Spin-Polarized Band-Structure Determination of the Si_2 Molecular Ground State by the Method of Full-Potential Linearized Augmented Plane Waves

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An electronic band-structure investigation of the charge topology and the eigenvalue spectrum of the Si_2 molecule is presented with use of the full-potential linearized augmented plane-wave method for thin films. The inclusion of spin polarization is found to be of fundamental importance in order to obtain the correct description of the ground state (paramagnetic calculations do not converge to any ground state) and to elucidate earlier controversies.

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In the past few years, the silicon molecule Si_2 has been of great theoretical interest[1-6] as a testing ground for different theoretical methods. In particular, Si_2 has been at the center of a controversy concerning the charge topology and the eigenvalue spectrum between pseudopotential (PP) band-structure[1,2,4] methods and all-electron linear combination of atomic orbital (LCAO), discrete variational method (DVM) molecular calculations.[3] All of these calculations were done by using (local) density functional theory,[7] and hence comparisons of the charge topology and the ordering of the uppermost states (as far as it affects the charge density) are of significance.

The ordering of the uppermost $1\pi_u$ and $2\sigma_g$ energy levels, which are derived from the atomic $3p$ levels, is the most obvious element of the controversy. The first two PP calculations[1,2] obtained a "triplet" ($^3\Sigma$) state ($2\sigma_g{}^2 1\pi_u{}^2$). After the LCAO-DVM molecular calculation[3] reported a ($^1\Sigma$) "singlet" state ($1\pi_u{}^4 2\sigma_g{}^0$), a new PP calculation also obtained the "singlet" ordering.[4] The main point underlying the charge-density topology controversy is whether or not correct physical conclusions can be drawn from densities obtained from PP calculations. There are large differences in the shape of the charge contours between the local PP[1,2] and the molecular calculations,[3] including differences in the number and position of maxima in individual level densities. The use of a first-principles nonlocal PP[4] (FPP) does improve the agreement. Although the appropriateness of the PP approach for the determination of valence charge densities and energy eigenvalues was demonstrated for the case of bulk silicon,[8] the Si_2 molecule seems to represent a more critical case for assessing the reliability of pseudopotential methods. In particular, the excellent agreement between a FPP calculation[4] and an LCAO-DVM calculation[3] has been taken as a demonstration of this reliability.[4] However, recent studies on the O_2 molecule[9] have pointed out the uncertainties of LCAO-type calculations in solving the all-electron local density equations. Therefore a comparison of pseudopotential results with LCAO-DVM results may not be conclusive and needs to be reexamined by comparing with more accurate solutions to the all-electron local density equations.

Since our recently developed full-potential linearized augmented-plane-wave (FLAPW) band-structure method[9,10] for thin films was found to be at least as accurate as a state-of-the-art LCAO-DVM molecular calculation[9,11] for eigenvalues and single-state charge densities for the oxygen molecule (O_2), we have undertaken a study of the challenging problem of the Si_2 molecule. In fact, we find similar descrepancies (of the order of 1 eV in the eigenvalues) between the LCAO-DVM[3] and our FLAPW results for the case of Si_2. In order to elucidate the controversy, we present results of paramagnetic calculations and the first spin-polarized results for Si_2. The $1\pi_u$ and $2\sigma_g$ levels are found to be nearly degenerate in the paramagnetic calculations and cause oscillations in the self-consistency procedure; the spin-polarized calculation yields a $^3\Sigma$ ground state, in agreement with experiment.[12]

In these calculations, the Si_2 molecules (bond length of 4.246 a.u.) are placed in an infinite two-dimensional hexagonal lattice with the axes of the molecules perpendicular to the film. A separa-

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tion of three bond lengths is sufficient for modeling the molecules as (nearly) noninteracting. For example, the $(l, m=6)$ multipole moments of the charge density in the spheres, which are a direct result of the artificial lattice environment, are found to be smaller by three orders of magnitude compared to the corresponding already small $(l, m=0)$ terms for $l \geqslant 6$. The local-density approximation[7] for the exchange-correlation potential is made: The paramagnetic calculations use the Hedin and Lundqvist[13] parametrization, while the spin-polarized calculation uses the spin-dependent potential of von Barth and Hedin[14] with the Hedin and Lundqvist paramagnetic limit.

In the spin-unpolarized FLAPW calculations, there is an oscillation during the self-consistency procedure in the occupation of the nearly degenerate $2\sigma_g$ and $1\pi_u$ levels. If the molecule is forced into a definite occupation of the levels, $^1\Sigma$ or $^3\Sigma$, then, according to Fermi statistics, the other configuration is found to be preferred, i.e., no convergence to a paramagnetic ground state exists. Figure 1 shows this reversal of the occupation and position of the eigenvalues for the self-consistent paramagnetic calculations for the assumed "singlet" and "triplet" configurations, neither of which is a ground state. The $1\pi_u$ and $2\sigma_g$ eigenvalues for the "triplet" case are nearly degenerate, while the splitting of these states for the "singlet" state is quite large.

In the first PP calculations,[1,2] the $1\pi_u$ and $2\sigma_g$ eigenvalues were found to be nearly degenerate.

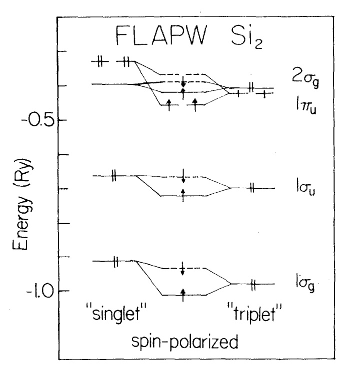

FIG. 1. The FLAPW eigenvalues for the paramagnetic calculations in the assumed "singlet" $(1\pi_u{}^4 2\sigma_g{}^0)$ and the "triplet" $(2\sigma_g{}^2 1\pi_u{}^2)$ configurations and for the spin-polarized results. Note the reversal in assumed occupation and calculated energy positions. The occupation of each is indicated by hash marks (arrows) for the paramagnetic (spin-polarized) results. The spin-down levels are given as dashed lines in the spin-polarized results.

Although the splitting of these two levels in the "triplet" state was only[2] 0.06 eV, if the "singlet" configuration was forced, then no convergence to a ground state was obtained.[2] The difference between the PP and our ordering of the "triplet" levels is due to quite small differences in the eigenvalues. (In a later paper,[4] the "singlet" ordering with a splitting of 0.03 eV is quoted for these results of Ref. 2.) The origin of these small differences in the ordering of the "triplet" state may be due to the different treatment of the core: They use a semiempirical local PP, while we use an all-electron fully relativistic core.

In contrast to these results, Miller *et al.*[3] used a LCAO-DVM molecular method and obtained a $^1\Sigma$ state. The $1\sigma_g$ and $1\pi_u$ eigenvalues compare well (0.1–0.3 eV) in absolute position with our "singlet" results, but the $2\sigma_g$ is much higher (1.1 eV) and the splitting of the $1\sigma_g$ and $1\sigma_u$ is larger (3.4 compared to 4.0 eV). These differences are quite similar to those found for the O_2 molecule.[9,11] In the case of O_2,[9,11] it was found that a far more complicated (and hence larger) LCAO-type basis was needed in order to approach the FLAPW results; in particular, the most difficult level for which to obtain convergence was the $2\sigma_g$ level.[11] Thus, if convergence to this level is not well achieved, then it is quite likely that in the LCAO-DVM calculation[3] the $2\sigma_g$ will be too high in energy to ever be occupied in Si_2. In light of these problems, the excellent agreement between the FPP[4] and the LCAO-DVM results[3] (within 0.07 eV, except for the $2\sigma_g$ which differs by 0.22 eV), is quite surprising.

The inability to obtain convergence to a paramagnetic ground state is not an artifact of either our method or local density theory. Using a Hartree-Fock molecular method, Moskowitz *et al.*[6] obtain the same result, i.e., although they find occupation in the lowest total energy $^3\Sigma$ "ground state" configuration $(2\sigma_g{}^2 1\pi_u{}^2)$, their energy eigenvalues are such that the $1\pi_u$ lies lower in energy, in agreement with our results. Unfortunately, these authors[6] do not comment on this problem and the eigenvalue of the $2\sigma_g$ state in the excited $^1\Sigma$ configuration is not obtained.

Since in an open-shell system, such as Si_2, spin polarization is expected to be important, we have also undertaken a spin-polarized FLAPW study of the Si_2 molecule in order to understand the difficulties in the paramagnetic calculations.[1-4,6] The resulting eigenvalues are also given in Fig. 1. The calculated ground state is $^3\Sigma$, in agreement with experiment.[12] The splitting of the spin-up and -down levels is quite large (in fact, larger than the differences between the "singlet" and "triplet" eigenvalues) and is due to the exchange interactions with the unpaired spin-up $1\pi_u$ electrons.

Since the low-lying $1\sigma_g$ level has a large density in the bond region, its detailed charge topology may be of importance for the correct description of the ordering and topology of the higher states, particularly within a self-consistent procedure.[9] Figure 2(a) presents the spin-up density of the $1\sigma_g$ level. (A plot of the spin-down density is visually indistinguishable from Fig. 2(a) on this scale.) An essential feature of this state is the shallow double-peak structure (the difference between the peaks and the center of the bond is ~1.5% of the height). This double-peak structure is of quite small dimension (~0.4 a.u.) and would require wave vectors $k \sim 15$ a.u.$^{-1}$ in a pure plane-wave basis to describe it correctly (a mixed basis[4] should be capable of describing this feature). The $1\sigma_g$ level of the LCAO-DVM calculation[3] [Fig. 2(c)] is in excellent agreement: Both the double-peak structure (the magnitude of the peak density is within 1% of the FLAPW total density for the level) and the rectangular shape of the contours are found. On the other hand, the agreement of the PP results, even outside the core region, is not so good. The semiempirical local PP[1,2] [Fig. 2(b)] has only a single peak (but of higher density) in the bond and the contours are round instead of the straighter lines of the FLAPW results. An *ad hoc* core orthogonalization of the wave functions does not improve the situation: The density at the center of the bond is increased even further and now the bond charge is elongated in the direction perpendicular instead of parallel to the axis. Use of a hard core nonlocal FPP with a mixed basis[4] [Fig. 2(d)] improves the agreement: The single peak has a density closer to the LCAO-DVM[3] and FLAPW results and the density in the core region is better described, but the contours in the bond region, although now better than the earlier PP[1,2] results, still have the wrong curvature. The overall agreement of the charge topology for the more extended $1\sigma_u$ and $1\pi_u$ levels between the FLAPW, the LCAO-DVM molecular,[3] and the nonlocal FPP[4] is quite good. (The $2\sigma_g$ density was not given in Ref. 4.)

Figure 3(a) gives the spin density for the $1\sigma_g$ level, while the closed shell (core, $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$) spin density is given in Figs. 3(b) and 3(c). The large valence level splittings (1 eV for the $1\sigma_g$) come from the high exchange polarizability of the levels.[15] For the Si_2 molecule, the spin-up density of the closed shells follows the density of the unpaired spin-up $1\pi_u$ electrons leaving a net spin-down density along the axis of the molecule (the $1\pi_u$ density vanishes on the axis by symmetry). The net spin density at the nucleus of

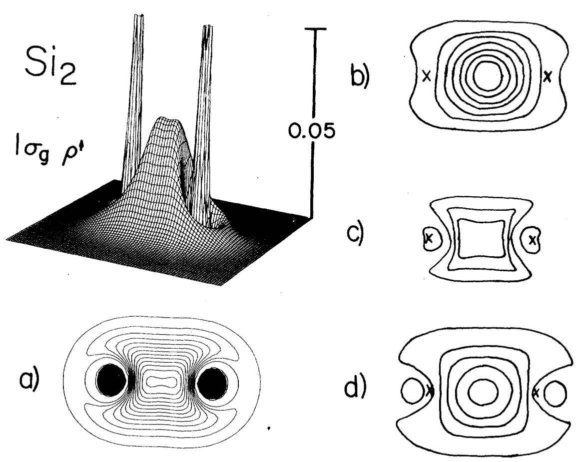

FIG. 2. (a) FLAPW $1\sigma_g{}^{\uparrow}$ density shown in three dimensions and as a contour plot at a spacing of 0.002 (in units of electrons/a.u.^{3}). Total $1\sigma_g$ density for (b) the local semiempirical PP (Ref. 2), (c) the LCAO-DVM molecular calculations (Ref. 3), and (d) the nonlocal first-principles PP (Ref. 4) with peaks of 83.4, 73, and 76.8 (electron pairs)/(400 Å^3), respectively. [Figs. 2(b)–2(d) after Fig. 1, Ref. 4.]

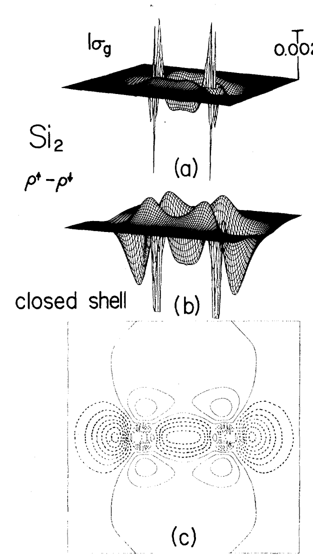

FIG. 3. Spin density for (a) the $1\sigma_g$ state and (b), (c) the closed shells (core, $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$) to the same scale in units of electrons/a.u.^{3} The contour spacing is 0.0004 and negative contours are dotted.

~ − 0.02 electron/a.u.[3] gives a contact contribution to the hyperfine field of ~ − 10 kG. However, it appears to be extremely difficult to measure the hyperfine field or the spin or charge densities of the Si_2 molecule for comparison with the present results since most experimental results on Si_2 have been obtained incidentally in flash photolysis experiments on other silicon compunds.[12]

These considerations of the spin densities shed light on the problems with a paramagnetic calculation. In a spin-unpolarized calculation there is, in some sense, an averaging of the spin-up and -down potentials and charge densities. It is quite reasonable that different methods will do the averaging in slightly different ways because of, e.g., basis effects or potential approximations, and this can then drive the system in two different directions, if (as is the case for Si_2) the effects of spin polarization are comparable to the differences between these two results. In this way, the spin-polarized results explain the origin of the controversy between the PP[1,2,4] methods and the LCAO-DVM molecular calculation[3] over the ordering of the uppermost levels of Si_2.

In conclusion, we have presented a FLAPW[9] self-consistent band structure investigation of the (nearly) free Si_2 molecule. Spin polarization was found to be of fundamental importance for a correct description of Si_2. The high polarizability of the spin density and the large effect of spin polarization on the energy eigenvalues provide an understanding of the origin of the controversy over the theoretical ground-state configuration of Si_2 between paramagnetic calculations using the PP band structure method[1,2,4] and the molecular LCAO-DVM.[3] We have also presented the first theoretical results for the contact contribution to the hyperfine field and for the magnetization density of the Si_2 molecule. Together with the results obtained[9] for O_2, the success of the present investigation demonstrates that a band-structure method designed for itinerant systems can also treat highly localized systems such as free molecules.

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