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[16] Using $\bar{c}=c/20=1.5\times10^7$ m/s, we obtain the Josephson plasma frequency $=\bar{c}/\lambda_J=4.28\times10^{11}$ Hz. This gives a cutoff voltage of 0.14 mV.

Semiconductor Charge Densities with Hard-Core and Soft-Core Pseudopotentials

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Bulk Si valence charge densities calculated in a completely parallel manner for a traditional weak pseudopotential, a pseudopotential with a strongly repulsive core, and the full potential are compared. The second and third are in excellent agreement, while the first displays a somewhat modified bond-charge shape.

Pseudopotentials have been used extensively in calculating the energy bands[1,2] and valence charge densities[3,4] of semiconductors. While earlier work primarily used an empirical pseudopotential consisting of a few Fourier components, recent work has introduced model potentials for the bare ions and screened them self-consistently with the valence charge.[5,6] Results differ little. In both cases, these "soft-core" pseudopotentials are weak and smooth, and a plane-wave expansion for the wave functions converges rapidly.

A rather different group of "hard-core" pseudopotentials has recently been introduced. These have been derived from atomic calculations[7-10] and hydrogenic ion levels.[11] They are strongly repulsive in the core region, so that valence wave functions, although nodeless, must decay strongly and thus have a slowly convergent plane-wave expansion. Such pseudopotentials have been used in molecular calculations,[7,10] where they accurately reproduce the results of parallel full potential or "all electron" calculations, and to derive radii used in empirically separating crystal structures[12] and fitting alloy heats of formation.[13]

In this Letter, the results of *completely parallel* self-consistent calculations using soft-core, hard-core, and full potentials are compared for the prototype covalent semiconductor Si. The charge densities predicted by the hard-core and full potentials are in excellent agreement; the soft-core charge density displays the correct contour topology and integrated bond charge, but a slightly distorted bond-charge shape. The energy bands given by all three potentials generally agree. The present results contradict the conclusions of Miller *et al.*[14] that soft-core potentials lead to topologically incorrect charge densities and eigenvalues with significant errors.

To represent correctly the scattering properties of the full potential, different angular-momentum components of a valence wave function should feel different pseudopotentials in the core region. Such l-dependent "nonlocality" has been used to improve the energy-band fit of empirical pseudopotentials, and the small added terms do not change the soft-core character.[4] The hard-core pseudopotentials, as derived, are l nonlocal. However, for Si, the s and p pseudopotentials are very similar,[7] and the d potential is fairly well shielded by the centrifugal barrier in the core region. To keep the comparison simple, local forms of the Si^{4+} potential have been used. The soft-core form of Schlüter *et al.* was used,[6] which is specified in reciprocal space as

$$V(q)=-\left(\frac{16\pi}{q^2}\right)\frac{\cos(0.791q)-0.352}{1-0.352}\exp(-0.018q^4), \tag{1}$$

where V and q are in atomic units. Similar results would be obtained from the form in Ref. 5. The local hard-core form used is that of Harris and Jones,[11] given in real space as

$$V(r) = -\left(\frac{4}{r}\right)\frac{1-\exp(-14r)}{1-\exp[14(0.98-r)]} + 0.1\{\exp[14(0.98-r)]-1\}\,\theta(0.98-r). \tag{2}$$

These are plotted, along with the full potential of the Si^{4+} ion, in Fig. 1.

The results reported here were calculated using a recently developed self-consistent version of Andersen's linear augmented-plane-wave (LAPW) method.[15] Wave functions are represented by plane waves in interstitial regions smoothly jointed to a pair of numerical radial functions for each l inside touching muffin-tin spheres. The charge and potential are of completely general form, and are represented by numerical radial functions for each symmetry-allowed angular-momentum component inside the muffin tins, and plane waves in the interstitial region. The Wigner interpolation formula[16] is used for the exchange and correlation potential,

$$V_{\text{ex-c}}(n) = n^{1/3}\left[-0.984 - \frac{0.944+8.90n^{1/3}}{(1+12.57n^{1/3})^2}\right] \tag{3}$$

with real-space synthesis of n followed by Fourier and spherical-harmonic analysis of $V_{\text{ex-c}}$. The core charge (where used) is recalculated at each iteration. Using approximately 50 plane waves and a $l \leqslant 4$ expansion for the wave functions, 440 plane waves and $l \leqslant 8$ for the charge and potential, and two special points[17] for the Brillouin-zone sample yields 0.1-eV overall convergence, verified by increasing each of these in turn. The same parameters are used for all calculations, so that systematic errors peculiar to the nature of the expansion are consistent throughout.

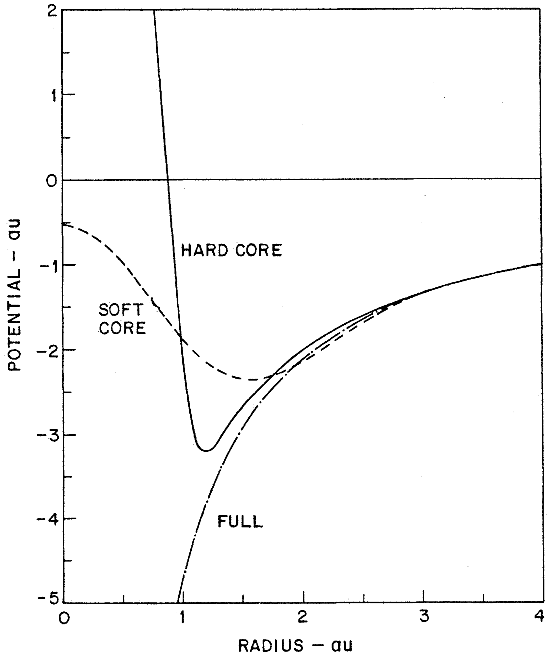

FIG. 1. Si^{4+} ion potentials used in the present calculations.

Valence charge densities for the three potentials are shown in Fig. 2. The full-potential and hard-core-potential results superpose almost perfectly everywhere except within 1 a.u. of the atoms. The soft-core results differ in the bond region and near the atoms. However, all three agree in the empty regions, indicating that the net integrated bond charge is correct for the soft core.

A more quantitative comparison of the bond region is given in Fig. 3. The full-potential and hard-core-potential charge densities are extremely flat in the bond region, and fall quite abruptly as the core is approached. The latter is essentially zero in the core region. The soft-core charge density is more nearly sinusoidal, and has nonzero amplitude in the core, approximating what one would expect if the hard-core charge density were convoluted with a smoothing function.

Two modifications of the soft-core Si charge density have been discussed. A nonlocal addition to the pseudopotential modifies the bond-region contours of Fig. 2(c) so that they are elongated parallel to the bond, in better qualitative agreement with Figs. 2(a) and 2(b).[4] However, this is achieved by a further increase in the core-region density, worsening the agreement in Fig. 3. Core orthogonalization of soft-core wave functions for the Si_2 molecule has recently been shown to improve their resemblance to full-potential results.[18] It is clear from Fig. 3 that applying the same procedure in the solid will decrease the average core-region density, but will do so at the expense of further enhancing the sharpness of the peak around the bond center. Core orthogonalization is an inappropriate modification with pseudopotentials that have been designed to give the correct wave-function *amplitude* outside the core.

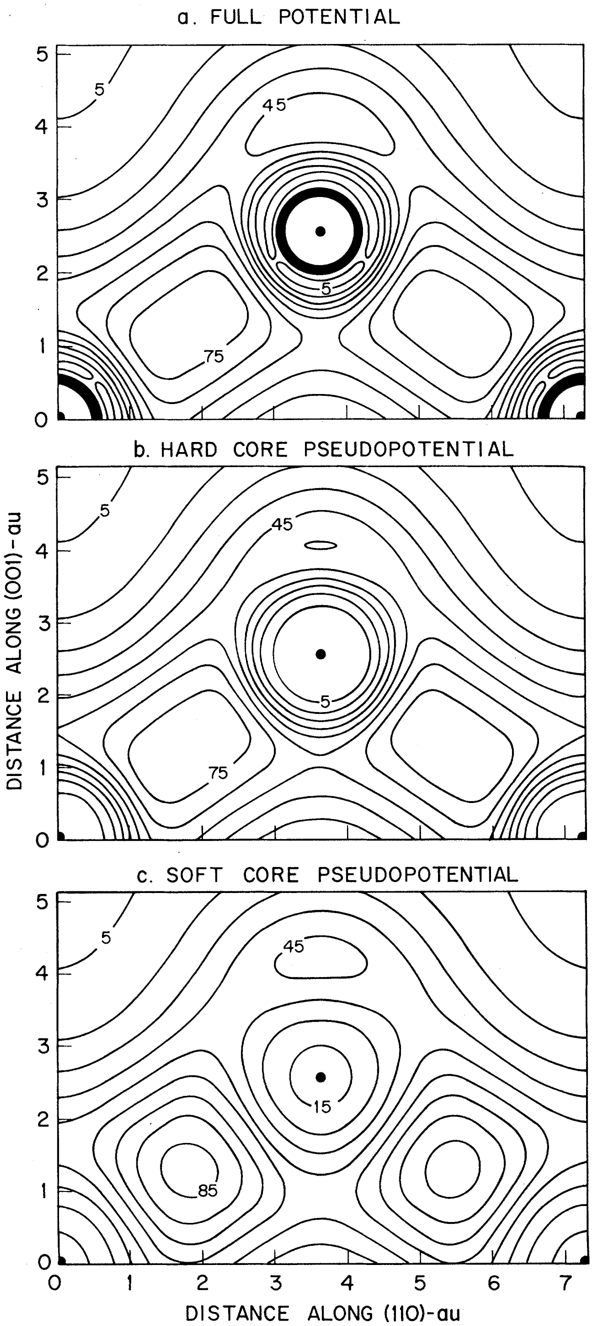

FIG. 2. Contour plots of Si valence charge densities in a.u. $\times 10^3$. Atom positions are indicated by dots.

A recent Si charge-density calculation by Zunger and Cohen using a nonlocal hard-core pseudopotential shows a distinctly split, or two-peaked, bond-charge density.[19] The discrepancy between this and the present results appears to arise from the fact that their Si^{4+} pseudopotential has a significantly smaller core radius (zero crossing) than the Harris-Jones pseudopotential[11] used

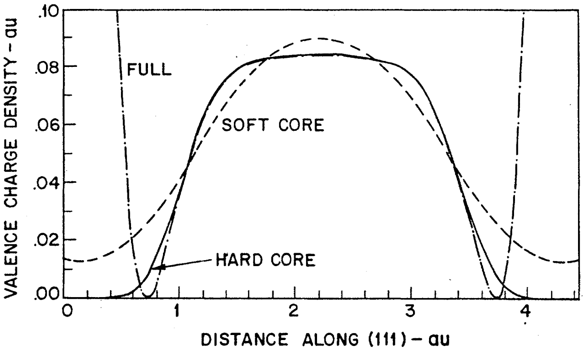

FIG. 3. Si valence charge densities along a bond.

here (or that of Ref. 8).

A Si valence charge density synthesized from x-ray data[20] is in good overall agreement with the results shown in Figs. 1(a) and 1(b). The peak density at the bond center of 0.102 a.u. is somewhat larger than those in any of the calculations. This value, as well as quantitative details of the bond-charge shape may reflect systematic errors in the core subtraction or anomalous dispersion correction of the data.

Band energies at Γ, X, and L symmetry points are given in Table I. The full-potential and soft-core–potential energies are in excellent agreement with independent orthogonalized-plane-wave[21] and plane-wave[19] calculations, respectively. The empirical nonlocal results by Chelikowsky and Cohen in the last column are in excellent

TABLE I. Band energies in eV at symmetry points for the full, hard-core, and soft-core potentials from the present self-consistent LAPW calculations, and for an empirical nonlocal pseudopotential (from Ref. 4).

Potential level	Full	Hard	Soft	Empirical
Γ_1	−12.02	−12.65	−12.79	−12.36
Γ_{25}'	0	0	0	0
$\Gamma_{15,c}$	2.49	2.59	2.80	3.42
$\Gamma_{2,c}'$	3.18	3.01	3.37	4.10
$\Gamma_{1,c}$	7.46	7.32	7.56	7.69
$\Gamma_{12,c}'$	7.86	8.87	8.40	8.19
X_1	−7.84	−8.38	−8.49	−7.69
X_4	−2.82	−3.13	−3.16	−2.86
$X_{1,c}$	0.55	0.58	0.64	1.17
$X_{4,c}$	10.32	10.88	11.94	
L_2'	−9.64	−10.25	−10.39	−9.55
L_1	−7.06	−7.52	−7.57	−6.96
$L_{3,c}'$	−1.16	−1.34	−1.35	−1.23
$L_{1,c}$	1.40	1.36	1.49	2.23
$L_{3,c}$	3.37	3.58	3.63	4.34

agreement with experiment,[4] and will be used as a standard for comparison. The full-potential calculation gives the best valence-band energies. Both the hard- and soft-core results place the bottom valence bands low by 0.4–0.8 eV. The upper valence and lower conduction bands agree quite well among the full, hard-core, and soft-core potentials. However, these conduction bands are too low by 0.6–0.9 eV. The local-density-functional approach is a ground-state method, and there is no theoretical basis for assuming that excited states should be given correctly. The gaps can be improved, although not uniformly, by modifying the exchange.[21] It is not clear that this is a universally applicable "fix," however, especially for more ionic materials. A practical means of going from a ground-state calculation to a reliable excitation potential remains an open problem. The soft-core–potential parameters could certainly be adjusted to produce better gaps, which gives this method a significant advantage over all-electron or first-principles pseudopotential calculations for spectral studies. The close agreement of the charge in Fig. 2(c) with that calculated from a local empirical pseudopotential[3] indicates that it would be insensitive to such adjustments. The largest discrepancy between the full-potential and hard-core–potential results is the Γ_{12}' level, which contains only *d* and higher-angular-momentum components, for which the repulsive core is a poor approximation.

The general conclusions of this study are that full, hard-core, and soft-core pseudopotentials all produce reliable charge densities and energy bands. Hard-core potentials are capable of more-accurate bond-charge shapes, and hence are more useful in sensitive structural separations. However, the rapid convergence of soft-core wave-function expansions, their subsequent usefulness in low-symmetry situations like surfaces and defects, and the ability to produce a more accurate excitation potential indicate the superiority of the soft-core approach for most applications.

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