and Kendrich (Ref. 2).

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# Reliability of Pseudopotential Charge Densities

M. Schlüter
*Bell Laboratories, Murray Hill, New Jersey 07974*

and

A. Zunger,(a) G. Kerker,(b) K. M. Ho, and Marvin L. Cohen
*Department of Physics, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*

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An analysis of the charge-density and energy-level separations for the $Si_2$ molecule is made using local semiempirical and nonlocal first-principles pseudopotentials. The results are compared with Hartree-Fock-Slater all-electron calculations. It is demonstrated that pseudopotential calculations for molecules are reliable, and that recent objections based on charge-density topology are unwarranted.

Recently, the reliability of the pseudopotential approach in correctly predicting electronic charge densities and energy levels of polyatomic systems has been questioned.[1,2] On the other hand, a large body of bulk semiconductor and surface calculations, carried out using local and nonlocal (empirical,[3] semiempirical,[4] and first-principles[5]) pseudopotentials, has been extremely successful in explaining numerous experiments. The recent criticism has been based on a comparison of first-principles all-electron calculation[1] and a local pseudopotential[6] calculation for the $Si_2$ molecule. In order to clarify the adequacy of the pseudopotential approach in general and to examine the specific criticism[1,2] on the correctness of the charge-density topology obtained using semiempirical local pseudopotentials[4,6] we have extended the original $Si_2$ calculations[6] and also applied nonlocal first-principles pseudopotentials.[5] We divide the problem into two categories: (1) the approach used in solving the variational eigenvalue problem and (2) the construction of the pseudopotential.

In Ref. 6, charge-density plots were presented to illustrate the general capability of a "supercell" plane-wave basis set in conjunction with a local pseudopotential to describe charge localization on a scale of molecular dimensions. Table I shows the effects of convergence on the molecular energy levels of $Si_2$.[7] The lower converged calculation[6] (column 2) employs 180 plane waves (plus 250 in second-order perturbation) and an intermolecular separation of three bond lengths while a highly converged calculation[8] (column 3) used 635 plane waves (plus 700) and a separation of four bond lengths (the exchange coefficient was

TABLE I. Energy-level spacings (in eV) for $Si_2$.

| | Semiempirical pseudopotential[a] (local) | Semiempirical (highly converged) (local) | All-electron[b] Hartree-Fock-Slater | First-principles pseudopotential (nonlocal) | (local) |
|---|---|---|---|---|---|
| $1\sigma_g$-$1\sigma_u$ | 4.90 | 4.27 | 4.00 | 3.99 | 4.12 |
| $1\sigma_u$-$1\pi_u$ | 3.54 | 4.13 | 3.45 | 3.35 | 3.61 |
| $1\sigma_g$-$2\sigma_g$ | 8.30 | 8.43 | 7.81 | 7.59 | 7.91 |
| $1\sigma_g$-$1\pi_u$ | 8.44 | 8.40 | 7.45 | 7.38 | 7.52 |
| $1\sigma_u$-$2\sigma_g$ | 3.40 | 4.16 | 3.81 | 3.56 | 3.82 |

[a] Ref. 6.

[b] Ref. 1.

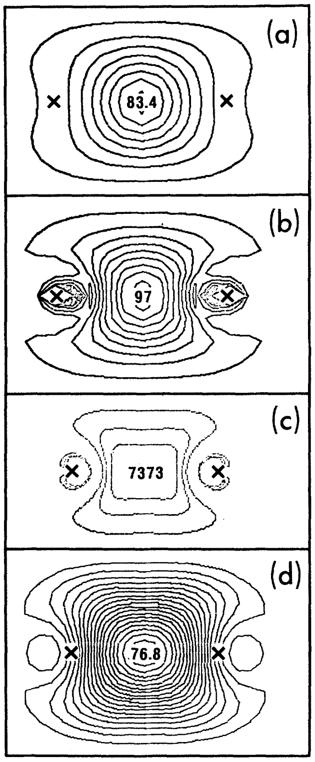

FIG. 1. Charge-density contours for the $1\sigma_g$ molecular orbital of $Si_2$. (a) Semiempirical local pseudopotential (Ref. 8). The contour step is 10 electrons per cell. (b) Orthogonalized local pseudopotential. Same contours as in (a). (c) All-electron Hartree-Fock-Slater (Ref. 1). Contours are shown at $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the indicated maxima. (d) First-principles nonlocal pseudopotential. The contour step is $\frac{1}{19}$ of the indicated maxima.

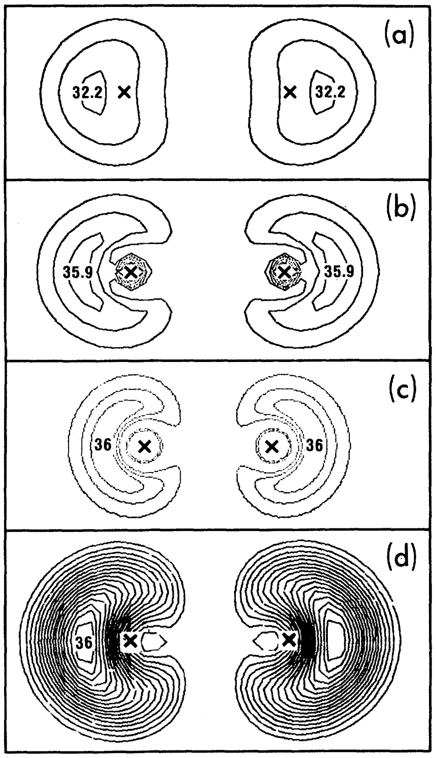

FIG. 2. Charge-density contours for the $1\sigma_u$ orbital of $Si_2$. Labels as in Fig. 1. (a) From Ref. 8, (c),from Ref. 1.

$\alpha = 0.794$). They are compared with the first-principles all-electron (core plus valence) results of Miller *et al.*[1] using a Slater basis set and $\alpha = 0.7$ (column 4). The highly converged plane-wave results can be reproduced with a mixed-basis set[9] (plane waves plus Gaussians) indicating their full convergence while the original calculations of Ref. 6 were not fully converged.

The replacement of the core-orthogonal all-electron valence orbitals by smooth, nodeless pseudopotential orbitals is based on the validity of the frozen-core approximation, and the quality of the results depends on the similarity of the pseudopotential orbitals as compared to the all-electron orbitals in the valence region. To illustrate to what degree the local semiempirical pseudopotential results reproduce the molecular all-electron charge density we have performed an *ad hoc* orthogonalization of the $Si_2$ pseudopotential orbitals to silicon atomic core states.

Figures 1–3 display (a) the converged unorthogonalized pseudopotential orbital charge density, (b) the core orthogonalized density, (c) the $a$-1 electron density,[1] and (d) the unorthogonalized pseudopotential charge density obtained from first-principles nonlocal potentials. The figures illustrate that core orthogonalization of local-semiempirical pseudopotential wave functions (not attempted in Ref. 1) can significantly change the *visual impression* obtained from contour plots to yield a topology of the bond charge comparable to the all-electron results. It should be noted, however, that *ad hoc* core orthogonalization is not rigorously correct for semiempirically chosen pseudopotentials on two counts: (i) It destroys the mutual orthogonality of the valence pseudo wave functions; (ii) since the semiempirically chosen wave functions are not linear combinations of the true all-electron core plus valence orbitals, orthogonalization does not recover pure valence wave functions. It is used here primarily to compare the topological nature of the pseudopotential and all-electron charge densities. Furthermore, *ad hoc* core orthogonalization enhanc-

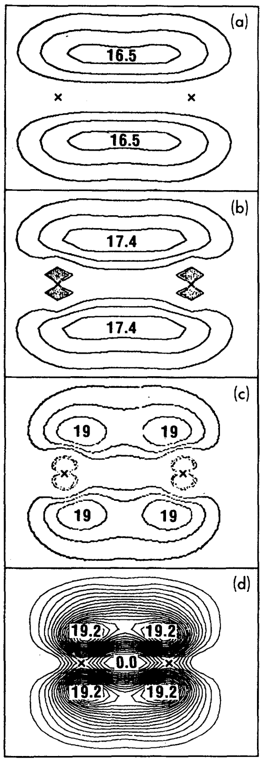

FIG. 3. Charge-density contours for the $1\pi_u$ orbital of $Si_2$. Labels as in Fig. 1 except for the contour steps in (a) and (b) which are 5 electrons per cell. (a) From Ref. 8, (c) from Ref. 1.

es the magnitude of the valence charge in the bond region: from 83.4, 33.2, 16.5, and 59.5 electrons per cell for $1\sigma_g$, $1\sigma_u$, $1\pi_u$, and $2\sigma_g$ in the unorthogonalized limit, to 97, 35.9, 17.4, and 64.2 electrons per cell after orthogonalization, compared to the all-electron results of 73, 36, 19, and 55, respectively. The maximum orbital densities obtained with the nonlocal first-principles pseudopotentials 76.8, 36, 19.2, and 53.7 compare well with the all-electron results.[1] These latter results are only minimally affected by core orthogonalization as the first-principles pseudopotentials are directly constructed to minimize the core projection of the valence pseudo wave functions[5] and thus exhibit highly repulsive cores.

The semiempirical pseudopotentials of Cohen *et al.*[6] and Zunger and Cohen[10] were constructed by adjusting parameters in an analytical form to match either the low-energy spectra of a neutral atom, a bare-ion $Si^{+4}$ system,[6] or the bulk band structures.[11] As this process does not determine the high-momentum regions of the potential, a conveniently smooth shape has been chosen in the core region, readily convergent in a plane-wave expansion. The shape in the core region, however, does have an effect on the *energy dependence* (and hence transferability) of the potential. When placed in a system different from that used for its construction, excess valence charge may flow into the core region characterized by a weak potential. The similarity of the pseudopotential wave functions to the all-electron form outside the core region can hence be altered. Indeed, the chosen semiempirical pseudopotential allows some valence change in the core region of the $Si_2$ molecule and, consequently, *ad hoc* core orthogonalization (which acts as an effective repulsive potential) introduces excess charge buildup in the valence region.

These problems are reduced by using first-principles pseudopotentials[5] which are obtained by a direct inversion of the atomic all-electron single-particle equations (in the density-functional representation), subject to a maximum similarity constraint between the pseudo and all-electron energies *and wave functions.* As a consequence, these pseudopotentials are both nonlocal and strongly repulsive in the core region. They are weakly energy dependent[5] and applicable to the study of crystal phase stabilities,[10] electronic structures of semiconductors[12] and transition metals,[12,13] and cohesive properties.[12,13]

Pseudopotential charge densities for $Si_2$ obtained from these potentials reproduce more accurately both the topology and the extrema of the all-electron results [see Figs. 1(d), 2(d), and 3(d)]. The present results have been obtained using a mixed basis[9] consisting of plane waves (237 functions) supplemented by $s,p$ Gaussians with exponents optimized to minimize the total molecular energy. The strength of the potentials does not allow the use of a simple plane-wave basis. An exchange coefficient of $\alpha = 0.7$ and a lattice spacing of four molecular bond lengths was chosen. We have also calculated the binding energy $E_b$ of $Si_2$ at the observed equilibrium distance, obtaining $E_b = 2.9$ eV, in moderate agreement with the all-electron results of Harris and Jones,[14] $E_b = 2.4$ eV and experiment ($E_b = 3.2 \pm 0.2$ eV).

Finally we address ourselves to the problem of the pseudopotential nonlocality. As all pseudopotentials are inherently nonlocal, one may question the appropriateness of replacing it by a local form.[6,8,10] The last column in Table I shows the molecular level spacing of $Si_2$ calculated with a local angular average of the Si first-principles potential. We conclude that nonlocality does not play an essential role for the occupied levels of Si (while excited states might differ by a volt or more) provided the local form is spatially sufficiently localized.[12, 14, 15]

In this study we have discussed general characteristic features of projected (pseudopotential) orbitals which for many problems of interest give physical insight and, if intepreted correctly, can be used in place of real orbitals. Furthermore, recently proposed pseudopotentials constructed either from first principles[5] or by explicitly fitting to all-electron *atomic* wave functions[14] are found to yield improved energies and charge densities for *molecules* and *solids* in close agreement with all-electron results.

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(a)Present address: Solar Energy Research Institute, Golden, Colo. 80401.

(b)Present address: Max-Planck Institute für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Germany.

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## ERRATUM

ELECTRONIC AND SPIN STRUCTURE OF UTe. M. Erbudak and J. Keller [Phys. Rev. Lett. 42, 115 (1979)].

The bibliographic entry in Ref. 12 is incorrect. It should read as follows: M. Erbudak, F. Greuter, J. Keller, F. Meier, B. Reihl, and D. Vogt, in Proceedings of the Twenty-fourth Annual Conference on Magnetism and Magnetic Materials, Cleveland, Ohio, 14–17 November 1978, to be published in J. Appl. Phys.