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Multiplet structure and charge distributions in silicon and germanium dimers

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Calculations of binding-energy curves and charge distributions have been carried out for low-lying states of Si_2 and Ge_2 using the local-density-functional formalism. Calculated spectroscopic constants are in good agreement with experiment for the states of Si_2 which have been identified, so that predictions for other states should be reliable. The binding-energy curves of the two dimers are remarkably similar, as are the *s-p* valence orbitals of silicon and germanium atoms. Charge-density differences are similar to those calculated previously for C_2 and orbital densities show pronounced differences from results of a recent pseudopotential calculation, even in regions far from the cores.

I. INTRODUCTION

In previous papers, we have shown that solutions of the Hohenberg-Kohn-Sham[1] (HKS) density-functional equations give a good description of low-lying states in first-row diatomic molecules[2] and alkali-metal dimers.[3] The linear muffin-tin orbital (LMTO) method used[4,5] has the advantage that heavier elements can be treated without increasing the basis. In this paper, equally good results are obtained for those states of Si_2 which have been identified spectroscopically, and we predict spectroscopic constants for other low-lying states of Si_2 and Ge_2. To the best of our knowledge, these are the first *ab initio* calculations of the multiplet structure of these dimers. We compare our results with parametrized extended Hückel calculations of Anderson.[6]

Many calculations for bulk silicon and silicon surfaces use the local pseudopotential method.[7,8] Though the method has not been applied to the calculation of energy curves for Si_2, Cohen *et al.*[7] published orbital densities, and we compare our results with theirs (Sec. V). Although the pseudocharge density is commonly assumed to equal the real charge density outside the core region, we find qualitative differences for the π_u-orbital density, indicating that either the pseudopotential used by Cohen *et al.*[7] was too simple or the plane-wave expansion was not converged.

In Sec. II we discuss in detail the application of HKS calculations to molecular multiplets and note some limitations of the approach. In Secs. III and IV we give the binding-energy curves and spectroscopic constants of states of Si_2 and Ge_2, respectively, and compare with experimental values where available. Section V contains a discussion of charge-density differences and orbital structure, and our concluding remarks concern the use of pseudopotentials in energy calculations. Details of the procedure used to solve the HKS one-particle equations and determine the energy have been given earlier.[2,3,5] In the present calculations, however, we allow for relaxation (though not polarization) of the outer-core levels, which are particularly extended in the case of germanium. In the alkali-metal dimers, this improvement caused only slight changes in the spectroscopic constants, but gave better agreement with experiment. Full details of the core-relaxation procedure will be given elsewhere.[9]

II. MULTIPLET DESCRIPTION IN HOHENBERG-KOHN-SHAM THEORY

The HKS approach draws a correspondence between an interacting system in its ground state and a noninteracting system with the same density. The ground-state energy is found by minimizing the density functional by solving a single-particle wave equation, so that the difficult problem of evaluating the many-particle wave function does not arise. An extension of the method[10] allows its application to the state of each symmetry which lies lowest in energy. The energy of a given state can then be found by minimizing the energy functional for all densities compatible with one-electron wave functions having the same symmetry properties as the state under consideration. In the case of the lowest-lying $^1\Sigma_g^+$ state of a molecule, for example, one must determine all densities of a noninteracting system which are compatible with this symmetry and belong to a single configuration.

To show that only single-configuration independent-electron wave functions are admissible, we consider the Hamiltonian[10]

$$H_\lambda = T + \lambda V_{\text{el-el}} + V_N + V_\lambda , \qquad (1)$$

which formally draws the analogy between interacting and noninteracting systems. T and $V_{\text{el-el}}$ are, respectively, the kinetic energy and Coulomb interaction of the electrons, V_N is the nuclear potential, and V_λ an external potential, with λ a number between 0 and 1. If V_1 is zero, then H_1 is the Hamiltonian of the interacting system, and we denote its lowest-lying eigenstate with quantum numbers μ by $|\psi_\mu^1\rangle$. If perturbation theory is valid, we may reduce λ infinitesimally and adjust V_λ so that the density is unchanged. By successive repetition of this procedure, $|\psi_\mu^1\rangle$ changes smoothly to $|\psi_\mu^0\rangle$, the corresponding eigenfunction for a noninteracting system of the same density. Since it is an eigenstate (not necessarily the ground state) of an independent-electron Hamiltonian, $|\psi_\mu^0\rangle$ is, in general, a simple sum of Slater determinants belonging to the same configuration, and is usually a single determinant. This argument shows that mixing configurations to describe $|\psi_\mu^0\rangle$ (Ref. 11), even if it yields a lower total energy, involves the use of the density functional outside its range of definition. It justifies our choice of configuration in calculating the ${}^1\Sigma_g^+$ state in C_2^{2} and corrects the discussion in Ref. 2 concerning configuration mixing in HKS theory.

In using the density functional scheme for multiplet structures, we approximate the exchange-correlation part, E^{xc}, by a simple local-spin-density (LSD) term. In atoms, this approximation is not generally adequate, since angular correlations cannot be described. For example, the $2p^2$ configuration in the carbon atom gives rise to fifteen states, three ${}^3P$ (approximately degenerate), five ${}^1D$ (degenerate), and a ${}^1S$ state. Of these, only the last has a spherically symmetric density. Within the central-field approximation the functional can describe only two states, a "singlet" $2p(\uparrow\downarrow)$ and a "triplet" $2p(\uparrow\uparrow)$, whose splitting (1.25 eV) is determined solely by the spin dependence of E^{xc}. This value agrees with the observed splitting between the ${}^3P$ ground state and a ${}^1D$ state. However, the ${}^1D$-${}^1S$ splitting (1.5 eV) is not described by the functional at all. To go beyond the central-field approximation does not solve this problem, since it seems impossible to find a simple approximation which guarantees the degeneracy of states having different densities. A more promising approach might be to retain the central-field scheme but to introduce an explicit l dependence of E^{xc}.

In molecules, the symmetry is lower and angular correlations are less important, so the situation is much more favorable. From the low-lying molecular orbitals we construct Slater determinants which have the required quantum numbers. With the corresponding occupation numbers held fixed, the density $n(\vec{x})$ and spin density $m(\vec{x})$ are calculated and the one-particle HKS equations iterated to self-consistency. Degeneracies still arise, however, if different states give rise to the same occupation numbers. For example, the lowest-lying states of O_2 (${}^3\Sigma_g^-$, ${}^1\Delta_g$, ${}^1\Sigma_g^+$) correspond to the configuration π_g^2. This configuration gives rise, however, to only two sets of occupation numbers: $\pi_g(\uparrow\uparrow)$ and $\pi_g(\uparrow\downarrow)$, and in the LSD approximation, therefore, the energy curves of the ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ are identical. Furthermore, since the ${}^3\Sigma_g^-$ differs from these states only in having a net spin $(m(\vec{x})\neq 0)$, its energy curve is essentially parallel to the others and lies ΔE below them, where

$$\Delta E = -\int d\vec{x}\, n(\vec{x})\{\epsilon^{xc}[n(\vec{x}), m(\vec{x})] - \epsilon^{xc}[n(x), 0)]\}. \tag{2}$$

TABLE I. Comparison of calculated spectroscopic constants of O_2 with experiment. Experimental values from P. H. Krupenie, J. Phys. Chem. Ref. Data 1, 423 (1972).

		E_B (eV)	$r_e(a_0)$	ω_e (cm^{-1})
${}^3\Sigma_g^-$		3.91	2.50	1400
	Expt.	5.213	2.282	1580
${}^1\Sigma_g^+$		2.90	2.52	1300
	Expt.	3.577	2.318	1433
${}^1\Delta_g$		2.90	2.52	1300
	Expt.	4.231	2.297	1509

In Table I, we show that the calculated spectroscopic constants are in semiquantitative agreement with experiment. The experimental curves have approximately the same vibration frequency and equilibrium internuclear separation, and the singlet-triplet splitting (1 eV) agrees with the calculation. The separation between ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ states (0.6 eV) is only one-quarter of the ${}^1D$-${}^1S$ splitting in the oxygen atom (2.2 eV), illustrating the greatly reduced angular correlations in the molecule.

The discrepancies between calculated and experimental values for O_2 (~ 1.5 eV in binding energy, 8% in equilibrium separation, and 15% in vibration frequency) are typical for sp-bonded molecules in the first row. As discussed in Ref. 2, this is due in part to the "common-κ" approximation we have used, which is only accurate when the eigenvalue spread is small. An estimate based on eigenvalues suggests that the error due to this approximation is approximately 1 eV, and is largest for F_2, where the eigenvalue spread is greatest. The recent calculations of Baerends and Ros,[12] who use a discrete variational method to solve the one-electron equations, imply somewhat larger, though consistent basis errors in E_B for these molecules (~ 2–3 eV). Their converged results give, however, only minor changes in ω_e and r_e, and lead to improved agreement with experiment. The predictive capability of any calculation requires, of course, that discrepancies with experiment be not only small, but consistent.

Multiplet structure in C_2, Si_2, and Ge_2 is more complicated than for O_2, because the $1\pi_u$- and $2\sigma_g$-orbital eigenvalues lie close together. In addition to states which correspond to the low-lying states of O_2 mentioned above, Slater determinants can be constructed with $^1\Sigma_g^+$, $^3\Pi_u$, and $^1\Pi_u$ symmetry. Of these six nondegenerate molecular states, only two have identical occupation numbers in the LSD approximation ($^1\Delta_g$ and $^1\Sigma_g^+$). Our results for the four lowest-lying states of C_2 agree well with experiment, apart from predicting a $^3\Pi_u$ ground state, rather than the closed π-shell $^1\Sigma_g^+$. The incorrect ordering of these may be due to the better description given by the LMTO basis for σ bonds or to an apparent tendency of the LSD functional to overestimate the exchange-correlation energy of a localized density distribution compared with that of a more diffuse density.[13] Experience with C_2 suggests that states in Si_2 and Ge_2 involving π electrons will lie too high compared with states involving mainly σ electrons.

III. MULTIPLETS OF Si_2

Binding-energy curves were calculated for 14 states of Si_2 with typically ten internuclear separations. The results for low-lying states (Fig. 1) and their spectroscopic constants (Table II) show striking differences from the corresponding results for C_2. Binding energies are much smaller, since the tails of the 3*s* and 3*p* valence states are more extended than the 2*s* and 2*p* states in carbon.[14] In addition, the level ordering is significantly different. The closed π-shell $^1\Sigma_g^+$ state, for example, is the experimental ground state in C_2 but lies well above the Si_2 ground state. The tendency of the LSD approximation to underestimate π-bond strengths is certainly no more than 0.5 eV, and does not affect our identification of the lowest-lying levels.

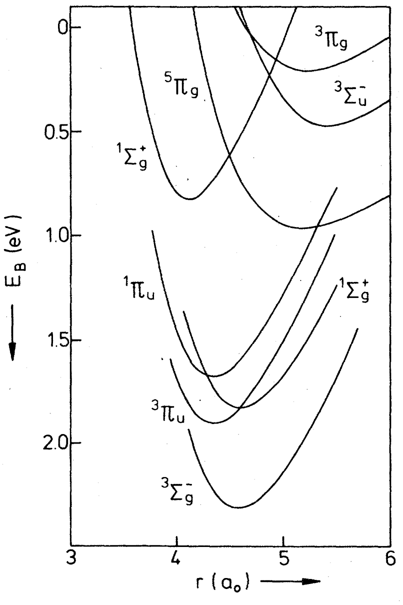

FIG. 1. Energy curves for low-lying states of Si_2.

TABLE II. Calculated spectroscopic constants for some low-lying states of Si_2. Experimental values from Refs. 15–19 (see text).

		E_B (eV)	$r_e(a_0)$	ω_e (cm^{-1})
$^3\Sigma_g^-$		2.32	4.60	430
	Expt.	3.0	4.24	510.98
$^3\Pi_u$		1.91	4.34	465
	Expt.		4.072	547.94
$^1\Sigma_g^+$		1.83	4.61	410
$^1\Pi_u$		1.68	4.35	440
$^5\Pi_g$		0.96	5.19	250
$^1\Sigma_g^+$		0.82	4.12	520
$^3\Sigma_u^-$		0.46	5.42	270
	Expt.	~1.1	5.032	271.32

The tendency to maximum occupancy of the $2\sigma_g$ orbital in Si_2 is clear from the self-consistent eigenvalues for the $^3\Sigma_g^-$ states in C_2 and Si_2 (Fig. 2), which show that the $1\pi_u$ level in C_2 lies relatively low compared with the $2\sigma_g$. Bonding-antibonding splittings are less pronounced in Si_2 and π bonding is sufficiently weak so that the $^5\Pi_g$ state, in which the $1\pi_g$ level is occupied, has a similar binding energy to the $^1\Sigma_g^+$ state. The loss in "bond energy" in the former is balanced by the energy lowering due to the existence of parallel spins. As noted in Sec. II, curves for states having essentially the same electron density but different spin densities are almost parallel. The $^3\Sigma_g^-$-$^1\Sigma_g^+$, $^3\Pi_u$-$^1\Pi_u$, and $^5\Pi_g$-$^3\Pi_g$ splittings are 0.49, 0.23, and 0.76 eV respectively.

Band spectroscopic data available for comparison[15-18] are much less extensive than in the case of C_2, although the $^3\Sigma_g^-$ ground state and its dissociation energy[19] are established. The value we obtain (2.32 eV) is in accord with the discrepancies found in other *sp*-bonded molecules, as are the 15% underestimate in the vibration frequency and 8% overestimate in equilibrium separation (see Table II). As it is unlikely that errors in other states are greater, our results support the assumption of Douglas[15] that the $^3\Pi_u$ state is low ly-

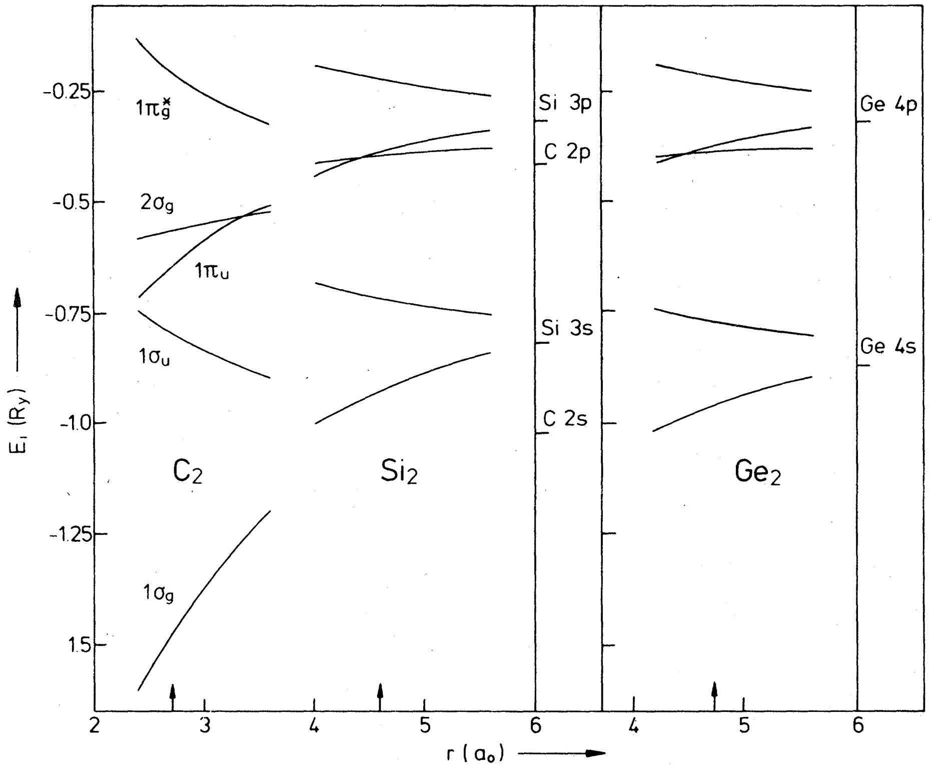

FIG. 2. Self-consistent HKS eigenvalues for the $^3\Sigma_g^-$ state of C_2, Si_2, and Ge_2, and for the isolated atoms. The orbital designations for Si_2 and Ge_2 correspond to those given for C_2. The arrows denote the calculated equilibrium separations in the three cases.

ing, rather than highly excited.[18] Other spectroscopic constants for this state agree with our results, as do values for the $^3\Sigma_u^-$ state, for which the estimated dissociation energy is 1.1 eV.[16] The error in the calculated value (0.5 eV) is consistent with the discrepancies in C_2.

A high-lying $^3\Pi_g$ state has been measured, and Douglas[15] has suggested the configuration

$$1\sigma_g(\uparrow\downarrow)1\sigma_u(\uparrow)1\pi_u(\uparrow\uparrow\downarrow)2\sigma_g(\uparrow\downarrow).$$

For this configuration we obtain $r_e = 4.12\ a_0$ (experiment $4.26\ a_0$), $\omega_e = 610\ \mathrm{cm}^{-1}$, and an energy minimum 1.9 eV *above* the energy of the separated atoms. According to our calculations, the $^3\Pi_g$ state with the lowest energy has the configuration

$$1\sigma_g(\uparrow\downarrow)1\sigma_u(\uparrow\downarrow)1\pi_u(\uparrow\uparrow)2\sigma_g(\downarrow)1\pi_g(\uparrow)$$

(see Table II).

Anderson[6] has reported extended Hückel (EH) calculations for three states of Si_2, and noted the weakening of π bonds compared with C_2. The EH results are, however, in less systematic agreement with experiment. The equilibrium separation, for example, is almost exact for the $^3\Pi_u$ state, too large for $^3\Sigma_g^-$ and too small for the $^3\Pi_g$ state.[20] The force constants for the $^3\Sigma_g^-$ and $^3\Pi_u$ states differ by a factor of 2, whereas they are similar both in the present calculations and experimentally.

IV. MULTIPLETS OF Ge_2

Binding energy curves for Ge_2 are given in Fig. 3, and the corresponding spectroscopic constants in Table III. The binding energy of the $^3\Sigma_g^-$ ground state is 2.0 eV compared with 2.81 ± 0.2 eV measured mass spectrometrically.[21] To the best of our knowledge, there are no band spectroscopic data on Ge_2. All other entries in Table III are therefore predictions, though subject, of course, to the systematic errors we find in all *sp*-bonded systems. Parameters for the upper $^1\Sigma_g^+$ state are not given, since the small overlap between the core functions and the valence LMTO's led to an unphysical energy lowering before the minimum was reached. This effect is less important for the other bound states, but it may lead to an underestimate of the vibration frequencies for the $^1\Pi_u$ and $^3\Pi_u$ states. From the energy curve resulting from overlapping atomic charge densities, we estimate $E_B \sim 0.5$ eV and $r_e \sim 4.3a_0$ for the $^1\Sigma_g^+$ state.

The similarity between the binding-energy curves for Ge_2 and Si_2 is quite remarkable. Apart from

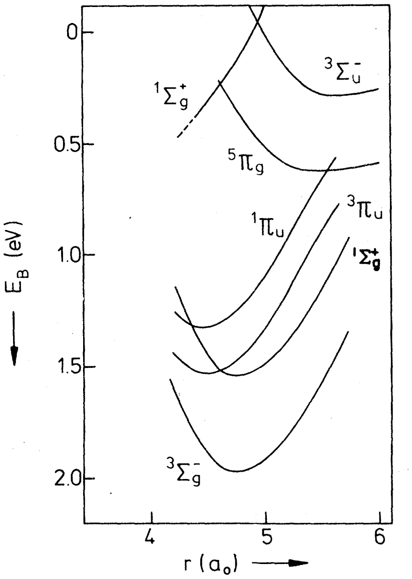

FIG. 3. Energy curves for low-lying states of Ge_2. As noted in the text, the nonvanishing of the 3d-core function for small muffin-tin radii can lead to an unphysical lowering of the energy. As a result, the minimum of the $^1\Sigma_g^+$ could not be determined.

the reversal of the almost degenerate $^3\Pi_u$ and $^1\Sigma_g^+$ states, the ordering is the same, and internuclear separations are only slightly greater in Ge_2. Force constants are similar, though vibration frequencies are substantially less due to the increased nuclear mass. In contrast to the EH results,[6] the raising of the $1\pi_u$ eigenvalue with respect to the $2\sigma_g$, observed for $C_2 \rightarrow Si_2$, does not continue for $Si_2 \rightarrow Ge_2$. As shown in Fig. 2, the valence eigenvalues for Ge_2 differ from those of Si_2 only in that the $1\sigma_g$ and $1\sigma_u$ levels lie slightly lower in energy. Not only are the eigenvalues very similar, the tails of the atomic valence orbitals are almost identical, as shown in Fig. 4.

TABLE III. Calculated spectroscopic constants for some low-lying states of Ge_2. Vibration frequencies are less precise than in Si_2 (see text).

	E_B (eV)	$r_e(a_0)$	ω_e (cm^{-1})
$^3\Sigma_g^-$	1.97	4.75	240
$^1\Sigma_g^+$	1.55	4.76	240
$^3\Pi_u$	1.53	4.49	250
$^1\Pi_u$	1.32	4.48	250
$^5\Pi_g$	0.62	5.76	150
$^3\Sigma_u^-$	0.28	5.65	160

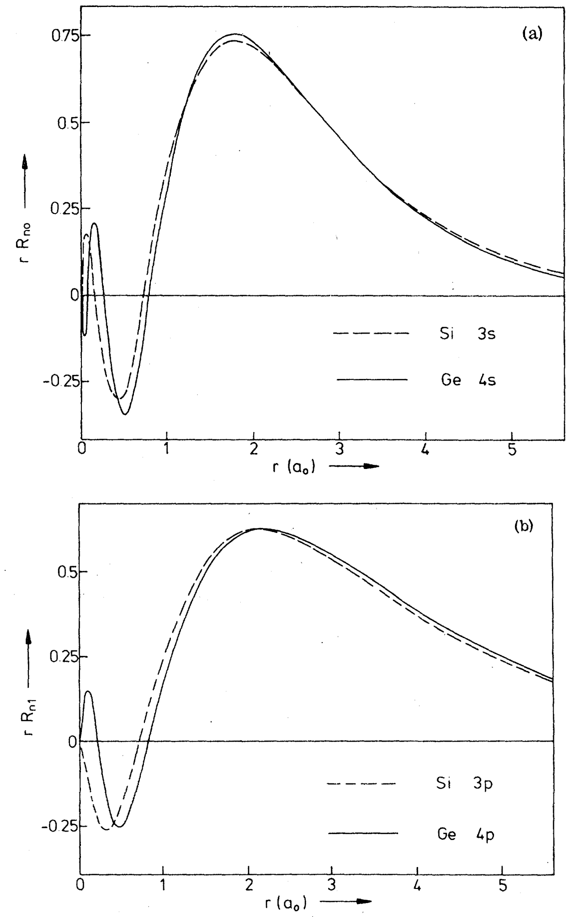

FIG. 4. Comparison of self-consistent valence orbitals $r\,R_{nl}(r)$ for Si and Ge atoms (a) s orbitals (b) p orbitals. Note the remarkable similarity outside the core.

V. CHARGE- AND ORBITAL-DENSITY DISTRIBUTIONS

The charge transfer which occurs on molecular bonding can be discussed most conveniently in terms of the density difference $\Delta n(\vec{x})$ between the molecular state in question and a superposition of spherically symmetrical atomic charge densities with the same geometry. In first-row molecules,[2] the present method gave plots of $\Delta n(\vec{x})$ which were similar to those determined from Hartree-Fock calculations, and the results for the $^3\Sigma_g^-$ ground state of Si_2 and Ge_2 at the equilibrium separations (Fig. 5) show features present in the earlier results for this state in C_2. Particularly notable is that the largest density changes occur inside the core region and close to the nuclei. As discussed

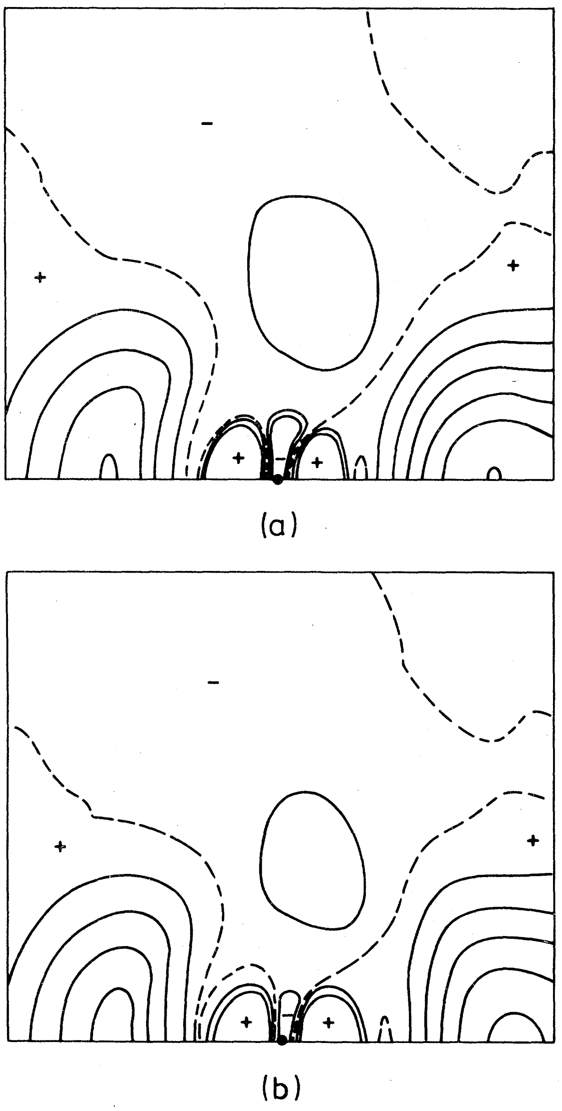

FIG. 5. Density difference $\Delta n(\vec{x})$ in ground state of (a) Si_2 (b) Ge_2 for separations close to the calculated equilibrium values. The zero contour is broken and the interval is 0.004 electrons a_0^{-3}. For reasons of clarity, contours in particularly dense regions are not shown. The main effect of bonding is a transfer of charge from the immediate vicinity of the nucleus to other regions along the bond axis.

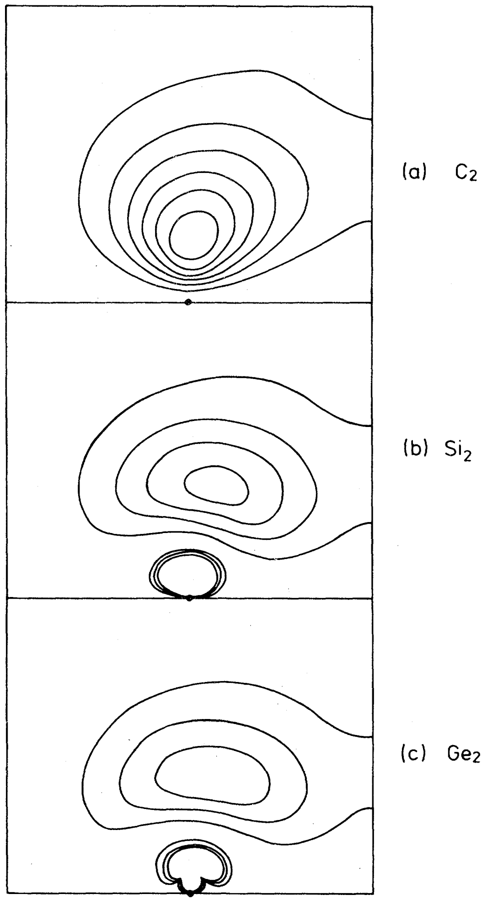

FIG. 6. Density plots for π_u orbital in (a) C_2: contour interval 0.008 electrons a_0^{-3}, (b) Si_2: contour interval 0.002 electrons a_0^{-3}, (c) Ge_2: contour interval 0.002 electrons a_0^{-3}. One quadrant is plotted with the midpoint of the molecule to the right of each frame, and the internuclear separations are close to the calculated equilibrium values.

in detail by Ruedenberg,[22] it is a misconception to equate bonding between atoms with the accumulation of charge in the overlap region. In *s*-bonded systems such as H_2 and the alkali-metal dimers,[3] much of the bonding comes from a lowering of the potential energy due to charge contraction around the nucleus. In the present case, the charge transfer is complicated by *s*-*p* hybridization and by small admixtures of *d* orbitals.

Although density-difference plots for a given molecule vary greatly from state to state, the orbital densities from which they are derived are relatively insensitive to the state and to internuclear separation. Recently, Miller and Haneman[23] pointed out that the orbital densities calculated by Cohen *et al.*[7] using a local pseudopotential method showed some unexpected results. In particular, the $1\pi_u$-pseudocharge densities showed maxima opposite the bond center, whereas results of a *p*-wave linear-combination-of-atomic-orbitals (LCAO) calculation[23] yielded maxima opposite the nuclei. In Fig. 6, we show our results for the $1\pi_u$ orbital density for the $^3\Sigma_g^-$ states of C_2, Si_2, and Ge_2 for separations close to equilibrium. The level has prominent p_x (p_y) character, but the lobes are drawn towards the bond region, due to overlap and a small d_{xz} (d_{yz}) component. The plots are qualitatively different from the pseudopotential results, even far from the cores, indicating that the pseudocharge density in this calculation is nowhere equal to the real charge density. This may be due to the inadequacy of the pseudopotential[24] or to the inherent difficulty in converging the plane-wave basis in an open structure such as a molecule or a surface. Other levels gave pseudocharge distributions more similar to ours outside the core region.

VI. CONCLUDING REMARKS

The results we have obtained for silicon and germanium dimers are further confirmations of the accuracy and usefulness of the local-density-functional scheme in calculating energies.[25] There is every reason to expect equally good results for the bulk and surfaces of these materials, provided the HKS equations are solved using a method, such as the LMTO method, which is valid for open structures. The availability of band spectroscopic data on dimers makes them an ideal testing ground for methods which are used to calculate bulk and surface properties. Since the local pseudopotential approach is so widely used, it is therefore rather disquieting that what little work has been published on Si_2 is in such poor agreement with the present *ab initio* calculations. A carefully constructed pseudopotential can certainly give excellent energies for small molecules, as shown, for example, by Bardsley *et al.*[26] for Na_2. These calculations, however, used a pseudopotential which was strongly l dependent and more detailed than those commonly employed in solid-state physics. Moreover, the determinantal trial functions were calculated from partially optimized Slater-type atomic orbitals, not from plane waves.

The applicability of pseudopotential concepts within the local-density-functional formalism depends on the role the core states play in the bonding. The orthogonality requirement between molecular orbitals means that core states influence not only valence orbitals of the same atom but those of other atoms with which they have sufficient overlap. This leads to a repulsive force due to the increase in valence kinetic energy. While such a force is present in calculations which employ a local pseudopotential, it is not obvious that its detailed dependence on internuclear separation can be sufficiently accurate to describe adequately the binding-energy curve in the region close to the minimum. In spite of this reservation, the present results are further evidence that the details of the core states are relatively unimportant. The similarity of the binding energy curves for Si_2 and Ge_2, which have very different cores, are in accord with our results for the alkali-metal dimers,[3] where trends in binding-energy curves followed closely the behavior of the tails of the valence orbitals.

If it is a general feature that the binding-energy curves are determined almost solely by the nature of the orbitals outside the core region, a description in terms of a "pseudodensity functional" would follow naturally. The core could be represented by a fixed potential adjusted so that the tails of the nodeless pseudoatomic functions agreed with those of a self-consistent atomic calculation.[27] In the context of HKS energy calculations, this choice of pseudopotential would seem more promising than fitting the eigenvalues of the bulk. We are currently recalculating the energy curves presented here using such an approach to test whether a simple local pseudopotential gives the energy variation with bond distance accurately or whether an l-dependent potential is essential to describe the core orthogonalization force.

ACKNOWLEDGMENTS

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[13] Compared with experiment, the functional favors consistently atomic configurations where localized orbitals are occupied. A study of this feature of the local-density-functional and of nonlocal modifications to the functional is currently in progress.

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[27] A similar approach has been developed by S. Topiol, A. Zunger, and M. A. Ratner [Chem. Phys. Lett. 49, 367 (1977)], who obtain remarkable results for excitation energies in first-row atoms.