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Comparison of Charge Densities and Pseudo Charge Densities for Si₂

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We compare the charge densities of the orbitals of Si₂ calculated from Hartree-Fock-Slater self-consistent-field wave functions and pseudo charge densities from a local pseudopotential and found considerable differences. Given that the former are correct, this means that physically misleading conclusions could be drawn from the pseudo charge density. While pseudopotential methods have added much insight, current pseudocharge calculations for molecules and surfaces could be unreliable indicators of the true charge density.

In the last five years, the surface properties of a large number of different materials have been determined by self-consistent calculations.¹ Most of these calculations have made use of a local form of a pseudopotential and plane-wave basis states. Usually, the pseudocharge-density (PCD) distributions of the calculated surface states have been presented with the results. Increasing importance is being attached to the details of these PCD distributions. For example, it was concluded recently that a new type of chemisorption bond was possible on the basis of PCD calculated for H adsorbed on Si(111).² In view of these developments, it is desirable to provide assessments of the reliability of PCD for surfaces.

It has been pointed out³ that a prerequisite of confidence in the pseudopotential (or any other approach) is that it be successful in both the bulk-solid and free-atom limits. Basically, the reason for this is that the surface case [2D (two-dimensional) translational symmetry, partially localized states] is intermediate between the bulk

case (3D translational symmetry, delocalized states) and the molecular case (no translational symmetry, localized states). Therefore unless a method is successful both in the bulk and atomic (or molecular) limits, it cannot be concluded that it will be successful in the surface case. It is well known that the local-pseudopotential, plane-wave method has some shortcomings in the bulk.⁴ It may well be suspected that these shortcomings are exacerbated in situations involving more localized states, like surfaces and molecules. There is some experimental evidence for this in the case of surfaces.^{5,6}

One of the major approaches to the surface solution, the SCLC method⁷ (after the authors Schlüter, Chelikowsky, Louie, and Cohen), has been applied in virtually identical form to the solution of the Si₂ molecule.^{8,9} The results of this calculation have been used to imply that the methods employed can successfully represent charge distributions for surfaces.¹⁰ Also it is proposed that the results of similar calculations be used in surface chemisorption studies.⁹ Therefore, we com-

pare the results of the SCLC calculation with a more conventional solution of Si_2 . The results of the comparison are used to assess the reliability of the pseudopotential approach in the surface case.

The molecular wave functions used in the present work have been obtained from a Hartree-Fock-Slater (HFS) self-consistent-field (SCF) calculation¹¹⁻¹⁴ with an internuclear separation of 2.25 Å. The frozen cores (1s, 2s, and 2p) were represented by the near-Hartree-Fock (HF)-limit atomic orbitals of Clementi and Roetti.¹⁵ The basis set for the valence molecular orbitals consisted of a double-zeta Slater-type orbital (STO) 3s and 3p set, with optimized atomic exponents from the compilation of Clementi and Roetti.¹⁵ In addition the basis set included a 3d STO (with exponent 1.29744). Orthogonalization on the frozen cores is achieved, without loss of variational freedom, by the inclusion of one additional STO (exponent from optimal minimal atomic STO basis¹⁵) for each frozen atomic core orbital. For first-row molecules, the HFS-SCF approach has been shown to yield charge densities in excellent agreement with HF-SCF calculations.¹⁴ Furthermore, ionization potentials of different orbitals calculated by the HFS-SCF method are often in better agreement with experiment than those from HF-SCF calculations.¹²

The HFS-SCF charge densities of the σ and π

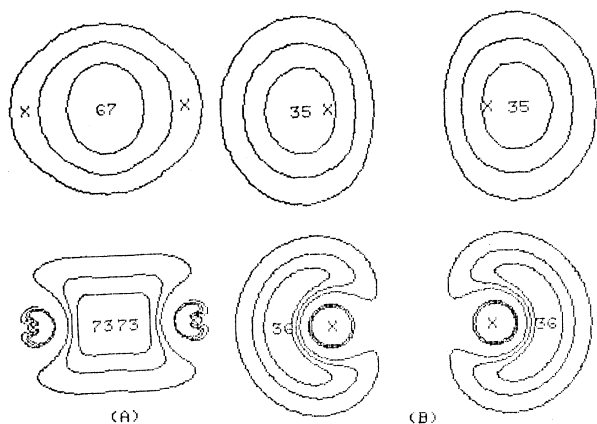


FIG. 1. Charge-density contours and pseudo charge-density (PCD) contours (adapted from Ref. 8) of Si_2 : (a) the $1\sigma_g$ orbital and (b) the $1\sigma_u$ orbital. The PCD is shown in the upper curves and the HFS-SCF charge density is shown in the lower curves. The positions and magnitudes of the maxima of the outer lobes are indicated by the numbers in units of $2e/(400 \text{ \AA}^3)$. The contours of charge density shown are $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the indicated maxima in each case.

valence orbitals are shown in Figs. 1 and 2 (lower curves) and Fig. 3(a). As expected, the charge densities of the Si_2 orbitals are similar to those of first-row homonuclear diatomics¹⁶ except for the presence of an extra nodal surface.

We compare these charge densities with the results of the plane-wave pseudopotential calculation for Si_2 .⁸ This was performed by placing the Si_2 molecule (bond length = 2.25 Å) in a hexagonal lattice so that the atoms of different molecules were separated by more than three bond lengths. The potential of each Si nucleus plus closed-shell electrons (pseudatom) was represented by a pseudopotential independent of energy and angular momentum ("local approximation"). The parameters of the pseudopotential were chosen by fitting atomic form factors. The basis states were plane waves and the problem was solved self-consistently using a Slater exchange term.

The pseudo charge density (PCD) of the σ and π orbitals resulting from this calculation are shown in Figs. 1 and 2 (upper curves) and Fig. 3(b). They were adapted from Fig. 2 of Ref. 8 where intermediate contours are also shown. The PCD does not, of course, correctly represent the form of the charge density near the nuclei. Better agreement in this region could presumably be obtained by orthogonalizing the plane waves to the core states but this was not done for the molecule or the surface calculations using this method.

The outer parts of the PCD show an overall resemblance to the orbitals of the molecular calcu-

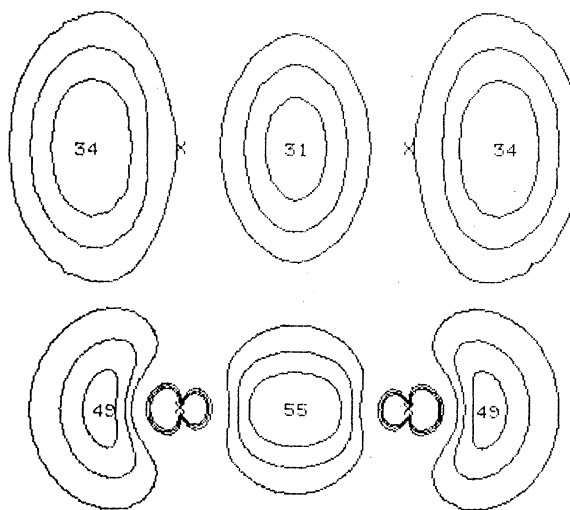


FIG. 2. Upper curve, pseudo charge density, and lower curve, charge density, for the $2\sigma_g$ orbital of Si_2 . Units and contours as in Fig. 1.

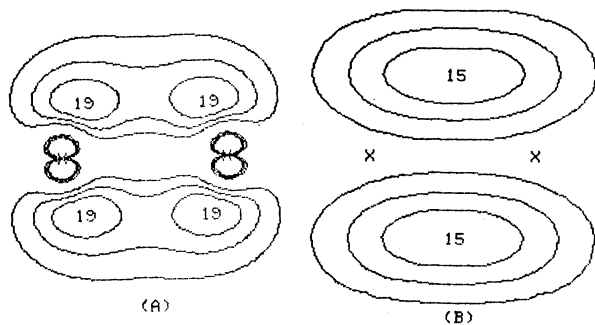


FIG. 3. (a) Charge density and (b) pseudo charge density for the $1\pi_u$ orbital of Si_2 . Units and contours as in Fig. 1.

lation. This may be considered a gratifying result for a method based on plane-wave basis states. However this does not mean that the PCD is sufficiently good to warrant physical conclusions being drawn from it. This is particularly so in the case of the bonding π orbital shown in Fig. 3. In this case, the maxima of the PCD are seriously misplaced in space and do not show the expected two separate maxima on either side of the nuclear axis given by the molecular calculation.

In order to make completely sure that the four maxima in $1\pi_u$ are not a basis-set effect, a calculation was performed with additional s and p basis functions at the center of the bond, so that the basis set was specifically adapted for the description of a π_u orbital of the SCLC shape. However the π_u charge contours showed no change while the orbital energies changed only slightly. This showed that the original basis set had been sufficient. (The only change worth noting was in the $1\sigma_g$, where the broad area of large density in the bond region no longer showed the two maxima indicated in Fig. 1.)

In the case of the σ orbitals, the maxima of the $1\sigma_g$ and $1\sigma_u$ PCD's are reasonably close to those of the HFS calculation, but considerable loss of detail is observed. The maxima of the $2\sigma_g$ are not in agreement, in particular in the bond region. We wish to observe here that the differences are not just due to the fact that the core part of the orbitals is absent in pseudo orbitals. Non-local pseudopotential calculations with another method,¹⁷ in which the same valence basis set was used as in the present molecular calculations, showed practically the same contours in the valence region, e.g., the kidney shape in $1\sigma_u$ and the four maxima in π_u . The agreement with the

full molecular calculation is essentially perfect after projection of the cores out of the pseudo orbitals.¹⁸ This suggests that the loss of structure observed in the SCLC orbitals is not necessarily due to the use of a pseudopotential as such. It may be due to use of a local form of the pseudopotential or to basis-state effects. It should be pointed out that the same pseudopotential and approximately the same number of plane-wave basis functions were used in the molecular case as in the surface case.

With respect to energies, Cohen *et al.*⁸ have stated that their energies were in good agreement with those from a HF calculation (data not given). Comparing with our HFS-SCF results, there are however considerable differences. With the SCLC results first, the orbital energies are (in eV): $1\sigma_g(-13.6, -12.06)$, $1\sigma_u(-8.7, -8.06)$, $2\sigma_g(-5.30, -4.25)$, and $1\pi_u(-5.16, -4.61)$. These results give different uppermost states (π_u for SLC, $2\sigma_g$ for HFS-SCF) which might be taken to suggest⁸ that the SCLC result is in better agreement with the experimental indication¹⁹ of a $^3\Sigma$ ground state for Si_2 . However, the proper determination of the molecular ground state requires a spin-unrestricted calculation. This was performed and showed the total energy of the $^3\Sigma$ state $[(2\sigma_g\alpha)^1 - (2\sigma_g\beta)^1(\pi_u\alpha)^2(\pi_u\beta)^0]$ and the $^3\Pi$ state $[(2\sigma_g\beta)^1 - (2\sigma_g\beta)^0(\pi_u\alpha)^2(\pi_u\beta)^1]$ differed by less than 3×10^{-3} eV (with the unoccupied orbital uppermost in energy in each case). Thus the two configurations are theoretically indistinguishable.

Figures 1 to 3 indicate that there are serious discrepancies between the PCD and the HFS charge density for Si_2 . Taking the HFS results as more reliable, the discrepancies shown by the PCD are such that physical conclusions drawn from it would be misleading. This therefore raises the possibility that similar errors may apply for results calculated for surfaces by the same pseudopotential method with a local approximation, and employing a similar plane-wave basis set (the SCLC method). The other surface pseudopotential method, due to Appelbaum and Hamann,¹ employs a similar pseudopotential but a different computational scheme. In view of the similarity of the results of the two methods,¹ the present results would be applicable as a guide to the reliability of both pseudopotential approaches.

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