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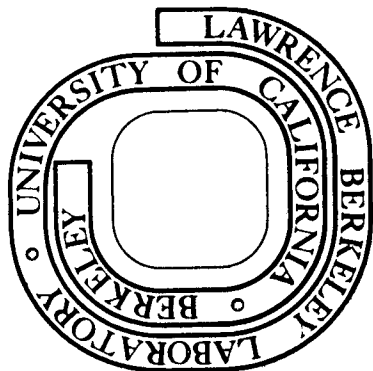
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Self-consistent Pseudopotential Calculations on Si (111)
Unreconstructed and (2 × 1) Reconstructed Surfaces*

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Abstract

A recently developed method for the self-consistent calculation of localized configurations has been applied to the Si (111) surface. Results have been obtained for an unrelaxed, relaxed and (2 × 1) reconstructed (buckled) surface. Densities of states and charge densities are presented and discussed. The salient experimental findings are reproduced.

In this letter we report self-consistent pseudopotential calculations on Si (111) surfaces. Three different surface models have been studied and the resulting calculated density of states curves and electronic charge density distributions have been examined to extract the essential physical features of the various models. In each case the calculations were carried to self-consistency following a recently developed procedure¹ which is based on the pseudopotential scheme.

Similar to the calculation of the electronic structure of a Si_2 molecule presented in ref. 1 the requirement of self-consistency proves to be absolutely necessary to account for the modified screening in the surface region.

The three different models for the Si (111) surface studied are:

a) An unrelaxed, unreconstructed surface, in which all surface atoms remain at their exact "bulk" positions,

b) A relaxed surface, in which the outermost atomic layer is rigidly relaxed inwards by an amount of $\Delta = 0.33 \text{ \AA}$. These two models have been studied by Appelbaum and Hamann² in the only previously existing self-consistent approach to the problem, and their results are basically confirmed by our calculations. In addition we find new types of surface states and are able to present density of states curves.

The third model we studied is

c) A (2×1) reconstructed surface, in which atoms of the outermost atomic layer are alternatively moved inward and outward to form a (2×1) planar unit cell. This model has been refined in a second step as first proposed by Haneman³ by moving atoms of the second atomic layer slightly laterally, the effect of which was small compared to the effect of the "buckling" at the first step. The predominant result of this (2×1) reconstruction is the splitting of the "dangling-bond" surface state in the gap into two peaks corresponding to two separate surface bands one of which is occupied. This

essential feature is in good agreement with experiments⁴ and is not obtained in the other two models.

The method used to obtain the electronic surface structure in a self-consistent fashion has been discussed in detail in our recent Si_2 molecule calculation,¹ therefore we only review the essential features in this paper. The local configuration in the present case is a 12-layer slab of Si, simulating two non-interacting surfaces. The slab is placed in a periodic lattice sufficiently spaced to prevent interaction between the different slabs (or surfaces). This artifact has the enormous advantage that the system can now in principle be treated as any periodic crystal and that the pseudopotential method in its standard form can be applied. A self-consistent treatment, however, is necessary to achieve the correct screening of the atoms in the neighborhood (~3 to 4 atomic layers) of the surfaces.

One problem which arises when simulating surfaces by finite slabs of atoms periodically repeated, is spurious structure in the density of states due to the "unreal" periodicity of slabs perpendicular to the surfaces.⁵ Spurious two-dimensional singularities occur. Their number increases with the number of atomic layers per slab. For the "true" surface case these singularities become "dense" and disappear. For finite slab calculations all structures in the density of states have to be investigated in this spirit. Similar problems are encountered when simulating an amorphous material by large unit cells periodically repeated.⁶

As for the molecule case¹ the calculations are initiated with an empirical pseudopotential carried over from crystalline calculations. From the resulting total charge density, screening and exchange potentials are derived and added to an atomic Si^{+4} ion-potential.⁷ New screening and exchange potentials are derived and the process is repeated until self-consistency (stability of the eigenvalues or stability of the input versus output potentials within 0.1 eV) is reached. At each step a density of states curve has been computed from 336 k-points in the two-dimensional Brillouin zone to guarantee a precise location of the Fermi level. The total charge density could then be derived from all states with energies below the Fermi level. From the self-consistent calculation an ionization potential of about $\phi = 4.0$ eV was obtained for the relaxed surface.

Density of states curves for the self-consistent results for the three surface models are presented in Fig. 1. Since these curves represent the total density of states for a 12 layer slab, their overall features strongly resemble those of the Si bulk density of states. To locate structures associated with surface states (no distinction is made in the present case between bona fide surface states and strong surface resonances) we investigated the charge density distributions for small energy intervals scanning the entire width of the valence bands. As already mentioned, because of the existence of artificial two-dimensional singularities

not all sharp structures in the density of states correspond to surface states. The locations of some of the very apparent surface states (for the relaxed case) are indicated by arrows in Fig. 1. Their energies are compared in Table 1 with experimental data obtained from UPS measurements⁴ and with previous calculations^{2,8} on Si (111) surfaces.

In particular we investigated the points Γ (center) and K (corner) of the two-dimensional hexagonal Brillouin zone. Model calculations⁹ indicate that K rather than M (edge midpoint) is a point of special interest to study surface states.

Let us first discuss the results at Γ . Below the energy zero which was chosen to coincide with the bulk valence band edge E_V we find (in agreement with Appelbaum and Hamann² and Pandey and Phillips⁸) three surface states. Two of them are degenerate and close to E_V representing the transverse back bonds with charge localized between the first and second atomic layer. The third state is localized at the bottom of the valence bands and is predominantly s-like around the outermost atoms. With the "dangling bond" state above E_V , which we shall discuss later, there are four surface states at Γ which agrees with the classical tight binding concept.⁸ The situation, however is different at K. We find only one "pure" transverse back bond K_{tb} , the remaining states $K_{\perp b}$ and $K_{\parallel b}$, having more longitudinal or s-like character. The interesting feature is that some states $K_{\perp b}$, (at -2.0 eV and

-9.7 eV) have most of their charge localized between the second and third layer in contrast to the state $K_{\ell b}$ (at -8.5 eV) which is a mixture of s-like and p-like states at the outermost atoms giving rise to a charge distribution between the first and second layer. In Fig. 2 we show a contour map of the charge of the state $K_{\ell b}$ at -2.0 eV. We would like to stress the fact that surface states apparently can "penetrate" into the second longitudinal bond which puts a limitation on the position of a "matching plane"² separating the surface region from the bulk. The appearance of surface states at K in the second longitudinal bond increases the number of surface states from four to five which has been predicted by model calculations⁹ but which is in contrast to the findings of Pandey and Phillips.⁸ At the point M the situation is expected to be similar but less pronounced with some of the surface states merging into the bulk continuum.⁹

Let us now examine the surface states in the energy gap above E_V . As shown in Fig. 1 we find for the unrelaxed, unreconstructed surface one very flat surface band about mid gap. This almost dispersionless band is half occupied, placing the Fermi level right at the peak. The charge distribution of these (either occupied or empty) mid gap surface states is very much "dangling bond"-like exhibiting a pronounced p-like charge centered at the outermost atoms. When the last atomic layer is relaxed inward, the back bonds

get stronger resulting in a mixing of the "dangling bond" states with lower lying back bond states. This increases the interaction between the individual "dangling bonds" via the second atomic layer and the dispersion of the surface band increases. In fact, the resulting density of states exhibits the asymmetric shape of critical points expected for a planar triangular network of s- or π -like orbitals. The critical points are labelled K_d and Γ_d in Fig. 1 indicating their origin in k -space. A charge density plot for the states K_d is shown in Fig. 3. It exhibits the very pronounced "dangling bond" character. The unoccupied states Γ_d show a stronger mixing with back bonds. As for the

unrelaxed case there is only one surface band which is half occupied. This changes qualitatively when we consider the (2×1) reconstructed surface. Enlarging the real space unit cell in one dimension corresponds to folding back the Brillouin zone in certain directions. Thus two surface bands will appear separated by a gap resulting from the potential perturbation of the reconstruction. If this gap is smaller or comparable to the dispersion of the surface bands it might not lead to a vanishing density of states between the bands. This situation is found for the self-consistent result of a (2×1) "buckled" surface (see Fig. 1) with atomic displacements of $\Delta_{in} = 0.11 \text{ \AA}$ and $\Delta_{out} = 0.18 \text{ \AA}$ as suggested by Haneman.³ The two peaks in the density of states now correspond to two separate bands,

thus allowing e.g. for an infrared surface absorption as observed by Chiarottiet al.¹⁰ The states of the two peaks in Fig. 1 show very interesting "real space behavior." Electrons in states originating from the lower peak labelled d_{out} predominantly sit on those atoms which have been moved outward (with a charge distribution resembling the one given in Fig. 3) and avoid the atoms which have been moved inward. Conversely the wavefunctions for unoccupied states of the peak labelled d_{in} are mostly concentrated around those atoms which have been moved inward. The surface thus exhibits a (2×1) pattern of 2-fold occupied "dangling bond" states. Roughly speaking, the unpaired electron of every second surface atom (in) is transferred to its neighboring atom (out) where it pairs up with another electron.

In addition to the appearance of two split surface bands we observe an overall shift towards lower energies placing the occupied surface state at about E_V . This trend is compatible with all available experiments⁴ which give a surface state at about 0.5 eV below E_V .

Our self-consistent calculations on the (2×1) reconstructed surface model thus give results which for the first time agree with the salient features of the experimental findings, i.e. split surface states, possibility of infrared absorption and lowering of the occupied surface band below E_V .

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- † Swiss National Science Foundation fellow.
- # National Science Foundation graduate fellow.
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Table 1

	SCLC relaxed	AH ^d	PP ^e	experiment (2x1)	(UPS) (7x7)
Γ	+1.2	+0.88	+1.04		
	-1.4(2x)	-1.95(2x)	-1.71(2x)		-1.5 ^a
	-12.6	-12.87	-12.90	-11.7 ^a	-12.3 ^a
K	+0.5 (0 for 2x1 reconstructed)		+0.11	-0.5 ^a -0.45 ^b -0.6 ^c	+0.1 ^a
	-2.0				-3.6 ^a
	-4.2		-5.65		
	-8.5		-8.35		-7.5 ^a
	-9.7		-9.60		

^aJ. E. Rowe, H. Ibach, Phys. Rev. Lett. 32, 421 (1974).

^bD. E. Eastman, W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

^cL. F. Wagner, W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).

^dReference 2.

^eReference 8.

Table Caption

Table 1. Calculated energies of several surface states of the relaxed surface at Γ (center) and K (corner) of the two-dimensional Brillouin zone. Also indicated are experimental (UPS) results for (2×1) and (7×7) reconstructed surfaces. The energy zero is taken at the bulk valence band edge E_V .

Figure Captions

Figure 1. Calculated density of states for a 12 layer Si (111) slab. The results for the unrelaxed (full line) and relaxed surfaces are superimposed. The labelling of the various surface states refers their locations in k -space and to the type of bond (transverse or longitudinal). Inserted is the density of states for the "dangling bond" of the (2×1) reconstructed surface.

Figure 2. Charge density contours in a (110) plane cutting the relaxed (111) surface of the longitudinal back bond state K_{lb} .

Figure 3. Charge density contours of the occupied part K_d of the dangling bond states for the relaxed surface model.

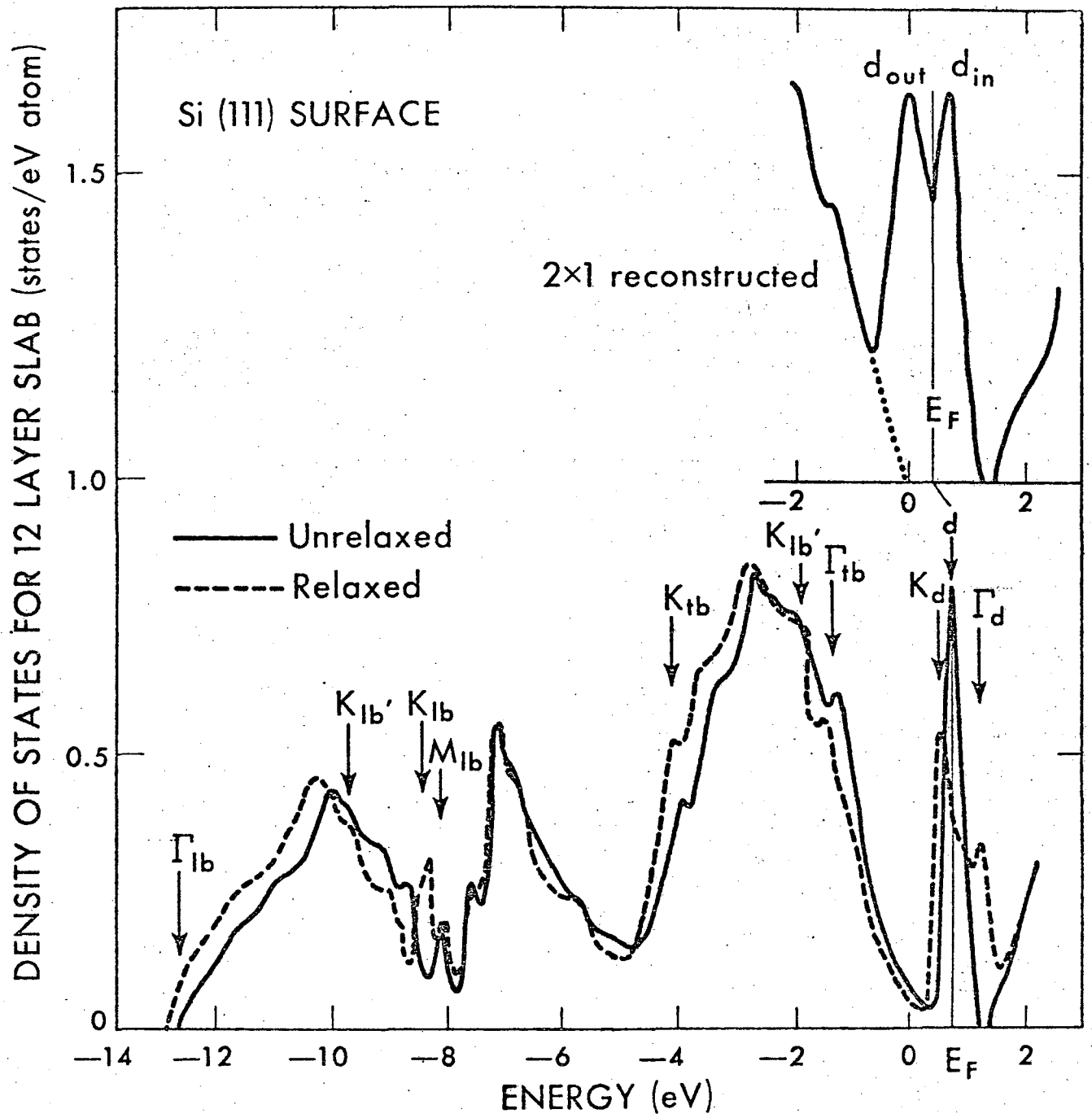


Figure 1

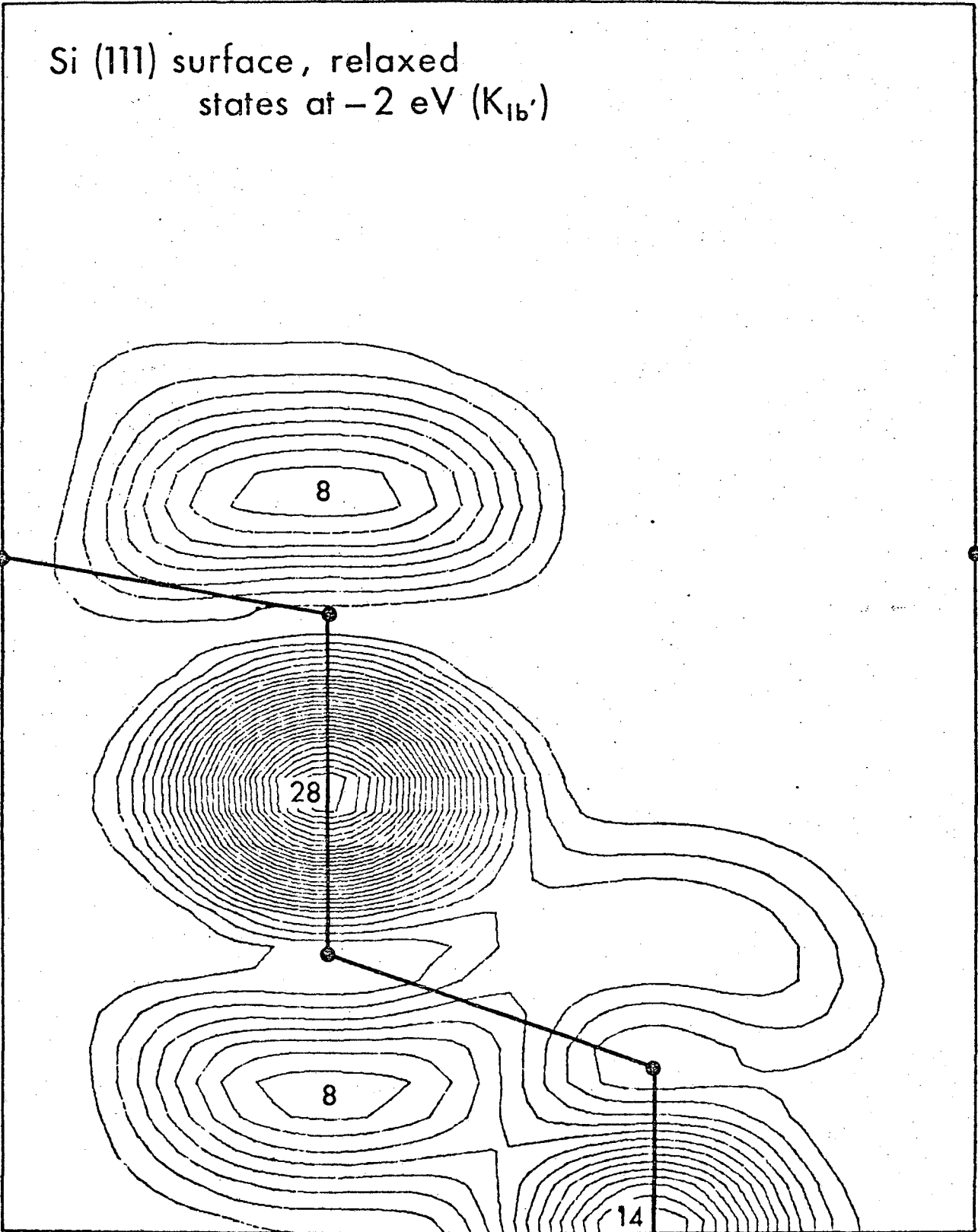


Figure 2

Si (111) surface, relaxed
states at + 0.5 eV (K_d)

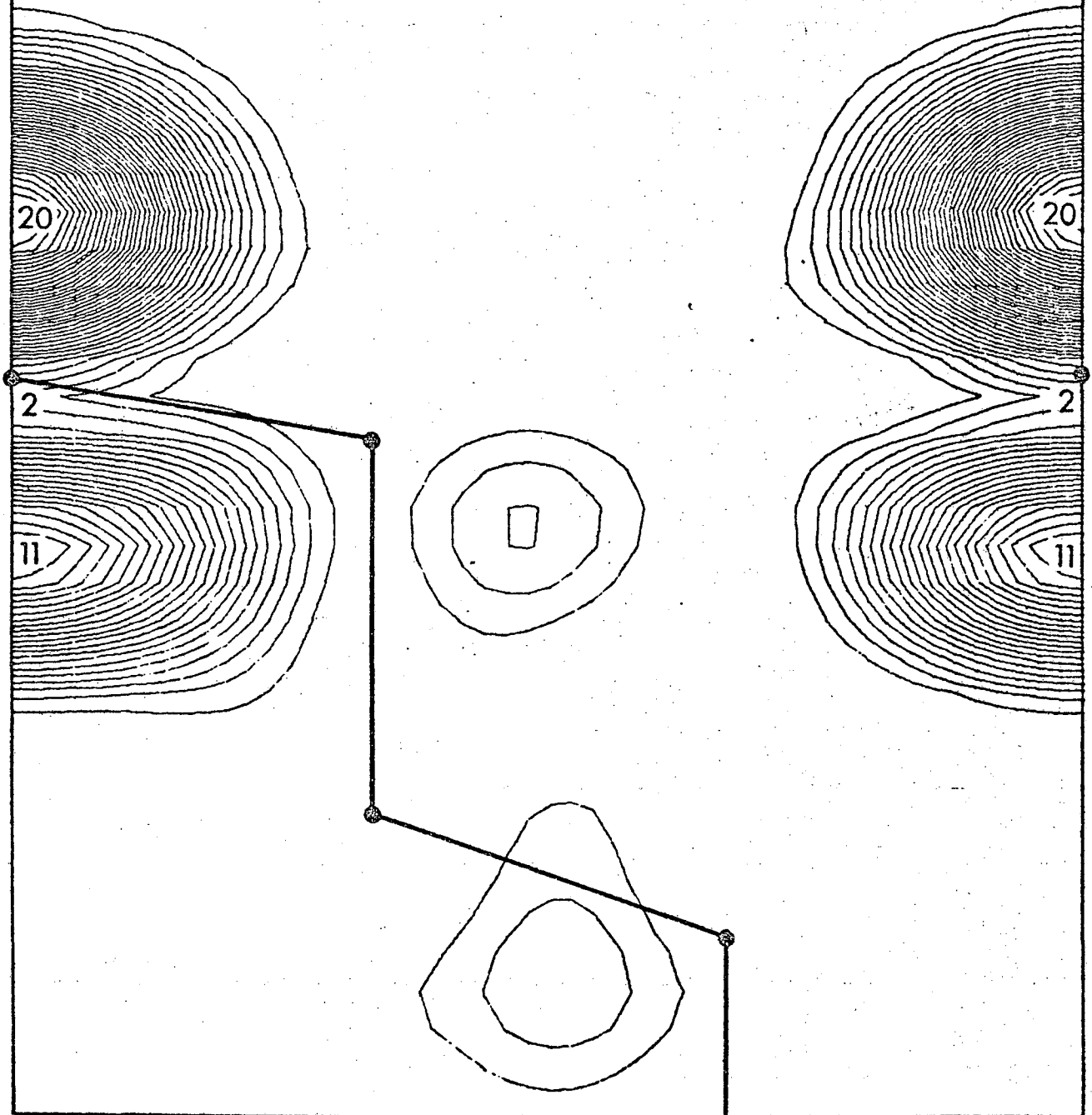


Figure 3

U S G O V E R N M E N T

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