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Self-Consistent Pseudopotential Method for Localized Configurations: Molecules*

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Abstract

A method is developed to use pseudopotentials in a self-consistent manner to describe localized configurations such as molecules, surfaces, impurities, vacancies, finite chains of atoms, adsorbates and solid interfaces. The method is described and specific application is made to the Si_2 molecule.

We have developed a method which extends the pseudopotential scheme to localized configurations. These calculations are done self-consistently and the approach is applicable to problems such as solid surfaces, localized impurity and vacancy states, atomic and molecular states, finite chains or layers, adsorbates, and interfaces between solids. The scheme has many of the advantages of the pseudopotential method in that it uses a simple plane wave expansion and the starting potential can be obtained from experimental data. It goes beyond the usual pseudopotential approach through the requirement of self-consistency. We treat here the case of a silicon diatomic molecule both to illustrate the method and to demonstrate the interesting results which are possible for molecular calculations. This is the first molecular calculation using self-consistent pseudopotentials to our knowledge.

Pseudopotential methods have evolved considerably since their introduction[1] in the late 1950's. The use of model potentials[2] and the empirical pseudopotential method (EPM)[3] have yielded a great deal of information about solid state properties such as band structure, optical response functions and electronic charge densities.[4] In all of these cases the systems considered were assumed infinite and periodic; and possible extensions of the method to local configurations in solids e.g. localized impurities or solids without long range periodicity were not obvious. An attempt[5] was made to use the pseudopotential scheme to study amorphous materials. Complex cells were repeated infinitely and the effects of the complexity of the unit cells on the calculated properties yielded information about how the prominent features of the structure (e.g. even and odd numbered rings of bonds) influenced the properties (e.g. electronic density of states). A true amorphous system was not generated, but information gained from studies of increasingly complex cells was extremely useful.

The method discussed here is somewhat related to the above scheme, and it is directly applicable to the specific problem of interest. The method is straightforward and initially involves putting the local configuration of interest into the structure factor. In the pseudopotential formulation, the crystalline pseudopotential form factors, $V(\underset{\sim}{G})$, are written in terms of atomic potential form factors, $V_a(\underset{\sim}{G})$ through the structure factor $S(\underset{\sim}{G})$,

$$V(\underset{\sim}{G}) = \sum_{\tau_a} S(\underset{\sim}{G})V_a(\underset{\sim}{G})$$

$$S(\underset{\sim}{G}) = e^{i\underset{\sim}{G}\cdot\underset{\sim}{\tau}_a} \qquad (1)$$

where $\underset{\sim}{G}$ is a reciprocal lattice vector and $\underset{\sim}{\tau}_a$ are the basis vectors to the various atoms in a primitive cell. The basic scheme is to include in $S(\underset{\sim}{G})$ the essential features of the local configuration. In the case of a molecule, the structure factor can be constructed to create a cell with a molecule and sufficient empty space around the molecule to provide isolation from the next molecule when the cell is repeated. For a surface, usual periodicity can be retained in two dimensions and a slab of space can be inserted to provide a surface in the third dimension. The impurity or vacancy problem requires a cluster of host atoms surrounding the site of interest. Ultimately the cell chosen is repeated indefinitely to allow the use of the pseudopotential method. A similar, but not self-consistent approach has been used by Kleinman et al.[6] to calculate surface properties in Al.

Self-consistency however is essential in obtaining realistic solutions since the calculations will start with potentials derived for bulk calculations. It is necessary to allow the electrons to react to the boundary conditions imposed by the local configuration and the resulting readjustment and screening is a fundamental part of the problem. For example, in the molecular case or the surface case, charge will first spill out into the regions chosen to be empty space between the configurations of interest. In practice the self-consistency requirement results in a potential which pulls the charge back to the molecule or surface in the appropriate way. Also, the self-consistent screening potential has to be completely general and is not necessarily a superposition of atomic potentials.

In the scheme described above, the configuration of atoms and spaces can be as complex as desired. The ultimate limitation on the number of atoms is the amount of computer time necessary to generate the eigenvalues and eigenfunctions through solution of the secular equation. The basis set is formed by Bloch waves expanded in terms of free electron eigenfunctions.

The starting potential can be an ionic model potential fit to atomic term values and screened appropriately or a potential obtained from measurements on bulk solid state properties. In both cases the results are the same once self-consistency is reached. The problems with the method come mainly via the artificial long-ranged symmetry imposed, but most of the consequences can be dealt with. Some examples are: the interaction between configurations; the fact that the potential which should depend continuously on wavevector, q, is approximated by form factors at $\underset{\sim}{q}$'s equal to the $\underset{\sim}{G}$'s of the chosen lattice structure; and the symmetry of the configuration to some extent dictates the choice of lattices. Most of the above potential problems are eliminated or reduced by taking large enough cells and cells of the appropriate structure or symmetry. In the diatomic molecule case which has $D_{\infty h}$ symmetry, the most convenient lattice structure is hexagonal with D_{6h} symmetry. Thus the ∞ rotational symmetry of the wavefunction is simulated by sets of six-fold "stars" of plane waves. Test calculations on the Si_2 molecule in a trigonal lattice with D_{3d} symmetry show that the self-consistent results are weakly dependent on the chosen "crystal structure" provided convergence is reached i.e. enough plane waves are taken into account.

The Si_2 molecule calculation was done in the following way. The molecule was placed in a hexagonal lattice with a c/a ratio chosen such that the distance between any two atoms not belonging to the same molecule was larger than three bond lengths. The molecule bond length was taken from experiment to be 2.25 Å in the ground state[7] which differs considerably from the 2.34 Å for the Si crystal. The first step in the self-consistent calculation was performed using the superposition of two atomic potentials taken from empirical crystal calculations. A continuous curve[3] of the form

$$V(q) = \frac{a_1(q^2-a_2)}{\exp(a_3(q^2-a_4))+1} \tag{2}$$

was fit to the few crystalline form factor values to provide potential values at the new "molecule $\underset{\sim}{G}$-vectors". The dispersion of the eigenvalues in $\underset{\sim}{k}$-space which is a measure of the interaction of the different molecules with each other was of the order of 0.8 eV at this stage; it decreased to about 0.2 eV in the course of self-consistency. From this starting calculation the total charge $\rho(\underset{\sim}{r})$ was evaluated in terms of its Fourier components $\rho(\underset{\sim}{G})$ and a Hartree-like screening potential

$$V_H(\underset{\sim}{G}) = \frac{4\pi e^2\rho(\underset{\sim}{G})}{\Omega_c|\underset{\sim}{G}|^2} \tag{3}$$

defined by

$$\Delta V_H(\underset{\sim}{r}) = -4\pi e^2\rho(\underset{\sim}{r}) \tag{4}$$

as well as an exchange potential given by

$$V_x(\underset{\sim}{r}) = -\left(\frac{3}{2\pi}\right)(3\pi^2)^{1/3}e^2\rho(\underset{\sim}{r})^{1/3} \tag{5}$$

were computed. The use of a statistical exchange of the above form for atoms, molecules and solids has been proven to yield satisfactory results. The calculation of $V_x(\underset{\sim}{r})$ requires knowledge of the function $\rho(\underset{\sim}{r})^{1/3}$. For this purpose

$\rho(\underset{\sim}{r})$ was evaluated on a grid of points (~10,000 per unit cell), the cube root was taken at each grid point and the result was transformed back into a Fourier series resulting in $V_x(\underset{\sim}{G})$. The sum of these potentials was added to a bare ion pseudopotential obtained from empirical atomic calculations.[2] The local "on the Fermi sphere" approximation to this orginally non-local potential was used and a continuous curve of the form

$$V_{ion}(q) = \frac{a_1}{q^2}\,(\cos(a_2 q)+a_3)e^{a_4 q^4} \qquad (6)$$

was fit to the results. The use of this atomic ionic potential in the molecular case is also justified by the following. If this potential is used in a self-consistent band structure calculation for the crystal excellent results are obtained. In fact the final self-consistent crystal potential is essentially identical to the original empirical crystalline potential (Fig. 1).

The computational procedure was then continued until self-consistency was reached. The process of reaching self-consistency can be speeded up by interpolating appropriately between output and input potentials for consecutive steps. We thus needed five steps to reach selfconsistency of the eigenvalues to within 0.05 eV. The resulting potentials $V_{ion}(\underset{\sim}{r})$, $V_H(\underset{\sim}{r})$ and $V_x(\underset{\sim}{r})$ are plotted in Fig. 1 along the line, connecting the two Si atoms. The total self-consistent potential is also shown and compared to the empirical input potential which gives the best description of Si-atoms in the crystalline phase. The interesting results are that:

a) the Hartree screening potential is essentially featureless

b) the exchange potential is comparable in strength to the total self-consistent potential

c) the total self-consistent potential is considerably deeper than the empirical starting potential because of the increased exchange potential.

Also indicated in Fig. 1 are the occupied molecular one-electron energy levels σ_S at -1.30 ryd, σ_S^* at -0.96 ryd, σ_p at -0.71 ryd and π_p at -0.69 ryd.

In Fig. 2 we display charge density contours for the four occupied molecular levels. The charge density values are given in $2e/\Omega_c$ where $\Omega_c = 400$ Å^3 is the unit cell volume. The lowest level σ_S contains mostly s-like charge in a bonding-like configuration with its maximum between the two atoms. The next higher level σ_S^* has antibonding s-like character. Some admixture of p-states quantized along the molecular axis is present. The wavefunctions of the third occupied level are predominantly p-like at the two atoms and overlap forming a σ-type bonding state. The fourth (occupied) and fifth (empty) level are quasi-degenerate. The occupation of one of these levels lifts the exact degeneracy in the course of self-consistency by about 0.05 eV which is smaller than the artificial dispersion of 0.2 eV of the levels. The wavefunctions are mostly p-like in character and form π-type bonding states. The σ_p^* and π_p^*

antibonding levels lie at higher energies and are unoccupied. This would leave the molecule in a singlet ground state configuration. Experimentally[7] the ground state is found to be a Σ triplet, (Hund's rule) which in our model is quasi-degenerate with the singlet state. The inclusion of spin-dependent correlation potentials would be necessary to distinguish between the two states. The total charge density corresponding to the four occupied levels is presented in Fig. 3; the units of the indicated values are the same as in Fig. 2. To obtain a measure for the amount of charge in the bond we proceed as in Ref. 4 and integrate the charge pile-up over a region defined by the outermost closed contour. This yields a value of $Z_B = 0.138$ (in units of e) which is within computational accuracy identical to the crystalline value of $Z_B = 0.125$.

Concluding we may say that the strength of this new kind of self-consistent calculation lies in the fact that it is a straightforward extension of the well established pseudopotential method which is known to yield highly accurate results for the electronic structure of crystals.

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Figure Captions

Fig. 1. Molecular potentials plotted along a line connecting the two Si atoms. Also indicated are the molecular orbital energies.

Fig. 2. Charge density contours for the four occupied molecular orbitals. The values are given in $2e/\Omega_c$ where $\Omega_c = 400\ \mathring{A}^3$ is the unit cell volume.

Fig. 3. Total charge density of the Si_2 molecule in the ground state.

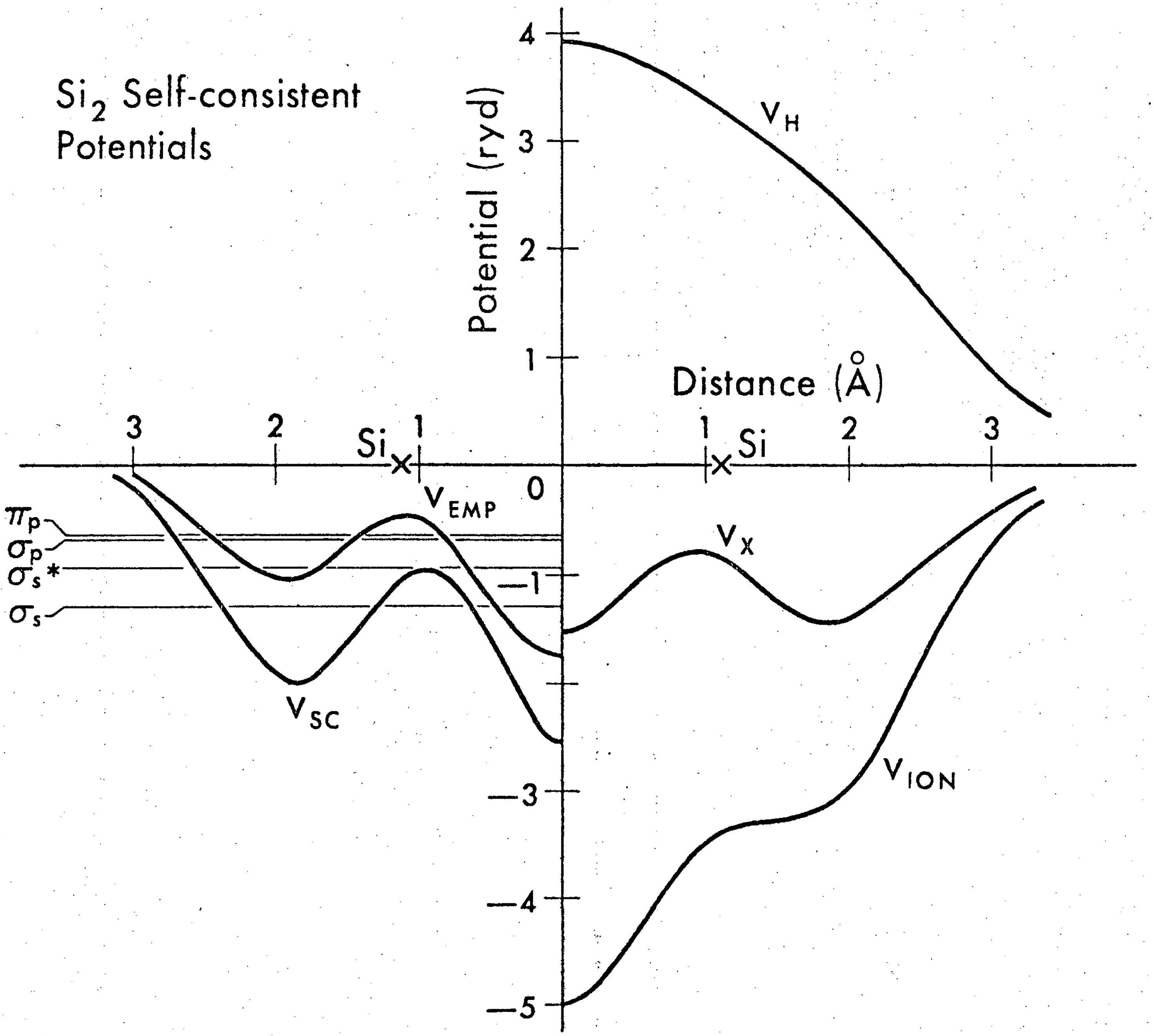
Si$_2$ Self-consistent Potentials
Potential (ryd)
4
3
2
1
0
−1
−3
−4
−5
Distance (Å)
3
2
Si
1
1
Si
2
3
V_H
V_{EMP}
V_X
V_{SC}
V_{ION}
π_p
σ_p
σ_s*
σ_s

Figure 1

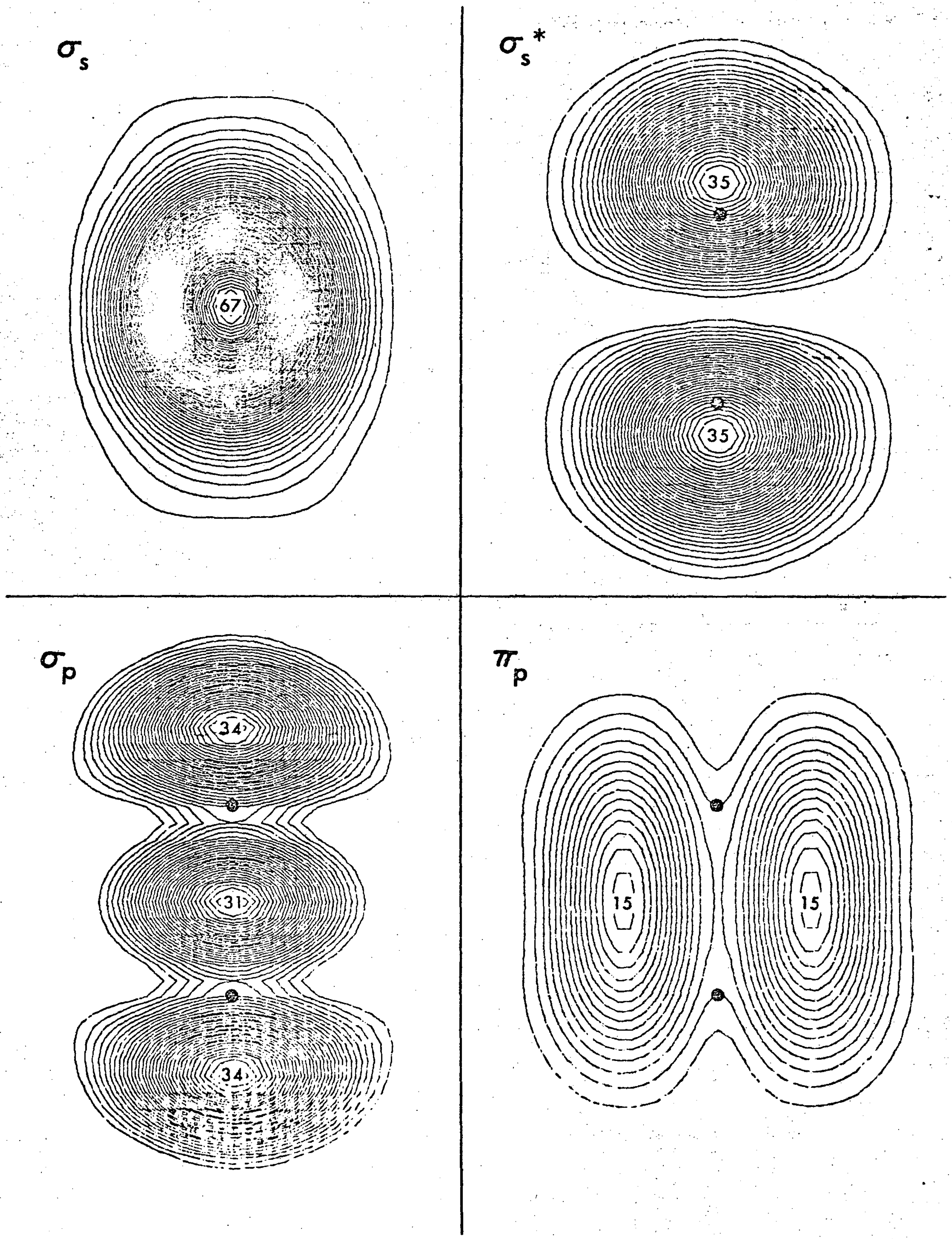
σ_s
67
σ_s*
35
35
σ_p
34
31
34
π_p
15
15

Figure 2

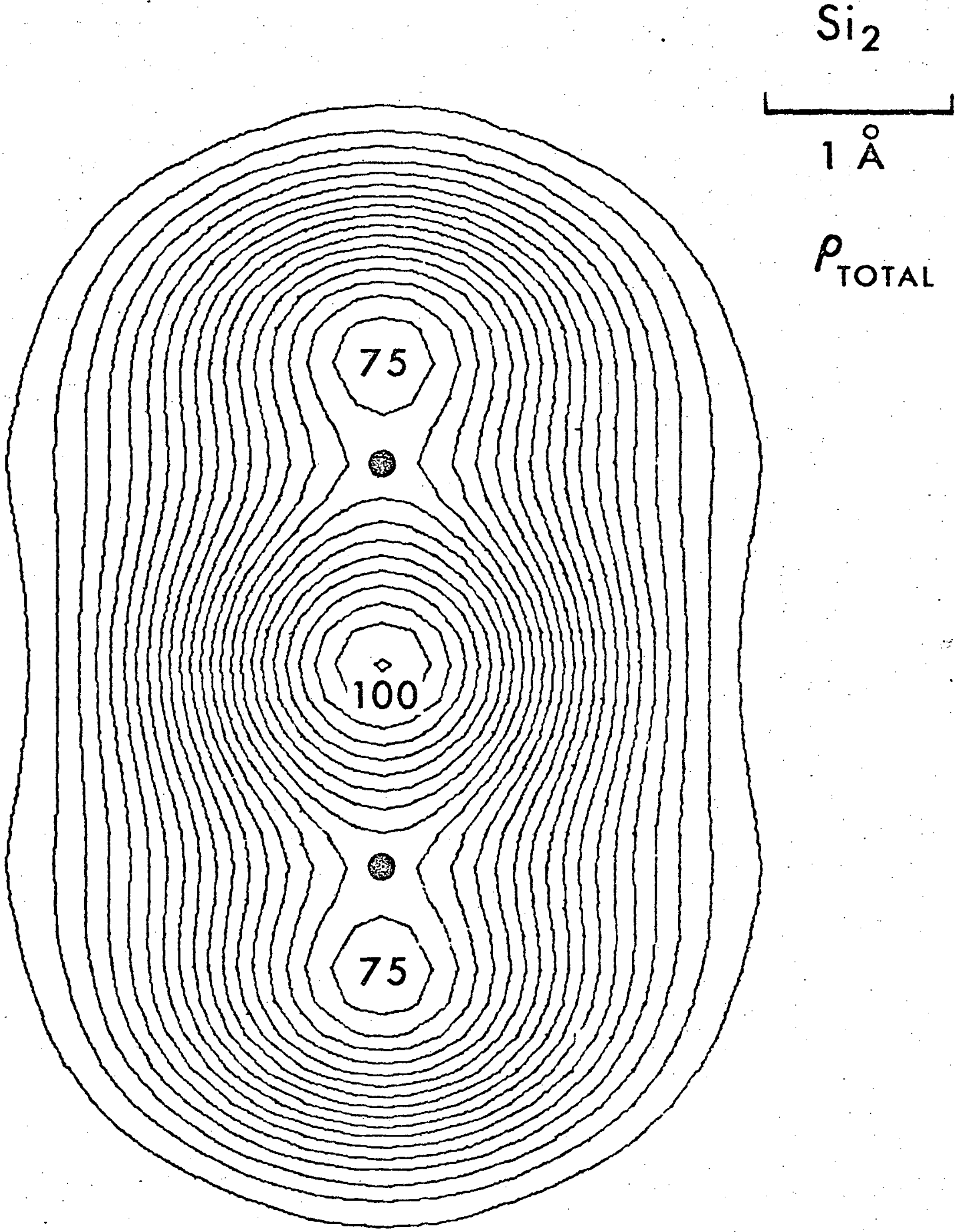

Figure 3

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