spin orbitals be paired, with one pair having the same space part and a different spin part. One of the great benefits of viewing the total wave function in this manner is that it allows us to view each orbital as a one particle state which describes the motion of one particle in the averaged field of all of the other particles. That is to say, it allows for an independent particle interpretation. However, there is a group of independent particle wavefunctions which are more general than Hartree-Fock, These are the GI wavefunctions (15). Now instead of having an antisymmetrized product, which can be written $\mathcal{A}\Psi$, where $\mathcal{A}$ is the antisymmetrizer, the total wavefunction is written $G_i^\gamma\Psi$ where G_i^γ is a more

complicated operator operating on both the space and spin wavefunctions. The G_i^γ operator creates a wavefunction which is an eigenfunction of $\hat{S}^2$, which satisfies the Pauli principle, and which does not require double occupation of the space orbitals. In particular, we wish to consider the particular sort of coupling for which the operator is G_F.

Consider the crystal to be composed of an even number of centers. In a small portion of the theoretical infinite crystal, this is no restriction. One would expect the entire system to be a singlet in the ground state so that it should be no restriction to consider a singlet system. For N electrons, there will be N/2 orbitals for each spin, usually denoted $\{\phi_a\}$ and $\{\phi_b\}$. For G_F coupling, it is no restriction to take all of the $\{\phi_a\}$ orbitals to be orthogonal, and all of the $\{\phi_b\}$ orbitals to be orthogonal. In general, the set $\{\phi_a\}$ will not be orthogonal to the set $\{\phi_b\}$. G_F coupling corresponds to taking all of the up spin orbitals and coupling them to obtain maximum spin, taking all of the down spin orbitals and coupling them to obtain maximum spin, and then coupling the two sets to obtain a singlet. Another way of saying this is to say that G_F coupling provides the proper treatment of spins for an alkali metal solid (16).

Within the G_F regime (17) we know that the total wavefunction is invariant (i) under transformations of the set $\{\phi_a\}$ among themselves and the set $\{\phi_b\}$ among themselves, and (ii) under transformations which take the set $\{\phi_a\}$ into the set $\{\phi_b\}$ and conversely. Symmetry transformations of type (i) commute with the G_F one-particle Hamiltonian but

those of type (ii) do not. Thus the G_F orbitals will have symmetries corresponding to the subgroup composed of elements of type (i). Of all of the subgroups of the full symmetry group of the molecule or solid, only those which do not contain elements which transforms the a orbitals and b orbitals into each other are possible symmetry groups for the orbitals. For the bcc space group, the most reasonable subgroup is the sc space group. In Figure 18 the bcc structure is shown as two interpenetrating sc structures. Note that the sites denoted a and b are not equivalent in the sc space group, thus we should expect a set of orbitals more concentrated on the a sites and a set of orbitals more concentrated on the b sites. However, since the two sets are related by a lattice translation, they are equivalent and we need only solve for one set.

This process leads to a good deal of simplification in terms of solving the problem. First of all, the problem may be solved in the Wigner-Seitz cell of one of the two interpenetrating cubic lattices. Such a Wigner-Seitz cell is pictured in Figure 19. This cell is twice the size of the bcc cell, which means that the Brillouin zone is half the size of the bcc Brillouin zone. Now the Fermi surface, instead of lying entirely within the Brillouin zone will extend past it in certain directions. In addition, each Hartree-Fock band should be split into two GF bands. Thus we should have, as in the case with lithium, two partially filled bands with a small band gap at the zone boundary.

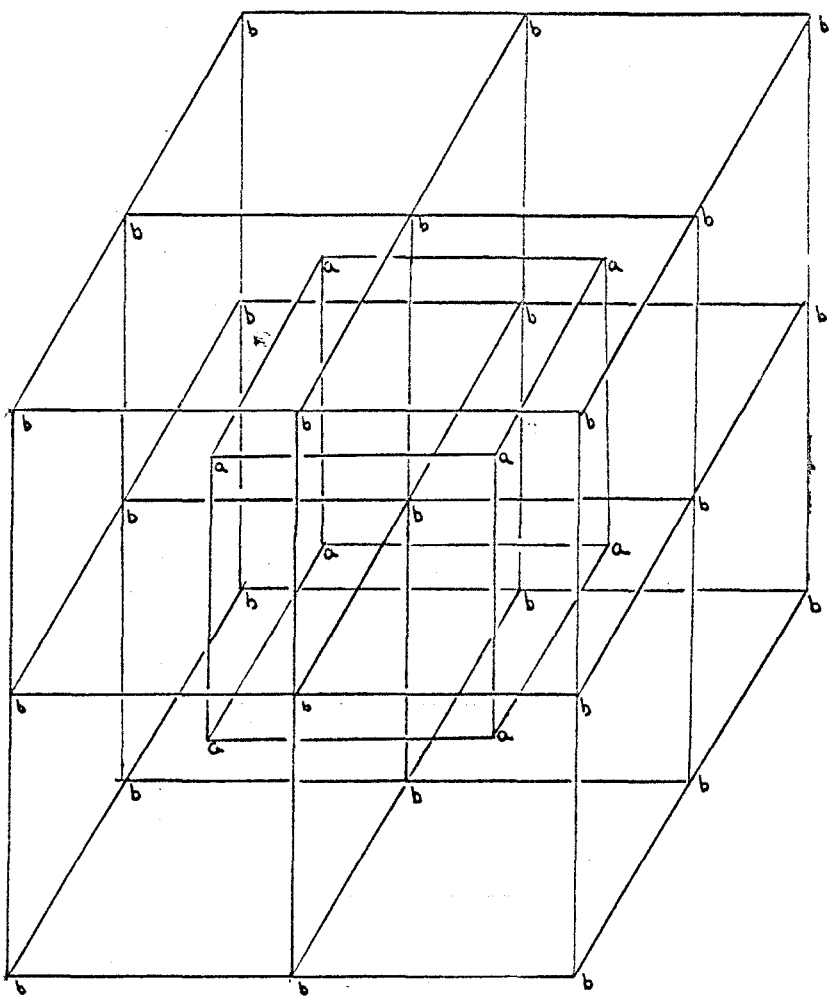

Figure 18

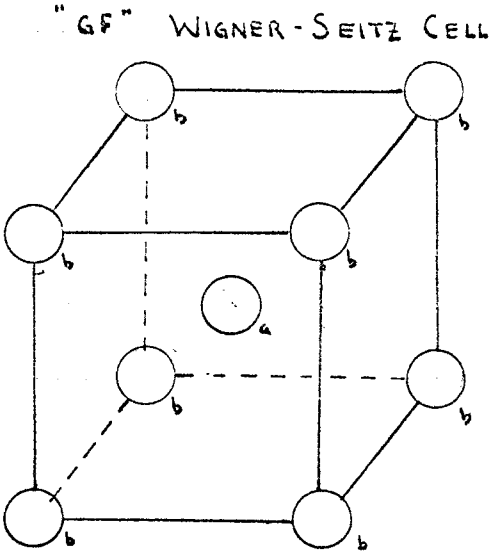

Figure 19

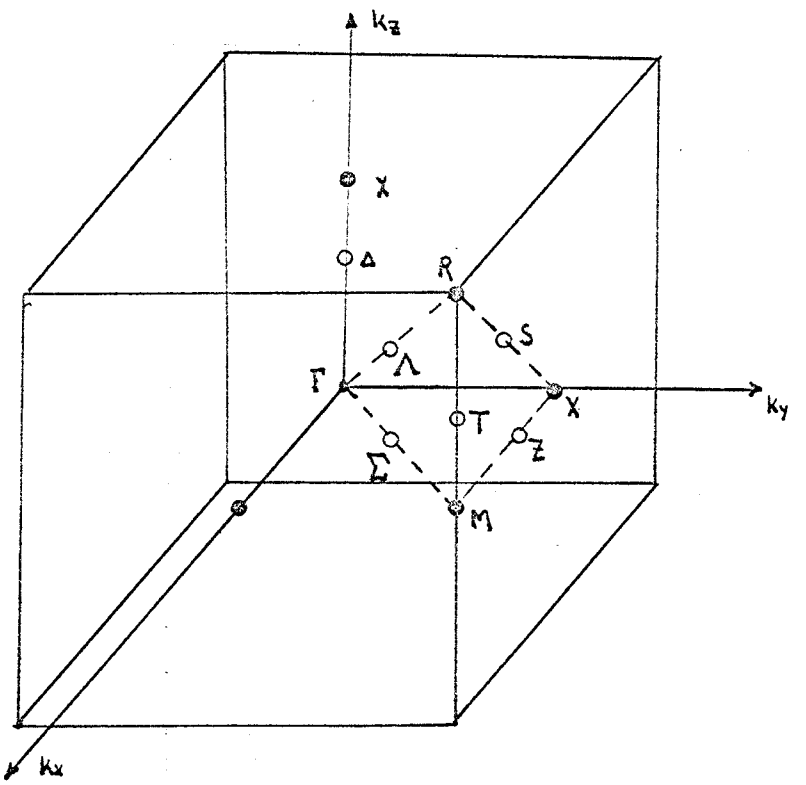

Figure 20

Simple Cubic Brillouin Zone with symmetry points

It is of interest to note that while GF provides the first real justification for the idea of two translationally equivalent lattices of opposite spin, the concept has been around for a while. If was originally proposed by Slater (18) for antiferromagnetic solids. Then when Löwdin (19) suggested the use of projected Hartree-Fock, he considered the idea of an alternant molecular orbital which might be applicable to systems satisfying Born-van Karman boundary conditions. The AMO concept was applied to Benzene (20) and was later used as a basis for disussing electron correlation in solids (25). Unfortunately, the mathematics served to obscure the basic points of the coupling, which the GF method does not, as well as to make the problem seem sufficiently intractible that it was not applied to any real solid.

The actual calculation is done in the following manner. First remember that the solution is for the orbital associated with the a site at the center of the Wigner-Seitz cell, not for electrons on the b sites. Furthermore, we want to solve the problem only with one cell using the total potential within that cell. The potential arises from two sources, an ion core on the a site and atoms at the corners. The ion core gives the regular interaction of an electron with the ion core, that is the pseudopotential for the atom. However, when the electron is close to a b site, the interaction is that of a spin up electron with a spin down atom, which is a singlet negative ion. That means that the potential from the b sites is a negative ion pseudopotential. (In actuality it turns out that the negative ion potential

is too long range to be correct, however the correct potential will be a negative ion like potential.) Furthermore, it is assumed that the contributions to the total potential due to the other ion cores is exactly cancelled by the electron cloud of the other cells. Thus the Hamiltonian for the system may be written

$$H = -\frac{1}{2}\nabla^2 + U_{CORE} + \sum_{\vec{R}_i} U_B(\vec{r}-\vec{R}_i)$$

where U_{CORE} is the atomic pseudopotential, U_B is the b site potential and $\vec{R}_i$ runs over the corners. The wavefunction is expanded in terms of plane waves which transform as the irreducible representations of the cub$^{e}_{A}$. That is, the one electron eigenstate Φ is expanded as

$$\Phi(\vec{k},\vec{r}) = \sum_{\vec{K}_i} C(\vec{K}_i)\exp\{i(\vec{k}+\vec{K}_i)\cdot\vec{r}\}$$

where $\vec{K}_i$ is chosen to run over a sufficient nember of reciprocal lattice vectors so that the solution converges. The potentials are expanded in terms of projection operators as previously explained. One then simply sets up the equations and performs the necessary integrations over the Wigner-Seitz cell. In so doing, we have found that it is not unduly complicated to perform the integrations over the actual cubic cell rather than over a sphere of the same volume or an inscribed sphere as is usually done. In practice, what is done is first to ignore the contribution of the b sites, assuming that their contribution is small and to perform the calculation with just the ion core potential. These results would be expected to be fairly correct although it was found in Li that the ordering of certain states was very dependent on using the total potential. This calculation was done in two steps.

These steps are a "zero order" calculation and a "first order" calculation described as follows.

The "zero order" calculation is derived from the potentials in the simplest way. Essentially, one uses the simplest form of the wavefunction which transforms as certain irreducible representations of the cube. The Hamiltonian is simply

$$-\frac{1}{2}\nabla^2 + U^{\ell}_{CORE}$$

U^{ℓ}_{CORE} means that for a state of a given symmetry, one considers only the potential for that symmetry, i.e. ℓ=s for s states, ℓ=p for p states, etc. The matrix elements between the simple plane waves give the energy eigenvalues, the matrix elements of U being simply the Fourier transforms of U. The lowest Fourier transforms for the sodium potentials are given in Table 5. The energy eigenvalues for various symmetry points on the Brillouin zone are given in Table 6 and in Figure 21 in the form of a band structure. The dashed lines are drawn to approximate the free electron like behavior one might expect and to show how the states might be expected to connect. The Fermi level is obtained by a simple free electron formula.

The "first order" calculation is performed in much the same way, however now the wavefunction is expanded in terms of a fairly large set of plane waves. The Hamiltonian is the one given above, again using only an a-site potential. The plane wave sets are chosen so that they transform as the desired irreducible representations of the cube. The eigen-

Table 5

Fourier Transforms of Na Pseudopotentials

$\vec{k}$	$V_{FT}(S)$	$V_{FT}(P)$	$V_{FT}(D)$
000	-.24973492	-.25304357	-.33914545
100	-.01234980	-.01405243	-.08620550
200	.00970926	.01244227	-.03660712
300	-.00089851	.00497590	-.02804581
400	-.00086445	.00505650	-.01743957
110	.00546427	.00539531	-.05679202
210	.00537631	.00918583	-.03538123
310	-.00024959	.00578013	-.02523715
410	-.00170537	.00411299	-.01737623
220	.00130678	.00687165	-.02841361
320	-.00117322	.00497857	-.02116104
420	-.00193491	.00347289	-.01546911
111	.00722802	.00874300	-.04601014
211	.00356753	.00816673	-.03275728
311	-.00055689	.00556175	-.02366743
221	.00058929	.00642427	-.02660229
321	-.00142692	.00468442	-.02012500
331	-.00191572	.00364075	-.01608302
222	-.00089255	.00526633	-.02233204
322	-.00182627	.00400162	-.01748654
332	-.00190122	.00318713	-.01437990
333	-.00166816	.00259169	-.01227969
444	-.00022572	.00121641	-.00782449

$\vec{k}$ in units of $2\pi/a$.

Table 6

Eigenvalues at High Symmetry Points

State	Zero Order	First Order
Γ_1	-.24973492	-.25467631
Γ_1'	.09147831	.09036017
Γ_{15}	.06904559	.03661126
Γ_{12}	-	.03871223
X_1	-.18467300	-.18843464
X_4'	-.16157942	-.16815147
X_2	-	.08781648
X_5'	-	.09316348
M_1	-.11414681	-.11813079
M_5'	-.10360757	-.10908693
M_3	-.06870303	-.07502271
R_{15}	.00738234	-.05209517
R_1	-.03092822	-.03802400
R_{25}'	-.00992280	-.01631622
R_2'	.02734030	.02503252

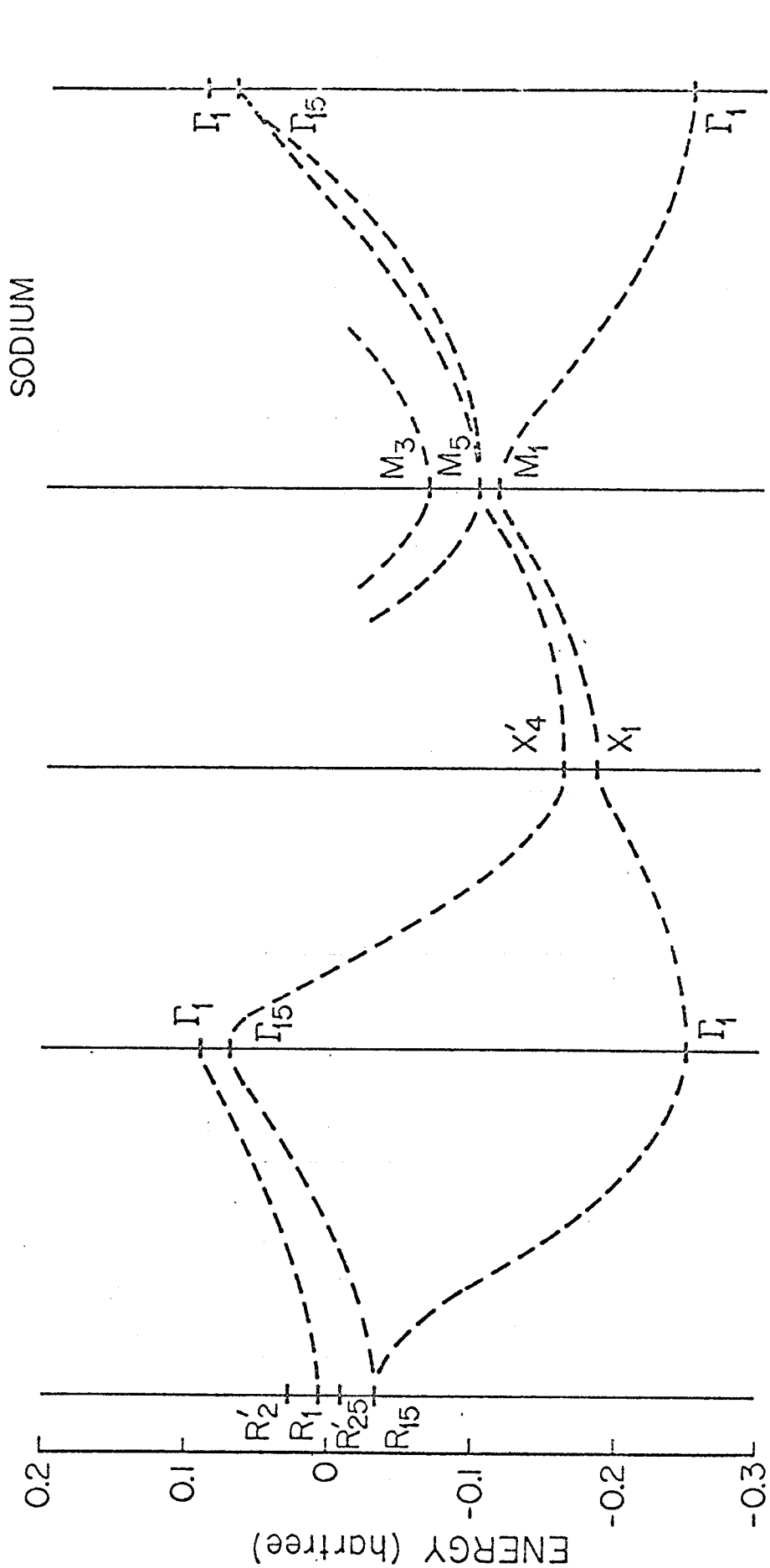
SODIUM
ENERGY (hartree)
0.2
0.1
0
-0.1
-0.2
-0.3
R'_2
R_1
R'_{25}
R_{15}
Γ_1
Γ_{15}
X'_4
X_1
M_3
M_5
M_1
$k = \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$
$k = \frac{2\pi}{a}(0,0,0)$
$k = \frac{2\pi}{a}\left(0, 0, \frac{1}{2}\right)$
$k = \frac{2\pi}{a}\left(c, \frac{1}{2}, \frac{1}{2}\right)$
$k = \frac{2\pi}{a}(0,0,0)$

Figure 21

values are then obtained by diagonalizing the Hamiltonian matrix. These results are also given in Table 6.

The next step should be to perform the complete band structure using both potentials, and then to correlate the experimental evidence to the band structure. For instance there are de Haas-van Alphen effect measurements on the Alkali metals (21) which indicate that the Fermi surface should be roughly spherical. There are also measurements on the electron moments performed by Compton scattering experiments (22) which give roughly the same information. The optical absorption spectrum of sodium shows a classical Drude region, an interband transition, and an indirect interband transition (23). The direct transition agrees qualitatively with the calculated results. One relatively interesting property of sodium is the soft X-ray emission spectrum (24). Here we find that near the Fermi surface there is a surge in intensity which could be explained quite readily if the X_1 state were to lie above the X_4' state. (Although either ordering could produce it, the X_1 above the X_4' is the more straight forward.)

While the present study indicates that we should expect to find good agreement with experimental values, only a complete band structure calculation, which includes the correct projection operators and the potentials on both sites could form a valid basis for comparison.

IV. CONCLUSION

First we see that the minimum kinetic energy orbital does form a good basis for unique, Hermitian, local potentials. While this method is somewhat limited in the sense that one must start with a Hartree-Fock orbital which describes one electron, it is still good where this condition is met. Second, the basic method developed for lithium does represent a valid development in that it will work for a second test case, sodium. This method should also be applicable to potassium, however the heavier alkali metals may not be accessible due to relativistic effects. Finally, we find for sodium a predominantly free electron like band structure similar to that of lithium but with a larger energy gap at the X point.

APPENDIX A

The general pseudopotential formalism for atoms and molecules, essentially as given by Cohen and Heine.(5)

Suppose we wish to solve for the valence orbital, ψ, in an atom or molecule. First we expand ψ in a few orbitals χ_n which have been orthogonalized to the core states ϕ_t. Thus we have

$$\psi = \sum_n c_n \chi_n \tag{1}$$

where $$\chi_n = f_n - \sum_t (\phi_t, f_n)\phi_t \tag{2}$$

the f_n being suitable smooth functions. Now we define

$$\phi = \sum_n c_n f_n . \tag{3}$$

Subsitution of (3) into (1) gives

$$\psi = \sum_n c_n (f_n - \sum_t (\phi_t, f_n)\, \phi_t) \tag{4}$$

$$= \sum_n c_n f_n - \sum_t (\phi_t, \sum_n c_n f_n)\, \phi_t \tag{5}$$

$$= \phi - \sum_t (\phi_t, \phi)\, \phi_t \tag{6}$$

We know that ψ satisfies the equation $H\psi = E\psi$. Thus we have substituting (6) for ψ,

$$H\phi - \sum_t (\phi_t, \phi) H\phi_t = E\phi - \sum_t (\phi_t, \phi) E \phi_t \tag{7}$$

$$H\phi + \sum_t (E - E_t)(\phi_t, \phi)\phi_t = E\phi \tag{8}$$

Thus if we define

$$V^R \phi \equiv \sum_t (E - E_t)(\phi_t, \phi)\phi_t \tag{9}$$

we see that we have the Phillips-Kleinman (1) form

$$(H + V^R)\phi = E\phi$$

where now V^R is a non-local potential and ϕ is a smooth "pseudo-orbital". Furthermore, V^R is repulsive since E_t, the core energies, are lower than E, and therefore serves to cancel some of the attractive potential in H.

We will now demonstrate the non-uniqueness of the "pseudo-orbital", ϕ, and thus of the potential. If Cn is a set of coefficients of energy E then so is

$$C_n' \equiv C_n + \sum_t a_t (f_n, \phi_t) \tag{11}$$

Thus we have

$$\phi' = \sum_n C_n' f_n = \sum_n C_n f_n + \sum_n \sum_t a_t (f_n, \phi_t) f_n$$

$$= \sum_n C_n f_n + \sum_t a_t \sum_n (f_n, \phi_t) f_n . \tag{12}$$

But $\sum_n (f_n, \phi_t) f_n = \phi_t$. Thus we have

$$\phi' = \phi + \sum_t a_t \phi_t \tag{13}$$

Now we have for ψ

$$\psi = \phi + \sum_t a_t \phi_t - \sum_{t'} (\phi_{t'}, \phi + \sum_t a_t \phi_t) \phi_{t'} \tag{14}$$

$$= \phi + \sum_t a_t \phi_t - \sum_{t'} (\phi_{t'}, \phi) \phi_{t'} - \sum_{t'} a_{t'} \phi_t \tag{15}$$

$$= \phi - \sum_t (\phi_t, \phi) \phi_t \tag{16}$$

And so we have that ϕ may be replaced by $\phi + \delta\phi$ where $\delta\phi = \sum_t a_t \phi_t$ and the valence orbital ψ is unchanged. Furthermore.

$$(H + V^R)(\phi + \sum_t a_t \phi_t) = E(\phi + \sum_t a_t \phi_t) \tag{17}$$

$$H\phi + \sum_t a_t H\phi_t + V^R\phi + \sum_t a_t V^R \phi_t = E\phi + \sum_t a_t E \phi_t \tag{18}$$

$$H\phi + \sum_t (E_t - E) a_t \phi_t + V^R\phi + V^R \sum_t a_t \phi_t = E\phi \tag{19}$$

However, from the definition of V^R we have that

$$V^R \sum_t a_t \phi_t = \sum_{t'} \sum_t a_t (E - E_{t'}) (\phi_{t'}, \phi_t) \phi_{t'} \tag{20}$$

$$(\phi_{t'}, \phi_t) = \delta_{tt'}$$

$$V^R \sum_t a_t \phi_t = \sum_t a_t (E - E_t) \phi_t$$

Thus the second and fourth terms of the left-hand side of (19) cancel to give

$$H\phi + V^R\phi = E\phi$$

$$(H+V^R)\phi = E\phi$$

Therefore, the local potential is not uniquely determined.

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