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Self-consistent antiferromagnetic ground state for La_2CuO_4 via energy-band theory

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We have used the pseudofunction method to compute self-consistent spin-polarized energy bands for La_2CuO_4. The ground state is found to be semiconducting and antiferromagnetic (AF) with a moment of $0.35\mu_B$. The net moment resulting from the occupation of 82 itinerant bands is localized on the Cu atoms only. Our results agree with experiments in which La_2CuO_4 is found to be semiconducting and AF with a moment on the Cu atoms of $(0.35\pm0.05)\mu_B$ (neutron scattering) or in the range $0.2\mu_B$ to $0.6\mu_B$ (muon-spin resonance). Sr is found to produce holes on the out of plane O contrary to the assumption used in many strong-correlation theories of superconductivity.

The pseudofunction (PSF) method[1] with a local-density potential[2] has been successfully used to compute spin-polarized energy bands for Ni and MnTe.[3] The good agreement with experiment encouraged the use of this method for the new superconducting materials such as Sr-doped La_2CuO_4, hereby denoted in short as (2:1:4). In this paper, we present self-consistent spin-polarized local-density energy-band results for pure and Sr-doped 2:1:4. The ground-state energy bands are semiconducting and antiferromagnetic (AF) with a moment of $0.35\mu_B$ on the Cu atoms. One Cu-O hybrid state is split off by the AF correlation to give a semiconductor. The moment is nonintegral because of the strong hybridization between O and Cu at the Fermi surface. A magnetic ground state is found to be stable even in the metallic state when Sr is substituted for La. For example, an AF state with a moment of $0.09\mu_B$ is obtained when half of the La atoms are replaced by Sr atoms. Thus, contrary to widespread belief, band theory quantitatively accounts for the magnetic properties of 2:1:4 and suggests that the magnetic state is not observed in doped samples as the disorder overcomes the magnetic order.

The spin-polarized band model with a local-density potential has been used by several investigators to attempt an understanding of the AF and semiconducting behavior of 2:1:4.[4] These spin-polarized calculations with other methods find the ground state to be nonmagnetic and metallic contrary to experiment. We believe the reason that these attempts did not yield the correct ground state is that the bands at E_f are too broad. Specifically, for nonmagnetic calculations, the 2:1:4 bands are doubly degenerate on the hexagonal face of the orthorhombic unit cell. Semiconductivity can be obtained only when this degeneracy is lifted. These bands are only 0.17-eV wide for the PSF method.[5] The other techniques find these bands to be approximately 0.5-eV wide. Thus, the magnetic correlation needed to split a 0.5-eV-wide band is far stronger than that needed for a 0.17-eV band. Finally, we show that the nonspherical part of the crystal potential need be expanded in at least 15 625 plane waves to obtain the AF ground state. We believe this to be the key to the differences with other methods.

There are many proposals of superconductivity based on the coupling via magnetic excitations both local and nonlocal. Such theories of superconductivity are well documented[6] in the literature and will not be referenced here. We will only point out that we find the d_{z^2} band to be at the Fermi energy as postulated by Lee and Ihm.[7] They accounted for superconductivity with a two-band model (broad band and narrow d_{z^2} band) which we find to be appropriate. A more detailed two-band model[8] using local densities of states from the band theory for the broad Cu-O band and a Cu-O band in the z direction can phenomenologically account for the magnetic and superconducting properties of pure and doped 2:1:4.

The spin-polarized PSF method has been tested for ferromagnetic Ni and antiferromagnetic MnTe.[3] The results for Ni agree with those in the literature. For MnTe, we find the antiferromagnetic state to be more stable than the ferromagnetic state in agreement with experiment. Calculations for MnTe with the linearized augmented plane-wave (LAPW) method[9] also find that the antiferromagnetic state is more stable than the ferromagnetic state. K on Si is another example of success for the PSF method. The PSF method predicted the K-Si bond length to be 3.3 Å (Ref. 10) whereas the pseudopotential method predicted the bond length to be 2.59 Å.[11] Subsequent, surface-extended x-ray-absorption fine-structure (SEXAFS) experiments[12] give a bond length of 3.15 Å which is very similar to the PSF result.

The PSF method has a local orbital basis set employing the full potential including the core states (see the Appendix for details). The computation is done in Fourier space for computational efficiency just as the time-consuming parts of matrix element evaluation is done with the fast Fourier transform. For 2:1:4, the potential is expanded in 15 625 plane waves. The very accurate expansion of the potential is essential in obtaining the 0.17-eV-wide band at the Fermi energy. A less accurate potential gives broader bands. Nine *s*, *p*, and *d* basis functions were used on the La and Cu atoms with *s*,*p* sets on the O atoms. The basis functions are continually charged during iteration to self-consistency in order to optimize the description of the charge density. Identical results are obtained whether or not the O atoms were started with a spin state. The calculation was first brought to self-consistency with only a single *K* point in the iteration. A four-point sample was next used. The final iterations were done with eight *k* points. The average deviation in the potential between the input and output potential at 10% mixing was 1.1 mRy, with a maximum deviation of 7 mRy. The moment of the Cu sites increased by about $0.02\mu_B$ on going from a four-point sample to an eight-point sample. Subsequently, the calculations have been redone in entirety with a general set of eight *k* points. The moment is unchanged to $\pm 0.01\mu_B$ and the bands are virtually identical.

In Fig. 1, the spin-polarized bands near E_f are plotted for 2:1:4. The band gap between filled and empty states varies from approximately 2 eV at Γ to 0.06 eV on the hexagonal face. The bands are relatively flat in the *Z* direction because of the layered structure and are not shown. For the hexagonal face, the bands are narrow and doubly degenerate for a self-consistent field (SCF) non-spin-polarized calculations.[5] For spin-polarized bands, the gap varies from 0.35 eV at *X* and *M* to 0.06 along the *M* to *N* and *N* to *S* directions. The necessity that bands be narrow on this hexagonal face thus becomes obvious since the spin effect which gives the semiconducting gap varies from 0.35 to 0.06 eV. This band is 0.17-eV wide for the PSF method[5] and approximately 0.5 eV for other methods.[4] At internal points of the Bril-

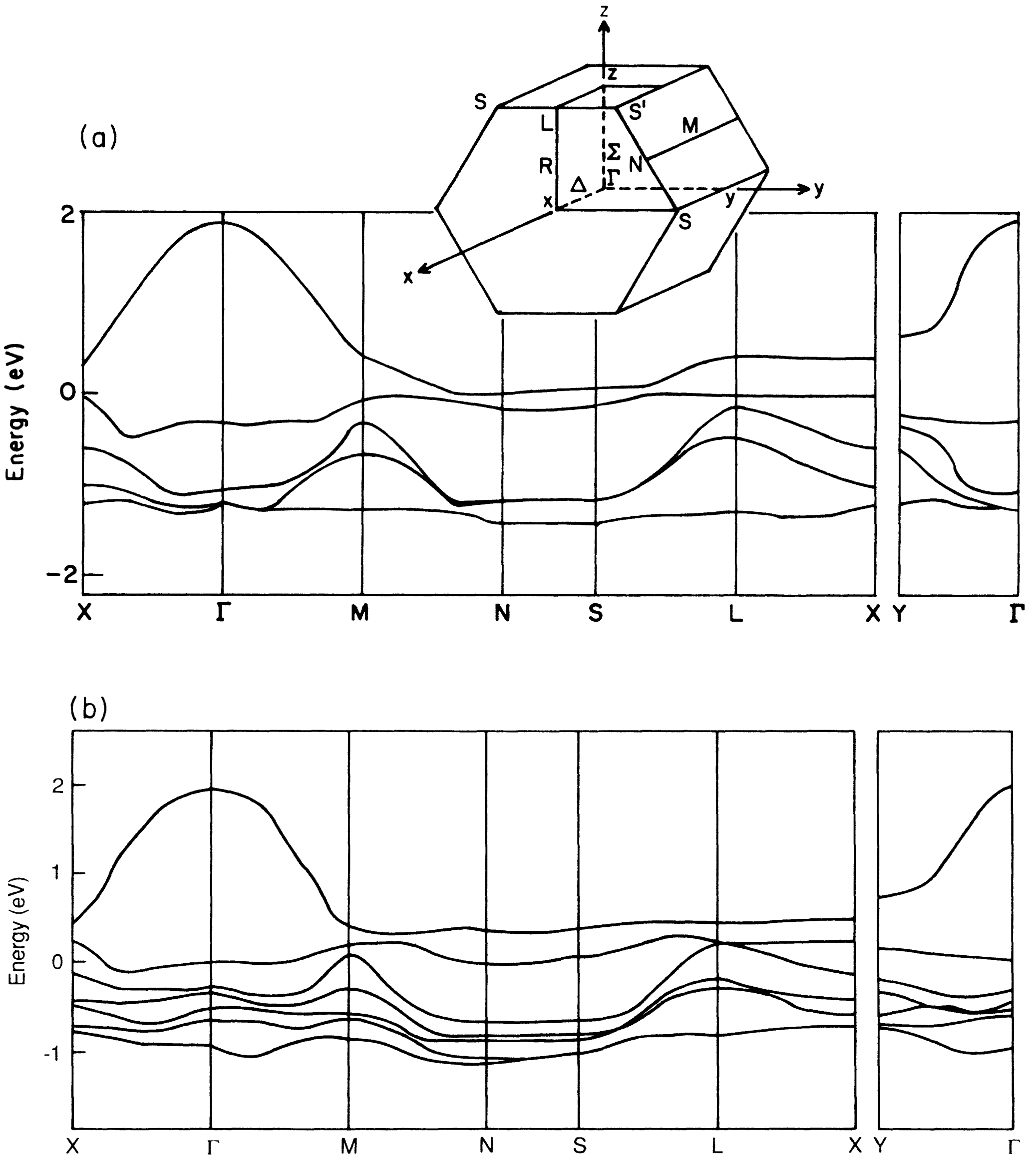

FIG. 1. Spin-polarized energy bands near the Fermi energy for (a) La_2CuO_4 and (b) $LaSrCuO_4$.

louin zone, the gap is large. This gap existed even for non-spin-polarized energy bands. Thus, the spin-polarization effect is only opening a gap at a small percentage of the points within the Brillouin zone. An approximate measure of the number of points at which antiferromagnetism opens a gap is a skin depth on the hexagonal face divided by the volume which would be a small number. This is probably a unique feature of the layered Cu-O materials because the number of electrons is important.

The indirect gap in Fig. 1(a) is as little as 0.01 eV. We were concerned that if the indirect gap were less than zero and a metallic state was obtained, the moment on the Cu atoms might become zero. Thus, the bands were iterated to SCF with an extremely poor sampling of k space using the points S, L, N, M, and X. The bands remain essentially unchanged except that the bands at L overlap the bands at N by 0.03 eV to give a metal. The moment on the Cu atoms increases to $0.39\mu_B$. This result indicates that our moment is not sensitive to small changes in band structure which produce metallic overlap. Alternatively, we believe nesting does not have to be exact to obtain the magnetic ground state as would occur at small Sr-dopant concentrations. Since band theory cannot be performed for small deviations from stoichiometry, we suggest that the above computations for a metallic state suggest that the antiferromagnetic state is stable for small dopant concentrations. Small dopant concentrations of Sr probably would not yield a metallic state because of the narrow bands at E_f and small overlap between carriers. Disorder would also create a mobility gap at low carrier concentrations.

It is important to understand the magnetic behavior as a function of Sr doping. The optimal superconducting transition temperature is observed at the large doping level of 0.15 Sr. Calculations have been performed on 2:1:4 where one-fourth and one-half of the La atoms are substituted by Sr. The dependence of the magnetic moment as a function of Sr is thus obtained.

The AF moment is obtained by integrating over all spheres. A value of $0.35\mu_B$ is obtained. An important understanding can be obtained by computing the charge within spheres about the different sites. In Table I, the amount of charge within the Cu sphere ($R=0.98$ Å), La sphere ($R=1.49$ Å), and O sphere ($R=0.86$ Å) is tabulated for spin-up and spin-down bands for both the pure and doped 2:1:4. The O atoms are labeled according to the type of coplanar metal atom. For 2:1:4, the first Cu atom has a net spin down of 0.35 electrons ($4.33-4.69$). The O atoms are identical in spin density indicating that the spin is localized to the Cu atom. Even though the band picture is an itinerant picture, moments localized to the metal atoms are obtained. For 25% Sr doping, the moments on the Cu are $0.35\mu_B$ and $0.32\mu_B$, which is indicative of small ferrimagnetism. At 50% doping, moments of $0.09\mu_B$ are obtained on the Cu atoms with antiferromagnetic behavior. The O atoms within the Cu-O basal plane do not have a moment at any level of Sr doping. For 25% Sr, the O atoms adjacent to the Sr and Cu(2) develops a small moment of $0.06\mu_B$. Thus, the moment on the Cu atoms will remain at a large value for Sr doping up to 25% with a slow decrease at higher levels. The O atoms may also participate depending on the doping level.

Spin-polarized energy bands calculated for $LaSrCuO_4$ are shown in Fig. 1(b). The bands are quite similar in appearance to those for pure 2:1:4. Because one-half of a band has been depopulated, the Fermi energy falls in the middle of the Cu-O band associated with the d_{z^2} orbital and O perpendicular to the plane.

Evidence for both spin and charge fluctuations via the apex O can be found in Table I. As the charge density and net spin on the O atoms in the base are independent of Sr content, we conclude that the basal O atoms do not participate in fluctuations. First, we consider fluctuations for 25% doping since this is closer to experiment at 0.15 Sr. Pure 2:1:4 has a charge of 9.03 ($4.34+4.69$) on the Cu atoms and 2.62 on all O. For 25% Sr, the net charge on Cu atoms is reduced to 8.98 electrons, an increase in Cu valence of 0.05 electrons. The O(La) and O(Sr) have moments of $0.06\mu_B$ by reducing its spin-up character by 0.06 e. One could envision fluctuations among the O(La) and O(Sr) atoms via bands at E_f that Sr has caused to be depopulated. Fluctuations require empty states near E_f. Table I shows these states to exist on the out of plane O.

TABLE I. Partial charge densities. The arrow indicates the spin direction.

	La_2CuO_4			$La_{1.5}Sr_{0.5}CuO_4$			$LaSrCuO_4$	
	↑	↓		↑	↓		↑	↓
Cu_1	4.34	4.69	Cu_1	4.31	4.67	Cu_1	4.33	4.42
Cu_2	4.69	4.34	Cu_2	4.66	4.34	Cu_2	4.66	4.57
La	0.46	0.46	La	0.46	0.46	La	0.45	0.45
La	0.46	0.46	La	0.44	0.44	La	0.45	0.45
La	0.46	0.46	La	0.45	0.45	La	0.33	0.33
La	0.46	0.46	Sr	0.34	0.34	Sr	0.33	0.33
O (base)	2.62	2.62	O (base)	2.61	2.62	O (base)	2.61	2.61
O (base)	2.62	2.62	O (base)	2.61	2.62	O (base)	2.61	2.61
O (La)	2.62	2.62	O (La)	2.56	2.62	O (Sr)	2.49	2.49
O (La)	2.62	2.62	O (Sr)	2.56	2.62	O (Sr)	2.49	2.49
O (La)	2.62	2.62	O (La)	2.61	2.57	O (La)	2.64	2.64
O (La)	2.62	2.62	O (La)	2.62	2.60	O (La)	2.64	2.64

A similar picture is obtained for 50% Sr doping. The net charge on the Cu sites is 8.75 (4.33+4.42) on Cu(1) and 9.23 (4.66+4.57) on Cu(2) as compared to 9.03 (4.34+4.69). Another important feature of Table I is that the O that is the nearest neighbor of Sr losses 0.13 electrons (2.62−2.49) within its sphere. This O is also bonded to the Cu that loses 0.22 (8.98−8.75) electrons within its spheres. Thus, the Sr doping, at least at this level, causes a hole to form on the Cu-O bond that is the nearest neighbor to the Sr atom. Similar but less dramatic results occur for 25% doping. This simply reflects that the band at the Fermi energy is composed mostly of the Cu-O character in the z direction, not the planar directions.

The difference between the 25% and 50% behavior is related to how the Sr is substituted for La. For 25%, the Sr is substituted only on one side of the Cu-O plane. For 50%, the Sr is placed symmetrically above and below the plane.

For very low levels of doping, a rigid-band model indicates that only bands on the hexagonal face would be depopulated and these have very important contributions from Cu-O bonds within the plane of Cu-O. Thus, at low levels of doping, states on the hexagonal face are depopulated and holes would be observed in the Cu-O plane. At large dopant levels of 15%, we would predict that the holes are in the Cu-O bond perpendicular to the plane. The exact spatial distribution would depend on the symmetry of Sr dopants relative to the plane.

It is well established experimentally that 2:1:4 is antiferromagnetic with semiconducting behavior.[13] Substitution of Sr for La leads to superconductivity. Neutron studies[14] indicate that the Néel state is destroyed by doping and that the spin-spin correlation length is reduced from 35 to 8 Å as the Sr concentration is varied from 0.02 to 0.18. More importantly, the local order is found to be the same for the doped and pure 2:1:4. Thus, it is stated[14] that no important differences in magnetic scattering were found in the normal and superconducting states. It is important to note that the interpretation of the neutron data is that doping affects the spin-spin correlations leaving the moment essentially unchanged from that of the pure state. Birgeneau *et al.*[14] caution that an unambiguous interpretation will require samples where the Meissner fraction far exceeds the 15% observed in the currently available samples. Birgeneau *et al.* also indicate that there are unexplained differences between samples.

Our calculations are in agreement with the above picture. A moment localized to the Cu atoms is obtained theoretically. This moment is practically unchanged up to a Sr concentration of 25%. We can similarly claim randomly placed Sr will disorder the moments. Our computed moment of $0.35\mu_B$ is quite similar to the experimental value from neutron [$(0.35\pm0.05)\mu_B$ (Ref. 15(b)] and muon-spin resonance [$(0.2-0.6)\mu_B$].[15(a)] It is certain that the moment is much less than $1.0\mu_B$ which would be obtained for spin 0.5.

Finally, whether or not the antiferromagnetic ground state is obtained is closely related to the number of plane waves with which the nonspherical potential is expanded. No AF ground state was obtained when the potential was expanded with 4913 or 9261 plane waves. An AF ground state was found for 24 389 plane waves. This calculation was not run to SCF due to extreme computer cost. The moment was $0.31\mu_B$ and increasing when the job was terminated. Since the number of basis functions was constant, the representation of the potential is critical.

There are other interpretations of the AF state of 2:1:4. The resonating valence bond picture[16] assumes a spin of $S=0.5$ on the Cu sites. An alternative strong-correlation picture[17] is that doping produces holes of spin 0.5 on the O sites in the plane. These local moment theories claim to account for much of the data but with adjustable parameters. Clearly a fundamental assumption is that Sr doping produces holes on the O sites within the Cu-O plane. Our energy-band results would place holes in the plane only for low doping levels. For larger values of doping as in the superconducting region, our energy-band results show holes on the O in the La plane not the Cu-O plane.

Spin and charge fluctuations have been mentioned as a possible mechanism for superconductivity. Our band-theory picture indicates a substantial coupling between planes via the O holes. Fluctuations within the plane can occur as a result of the fluctuations on the O. These fluctuations produce an attractive pairing interaction leading to a $T_c=280$ K for 0.15 Sr doping of 2:1:4.[18] An important feature of our band results is the capability of coupling within and between planes.

To support our claim that the width of the bands at E_f are sensitive to how well the potential is represented, a comparison is made for two different representations of the potential with the wave functions remaining identical. Figure 2 shows the narrow band for 4913 and 15 356

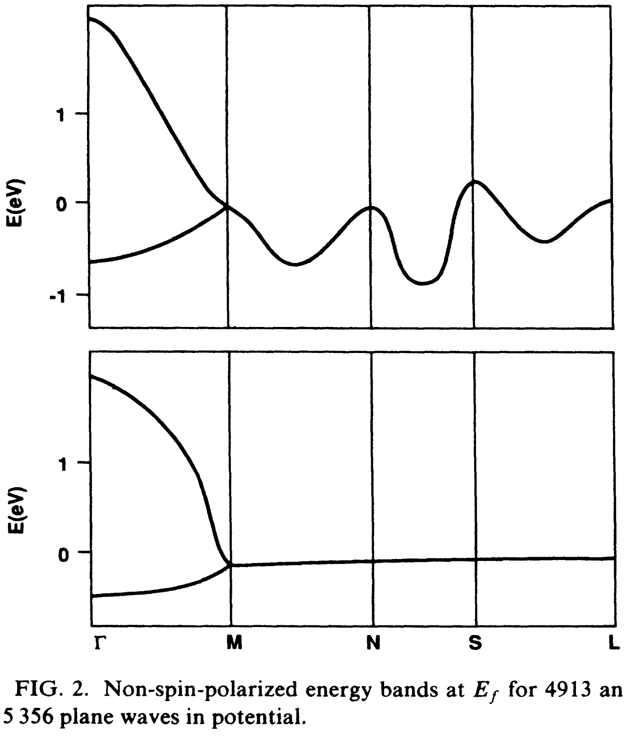

FIG. 2. Non-spin-polarized energy bands at E_f for 4913 and 15 356 plane waves in potential.

plane waves in the potential, respectively. The band is narrow if the potential has many plane waves. Only the band at E_f has been included for clarity. The band for 4913 plane waves is similar to that in the linear muffin-tin orbital (LMTO) calculations. The agreement cannot be exact because the LMTO calculation relies on the approximation of overlapping spheres and the PSF calculation relies on truncating the potential to 4913 plane waves. In further support of the accuracy of the PSF method, previously we have shown that the correct thermodynamic properties are computed for bulk Si (Ref. 19) and that the correct bond length can be computed for a CO molecule.[1] We have also computed the correct surface structure of Si.[1]

In summary, the itinerant energy-band model yields a band structure which has a moment of approximately the correct magnitude on the Cu site. Calculations for Sr doping support the notion of spin or charge fluctuations on the Cu and O sites. No evidence for localized holes of spin 0.5 on the planar O sites is obtained. Our results support the interpretation put forth by Birgeneau *et al.* that Sr disorders long-range spin-spin correlations leaving the local Cu moment relatively unchanged.

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APPENDIX

The PSF method has been described in detail[1] with application to CO and Si. Here, we will provide an outline of the method and all information that would be required to repeat our calculations. The unit-cell parameters and atom positions have been determined by Jorgenson *et al.* The unit cell is divided into muffin-tin and interstitial regions. The muffin-tin radii R_{MT} are 2.81 a.u. for La, 1.84 a.u. for Cu, and 1.62 a.u. for O. The potential is divided into spherically symmetric potentials within the muffin tins and a nonspherical potential that extends throughout the unit cell including the spheres. To form the PSF wave functions, we construct linearized muffin-tin orbitals exactly as in the LMTO or LAPW methods using the radial solutions ϕ and ϕ. ϕ is the energy derivative of ϕ, the solution of the muffin-tin potential for a given energy. The energy parameter is chosen to be an average band energy as in the linearized methods.

Beyond this point, the PSF method differs from other methods. First, we define two new radii R_{in} and R_{out} for all the muffin tins. R_{in} is chosen to be 0.95 R_{MT}. R_{out} is chosen to be 1.25 R_{MT}. The PSF wave function at site n for angular momentum lm is now defined as

$$\psi_{\mathrm{PSF}_{nlm}}=\begin{cases} a_{nlm}j_{lm}(k_1,r_n)+b_{nlm}j_{lm}(k_2,r_n), & r<R_{\mathrm{in}}\ , \\ N_{lm}(\phi(E,r_n)+\omega_{lm}\phi_{lm}(E,r_n)), & R_{\mathrm{in}}<r<R_{\mathrm{out}}\ , \\ -K_{lm}(k,r_n), & R_{\mathrm{out}}<r\ . \end{cases}$$

The parameters ω_{lm} and N_{lm} are chosen for continuity of the function and its radial derivative at R_{out}. The Neuman function K_{lm} has an energy parameter of -0.3 Ry. Within the distance R_{in} the parameters a_{nlm} and b_{nlm} are also chosen for continuity of the PSF function at R_{in}. The energies for the Bessel functions j_{lm} are $k_1^2=0.1$ Ry and $k_2^2=0.2$ Ry. The above procedure is followed for the *s*, *p*, and *d* orbitals on the La and Cu sites and the *s* and *p* orbitals on the O sites. The results are not sensitive to the choice of energy parameters k_1 and k_2 within the radius R_{in}. The tail-parameter energy -0.3 Ry is the result of calculations on many different systems. The resultant energy bands are not very sensitive to the tail parameter if a value near -0.3 Ry is used. The above-defined PSF orbitals are smooth throughout space thus enabling straightforward Fourier transforms as previously shown.[1] The criterion for the number of plane waves in the transform of the PSF orbitals is that R_{MT} times the maximum reciprocal-lattice vector be 7.0 in the three reciprocal-space directions thus defining a polyhedron in reciprocal space instead of a sphere.

The PSF orbitals are now defined by a linear combination of plane waves. The PSF orbitals are orthogonalized to the core states by augmentation as in the LAPW method. The solution of the Hamiltonian is fully described in Ref. 1 and is not repeated here. The charge density is in terms of spherically symmetric parts within the muffin tins and a Fourier series representing the nonspherical contribution. This plane-wave sum contains approximately eight times the number of plane waves in the wave function.

The self-consistency loop follows that of the standard band theory. The charge density is used to define a new potential which is mixed with the old potential. New PSF orbitals are constructed and the Hamiltonian is solved again until the input and output potentials are the same to a small deviation. The PSF orbitals change as one iterates to self-consistency. The PSF orbital molds to the charge density and changes as the charge density changes especially in the bond formation region between atoms. The applications described here and in Ref. 1 indicate that the plane number waves in the potential is vitally important for computation of properties. This dependence is shown in detail for a CO molecule.[1] In this paper we have shown that a bandwidth similar to that for other methods is obtained for a small number of plane waves.

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