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Illustration of the linear-muffin-tin-orbital tight-binding representation: Compact orbitals and charge density in Si

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Plots of the tight-binding (TB) orbitals recently derived by exact transformation of the conventional set of linear muffin-tin orbitals (LMTO's) are presented for crystalline silicon. The TB-LMTO's are found to be extremely compact. As a simple application we show how non-spherically-averaged charge densities may be obtained from standard LMTO calculations. For silicon this charge density is found to be in excellent agreement with the one obtained from a linear augmented plane-wave full-potential calculation. This is true even when the LMTO calculation employs the atomic-sphere approximation for the one-electron potential. A self-contained account of the TB-MTO formalism is presented and a simple way of including the quadratic energy dependence of the MTO's is derived.

I. INTRODUCTION

Muffin-tin orbitals[1-9] (MTO's) constitute a popular and efficient basis set for first-principles electronic-structure calculations in solids.[10] Its advantages are the following: (i) It is applicable to materials composed of atoms from any part of the Periodic Table. (ii) It is minimal in the sense that, per site, only one *s* orbital, three *p* orbitals, possibly five *d* orbitals and, for *f*-band materials, seven *f* orbitals are needed. (iii) Its energy dependence may be retained in Green's-function calculations and neglected in band-structure calculations. The energy-independent set, the linear MTO's (LMTO's), is correct to first order in energy [i.e., $|\chi(\varepsilon)\rangle = |\chi(\varepsilon_\nu)\rangle + |\ddot{\chi}(\varepsilon_\nu)\rangle(\varepsilon-\varepsilon_\nu)^2/2+\cdots$, with no first-order term, with $|\chi(\varepsilon)\rangle$ being the MTO and $|\chi(\varepsilon_\nu)\rangle$ being the LMTO]. (iv) The set is complete for the muffin-tin potential used for its generation but is not restricted to treating muffin-tin potentials. (v) The MTO's may be expanded about other sites in terms of numerical, radial functions, spherical harmonics and canonical structure constants. This, together with the atomic-sphere approximation (ASA) according to which the MT spheres or the Wigner-Seitz (WS) cells are substituted by overlapping "space-filling" WS spheres, leads to a factorization of the matrix elements of nearly any operator into products of structure constants and radial integrals. The ASA has proved a convenient starting point for simplified, analytical theories of the electronic structure, magnetism, total-energy differences, etc.

The basic disadvantage of the conventional solid-state MTO's is their *infinite range*. This has limited their applications to those cases where the structure constants can be summed by the Ewald procedure, that is, where the sites form a periodic lattice (this includes the cases of impurities and compositional disorder). Moreover, with orbitals of infinite range, the electronic wave function in a given cell has contributions from orbitals throughout the solid, and the only two ways of representation are through a plane-wave expansion and through a partial-wave, one-center expansion with Bloch-summed structure constants as mentioned in (v) above. Whereas the latter expansion converges rapidly only in the interior of the MT's the former expansion merely represents the envelope of the MTO, the so-called pseudo-MTO, valid in the interstitial region. Thus, despite the smooth nature of the MTO its atomic wiggles and infinite range often requires a composite partial-wave—plane-wave representation. For the one-electron Hamiltonian and overlap matrices the partial-wave representation together with integrals over the WS spheres yield the so-called ASA contributions and the remainder, for which only the plane-wave representation is needed, are the so-called combined-correction terms which are rather small.

For the charge density it has proved highly convenient and surprisingly accurate to use merely the spherically symmetric part obtained from the partial-wave expansion in the WS sphere. This approximation is commonly used in self-consistent calculations and we refer to it as *the ASA for the charge density*. Since the wave functions and the full, non-spherically-averaged charge density were so far difficult to represent throughout the cell, and since they are not needed during a self-consistent calculation in the ASA, wave-function and charge-density plots are not features of standard LMTO computer programs.[4] Existing plots[11] merely use the pseudo-LMTO's.[12] The total-energy functional which is being minimized in standard self-consistent LMTO-ASA calculations is not the proper one but a functional of merely the ASA density for fixed atomic-sphere radii; its Hartree term is the Coulomb self-energy of spherical charge densities inside WS spheres whose overlaps are neglected.[2,4] When the spheres can be closely packed like in fcc and bcc arrangements (the diamond structure is, for instance, packed like bcc with two atomic spheres and two empty spheres per cell), the ASA total energy normally deviates from the proper total energy by only hundredths of a rydberg, but the choice of sphere radii can be critical. If the combined correction terms are included in the calculation of the one-electron energies, and the charge density is approximated by a uniform background plus spherical contributions, calculated total-energy differences between high-symmetry structures usually have millirydberg accuracy or better. Even so, it is unlikely, that the minimization of a MT total-energy functional[13] can yield accurate results for symmetry-lowering displacements of the atoms. For such purposes the proper functional *without shape approximations for the charge density* is needed and it is an aim of the present paper to demonstrate how this charge density may be conveniently generated within the MTO framework.

The infinite-range problem for the solid-state MTO's was recently solved.[8,9] It originated from the requirement that the MTO set be minimal, because this forces the tail of *each* orbital to be an approximate solution of Schrödinger's equation in the interstitial region. Here, the one-electron kinetic energy, $\varepsilon - V(\mathbf{r})$, for the occupied valence states is numerically small, typically between -0.2 and $+0.8$ Ry, and the convenient choice made for solid-state MTO's is that they satisfy Laplace's equation $\Delta \chi = 0$ in the interstitial region, i.e., their "wave number" (κ) is zero.[1] The conventional *s*-MTO thus falls off like $1/r$, the *p* orbitals like $1/r^2$, the *d* orbitals like $1/r^3$, etc. Now, the recently proposed set of tight-binding (TB) MTO's are simply short-ranged linear combinations of the conventional set.

In the present paper we first show how the TB-MTO's may be represented in real space and, by the example of crystalline Si, we demonstrate that they have extremely short range. Secondly, we show how to use this TB representation to obtain charge-density plots from LMTO calculations. For Si we demonstrate that the charge density obtained from a standard, self-consistent LMTO-ASA calculation is in excellent agreement with the one obtained from a self-consistent, full-potential linear augmented plane-wave (LAPW) calculation.[14]

The eigenvalues and eigenvectors resulting from LMTO band calculations are correct to third and second order, respectively, in the deviation of the eigenvalue from the chosen energy, ε_ν, of the LMTO. The LMTO itself is however only correct to first order. In standard calculations the ASA charge density is therefore made correct to second order by use of the so-called tail-cancellation condition valid in the ASA, the one-center expansions of the wave functions, and the Taylor series to second order in energy of the radial wave functions $\phi_{Rl}(\varepsilon, r)$. We now devise a similar technique, which however does not rely on the ASA, for obtaining the full charge density correct to second order.

It is obvious that a next step will be to insert the MTO density in the proper, rather than the ASA or MT, total-energy functional. This, as well as other applications of the MTO-TB representation, will be published elsewhere.

Since this paper is the first of a planned series it is organized as follows. In Sec. II we give a self-contained account of the recent MTO formalism,[8,9] but we focus on the orbitals rather than on the Hamiltonian and overlap, or Green's-function matrices. As a demonstration we plot two sets of TB LMTO's for Si using structure constants screened, respectively, on bcc and diamond lattices. In Sec. III we show how the charge density may be obtained from various starting points, the simplest being a calculation using the ASA for the potential and the orthogonal LMTO representation given in Sec. III F. The Si charge density presented in Sec. III H was calculated in this way. In Sec. III E we explain how to obtain ASA Green's functions in the TB representation, and in Sec. III G we give the second-order correction to the charge density. Section IV is the summary.

II. CONVENTIONAL AND SCREENED LMTO's

A. Envelope functions and structure constants

As mentioned in the Introduction, for an LMTO, $\chi^0_{RL}(\mathbf{r}-\mathbf{R})$, belonging to the *conventional* set[1–4] (denoted by the superscript^0) the envelope function is simply the Laplace-equation solution

$$K^0_{RL}(\mathbf{r}_R) \equiv (r_R/w)^{-l-1} Y_L(\hat{\mathbf{r}}_R) , \tag{1}$$

apart from a normalization constant. Here and in the following the sites of the orbitals are denoted by $\mathbf{R}$,

$$\mathbf{r}_R \equiv \mathbf{r}-\mathbf{R} , \quad r_R \equiv |\mathbf{r}-\mathbf{R}| ,$$

and Y_{lm} is a spherical or cubic harmonic. w is the average WS radius and thus a measure of the site density; it is introduced in order to make the envelope functions independent of the scale of the structure. The envelope (1) has the form of the electrostatic potential from a single 2^l pole at $\mathbf{R}$. It is regular, except at $\mathbf{R}$, and it may be expanded about any other site, $\mathbf{R}'$,

$$K^0_{RL}(\mathbf{r}_R) = -\sum_{L'} J^0_{R'L'}(\mathbf{r}_{R'}) S^0_{R'L',RL} , \tag{2}$$

in terms of the regular Laplace-equation solutions

$$J^0_{RL}(\mathbf{r}_R) \equiv (r_R/w)^l [2(2l+1)]^{-1} Y_L(\hat{r}_R) . \tag{3}$$

Their form is independent of the orbital ($\mathbf{R}L$) and the site ($\mathbf{R}'$) of the expansion. The expansion (2) converges for $\mathbf{r}$ inside the sphere centered at $\mathbf{R}'$ passing through $\mathbf{R}$. The expansion matrix, $S^0_{R'L',RL}$, is the conventional canonical structure matrix which, due to the particular normalizations chosen in (1) and (3) for the functions K^0 and J^0, is Hermitian and only depends on $\mathbf{R}$ and $\mathbf{R}'$ in the combination

$$(|\mathbf{R}-\mathbf{R}'|/w)^{-l'-l-1} Y^*_{l'+l,m'-m}(\hat{\mathscr{R}}) ,$$

where $\mathscr{R} = \mathbf{R}-\mathbf{R}'$. Explicit expressions may be found in Refs. 1, 2, 4, and 5.

For a *general* LMTO representation, which is characterized by the "screening numbers" α_{Rl}, (α_{Rl} is usually independent of $\mathbf{R}$, and $\alpha_l \equiv 0$ for $l > l_\alpha \leq 2$), the envelope functions are defined to be those Laplace-equation solutions, $K^\alpha_{RL}(\mathbf{r}_R)$, which are proportional to $K^0_{RL}(\mathbf{r}_R)$ for $\mathbf{r}$ in the neighborhood of $\mathbf{R}$ and whose tail expansions

$$K^\alpha_{RL}(\mathbf{r}_R) = -\sum_{L'} J^\alpha_{R'L'}(\mathbf{r}_{R'}) S^\alpha_{R'L',RL} \tag{4}$$

involve the functions

$$J^\alpha_{RL}(\mathbf{r}_R) \equiv J^0_{RL}(\mathbf{r}_R) - \alpha_{Rl} K^0_{RL}(\mathbf{r}_R) . \tag{5}$$

Here, again, the form of J^α is independent of the orbital and its site. It is obvious that $K^{\alpha}_{RL}(\mathbf{r}_R)$ must be a superposition of conventional envelope functions (1) placed at all sites where the corresponding matrix elements of αS^{α} do not vanish and, hence, $K^{\alpha}_{RL}(\mathbf{r}_R)$ has the same form as the electrostatic potential from a 2^l pole at $\mathbf{R}$ *screened* by multipoles at all sites. The explicit expressions for this superposition and for the screened, canonical structure matrix, S^{α}, in terms of S^0 and α, may be obtained by insertion of (5) in (4) and subsequent comparison with (2).

For this and further purposes it is convenient to use the following combined matrix and ket-bra notation. Firstly, the functions $K^{0}_{RL}(\mathbf{r}_R)$ and $K^{\alpha}_{RL}(\mathbf{r}_R)$ are denoted as $|K^{0}_{RL}\rangle^{\infty}$ and $|K^{\alpha}_{RL}\rangle^{\infty}$, respectively. The superscript ∞ indicates that these functions extend in all space. Secondly, we divide space into WS cells around the sites in such a way that each expansion (2) holds throughout its WS cell. Omission of the superscript ∞, like in $|K^{0}_{RL}\rangle$, $|J^{0}_{RL}\rangle$, and $|J^{\alpha}_{RL}\rangle$ now indicates that these functions are truncated outside the WS cell around $\mathbf{R}$. Thirdly, the functions $|K^{\alpha}_{RL}\rangle^{\infty}$ are considered elements of the row vector, $|K^{\alpha}\rangle^{\infty}$, while the functions $K^{\alpha}_{RL}(\mathbf{r}_R)^*$ are considered elements of the column vector, ${}^{\infty}\langle K^{\alpha}|$. This vector notation is used for all functions. Fourthly, $S^{\alpha}_{R'L',RL}$ are the elements of a matrix, S^{α}, and α_{Rl} are the elements of a *diagonal* matrix, α, whose elements are independent of m.

With this notation we may use (1) and (2) to express the conventional set of LMTO envelopes as

$$|K^0\rangle^{\infty}=|K^0\rangle-|J^0\rangle S^0\,, \tag{6}$$

provided that the on-site elements $S^{0}_{RL',RL}$ are taken to be zero. Analogously, from (4),

$$|K^{\alpha}\rangle^{\infty}=|K^0\rangle-|J^{\alpha}\rangle S^{\alpha} \tag{7}$$

and, if we now insert the definition (5) of J^{α}, we obtain

$$|K^{\alpha}\rangle^{\infty}=|K^0\rangle(1+\alpha S^{\alpha})-|J^0\rangle S^{\alpha}\,, \tag{8}$$

which is a superposition of $|K^0\rangle^{\infty}$ as given by (6) if and only if the "screened" structure matrix satisfies the "Dyson equation"

$$S^{\alpha}=S^0(1+\alpha S^{\alpha})=S^0+S^0\alpha S^{\alpha} \tag{9}$$

or, equivalently,

$$S^{\alpha}=S^0(1-\alpha S^0)^{-1}=\alpha^{-1}[(\alpha^{-1}-S^0)^{-1}-\alpha]\alpha^{-1}\,. \tag{10}$$

The superposition is

$$|K^{\alpha}\rangle^{\infty}=|K^0\rangle^{\infty}(1+\alpha S^{\alpha}) \tag{11a}$$

or, explicitly,

$$K^{\alpha}_{RL}(\mathbf{r}_R)=(r_R/w)^{-l-1}Y_L(\hat{r}_R)+\sum_{R'}\sum_{l'=0}^{l_\alpha}(r_{R'}/w)^{-l'-1}\alpha_{R'l'}\times\sum_{m'}Y_{L'}(\hat{\mathbf{r}}_{R'})S^{\alpha}_{R'L',RL}\,. \tag{11b}$$

In the electrostatic analogue αS^{α} is seen to be the screening charge (note that S^{α} usually has on-site terms). Since $\alpha_{R'l'}\equiv 0$ for $l'>l_\alpha$ the l' sum in the superposition (11) is *finite*. This is in contrast to the one-center expansion (4) where the l' sum is infinite. Like in (11) the screened L orbital, $\chi^{\alpha}_{RL}(\mathbf{r}_R)$, will be a superposition of conventional s, p, and possibly d (plus f, if $l=3$) orbitals only. The problem is now to find a set of α values such that S^{α} is so localized that not only the L' sum but also the $\mathbf{R}'$ sum in (11) is manageable.

The construction of localized envelope functions is according to (10) possible for any set of α's for which $\det(\alpha^{-1}-S^0)\neq 0$. For the α's independent of $\mathbf{R}$ and sufficiently small and positive such sets exist because $S^0(\mathbf{k})$, the conventional canonical bands,[2] are upwards bound. The screened canonical structure matrix for such a set thus decreases exponentially with the relative, interatomic distance, $d/w\equiv|\mathbf{R}-\mathbf{R}'|/w$. The set found by trial and error[8,9] to yield the best localization of S^{α} for a number of closely packed lattices, and for $l_\alpha\equiv 2$, is

$$\alpha_s=0.3485\equiv\beta_s\,,\quad \alpha_p=0.053\,03\equiv\beta_p\,,$$

and

$$\alpha_d=0.0107\equiv\beta_d \tag{12}$$

The range of the corresponding, so-called TB structure matrix, S^{β}, is essentially limited to the first- and second-nearest neighbors and it behaves approximately as $\exp(-4d/w)$. It is given for the fcc, bcc, and sc structures in Table I of Ref. 8 and for further structures, including diamond, in Ref. 15. The TB structure matrix for the diamond structure differs from the one of the bcc structure by having $w_{\text{dia}}=2^{1/3}w_{\text{bcc}}$ and $\alpha_{El}=0$, where E refers to the tetrahedral interstitial sites. The screening numbers for the atomic sites, i.e., the diamond lattice, are still given by (12). For this more open structure S^{β} extends to the third-nearest neighbors. The TB structure matrix for an *arbitrary* structure may be obtained by solution of (10) for a small cluster containing at the order of 30, sites or by iteration of the "Dysons equation" (9) in real space using as a starting point the approximate S^{β} given in Table I. This will be demonstrated in detail in Ref. 15. With the structure matrix limited to first-, second-, and possibly third-nearest-neighbor hopping the corresponding envelope functions $|K^{\beta}\rangle^{\infty}$ can easily be represented by the direct superposition (11) and, in the bcc structure, each $|K^{\beta}_{RL}\rangle^{\infty}$ is the sum of $(8+6)\times 9=126$ terms. The envelope of the TB s orbital of the bcc structure is shown in Fig. 6 of Ref. 8.

TABLE I. Interpolation formula for the TB structure matrix: $S^{\beta}_{ll'm}=Ae^{-\lambda d/w}$.

S^{β}	A	λ
$ss\sigma$	-184.7	3.293
$sp\sigma$	371.7	3.301
$pp\sigma$	791.0	3.331
$sd\sigma$	-575.0	3.440
$pd\sigma$	-1422.0	3.535
$dd\sigma$	-3685.0	3.905
$pp\pi$	-359.9	3.935
$pd\pi$	837.0	3.965
$dd\pi$	1997.0	3.998
$dd\delta$	-844.0	4.708

In order to construct the set of TB LMTO's $|\chi^{\beta}\rangle^{\infty}$ we now merely need to define the conventional set of LMTO's $|\chi^{0}\rangle^{\infty}$ by augmentation of the envelope set $|K^{0}\rangle^{\infty}$ inside the MT (or WS) spheres and then use the superposition (11). For reasons of notation,[16] and in view of applications in the following section and coming publications, we shall, however, follow the development sketched in Ref. 9 and define the LMTO's in general, that is, for a general α and, furthermore, define them as the linear approximation to the *energy-dependent* MTO's which we now introduce.

B. Muffin-tin orbitals and potential functions

Whereas the envelope set is canonical (that is, scale, potential, and energy independent) the MTO set is uniquely designed for the one-electron potential, $V(\mathbf{r})$, to be treated as follows.

Inside each WS cell the potential is spherically averaged into $v_R(r_R)$ and the corresponding radial Schrödinger equations are solved as functions of the one-electron energy ε yielding the regular, radial functions $\phi_{Rl}(\varepsilon,r_R)$. If these are normalized to unity in the MT sphere of radius s_R, i.e.,

$$\int_0^{s_R}\phi_{Rl}^{\gamma}(\varepsilon,r)^2 r^2 dr=1\ , \tag{13}$$

they are given the superscript γ for reasons which will be clear later. The partial waves are

$$\phi_{RL}(\varepsilon,\mathbf{r}_R)\equiv\phi_{Rl}(\varepsilon,r_R)Y_L(\hat{\mathbf{r}}_R) \tag{14}$$

and the functions $|\phi_{RL}(\varepsilon)\rangle$ are truncated outside their MT sphere.

From the envelope function[7] one now forms the energy-dependent muffin-tin orbital (MTO) by substituting each radial function $|J_{R'l'}^{\alpha}\rangle$ inside its MT sphere by some *regular* function, $|\widetilde{J}_{R'l'}^{\alpha}\rangle$, which matches continuously and differentiably onto it at $s_{R'}$, i.e.,

$$J_{R'l'}^{\alpha}(r_{R'})\rightarrow\widetilde{J}_{R'l'}^{\alpha}(r_{R'})\ , \tag{15a}$$

and by substituting the radial function $|K_{RL}^{0}\rangle$ inside its MT sphere by the proper linear combination of $|\phi_{Rl}^{\gamma}(\varepsilon)\rangle$ and $|\widetilde{J}_{Rl}^{\alpha}\rangle$, i.e.,

$$\begin{aligned}K_{Rl}^{0}(r_R)\equiv(r_R/w)^{-l-1}&\rightarrow\phi_{Rl}^{\gamma}(\varepsilon,r_R)N_{Rl}^{\alpha}(\varepsilon)+\widetilde{J}_{Rl}^{\alpha}(r_R)P_{Rl}^{\alpha}(\varepsilon)\\&\equiv\phi_{Rl}^{\alpha}(\varepsilon,r_R)N_{Rl}^{\alpha}(\varepsilon_\nu)+\widetilde{J}_{Rl}^{\alpha}(r_R)P_{Rl}^{\alpha}(\varepsilon)\ .\end{aligned} \tag{15b}$$

Again, for reasons to become clear later, we have defined

$$|\phi^{\alpha}(\varepsilon)\rangle\equiv|\phi^{\gamma}(\varepsilon)\rangle N^{\alpha}(\varepsilon)/N^{\alpha}(\varepsilon_\nu) \tag{16}$$

in the last equation, and ε_ν is an arbitrary energy near the center of interest. Continuous and differentiable matching leads to the expressions

$$P^{\alpha}(\varepsilon)=\frac{W\{\phi(\varepsilon),K^{0}\}}{W\{\phi(\varepsilon),J^{\alpha}\}}=\frac{P^{0}(\varepsilon)}{1-\alpha P^{0}(\varepsilon)} \tag{17}$$

for the potential function and

$$N^{\alpha}(\varepsilon)=\frac{W\{J^{\alpha},K^{0}\}}{W\{J^{\alpha},\phi^{\gamma}(\varepsilon)\}}=[(w/2)\dot{P}^{\alpha}(\varepsilon)]^{1/2} \tag{18}$$

for the so-called normalization function. In these equations we have dropped the subscripts Rl. Moreover

$$W\{a,b\}\equiv s^2[a(s)b'(s)-a'(s)b(s)] \tag{19}$$

is the Wronskian,

$$W\{K^{0},J^{\alpha}\}=w/2\ , \tag{20}$$

and

$$P^{0}(\varepsilon)=2(2l+1)\left[\frac{w}{s}\right]^{2l+1}\frac{D(\varepsilon)+l+1}{D(\varepsilon)-l}\ , \tag{21}$$

with $D(\varepsilon)\equiv s\phi'(\varepsilon,s)/\phi(\varepsilon,s)$, is the conventional potential function. In (18) the overdot denotes an energy derivative,

$$\dot{P}^{\alpha}(\varepsilon)^{1/2}\equiv\left[\frac{\partial}{\partial\varepsilon}P^{\alpha}(\varepsilon)\right]^{1/2}\ ,$$

and a particular sign has been chosen for the square root. Throughout this paper we use atomic rydberg units. The last equation (18) follows from the Wronskian relation

$$\begin{aligned}W\{\dot{\phi}^{\gamma}(\varepsilon),\phi^{\gamma}(\varepsilon)\}&=\langle\phi^{\gamma}(\varepsilon)|-\Delta+v-\varepsilon|\dot{\phi}^{\gamma}(\varepsilon)\rangle\\&=\langle\phi^{\gamma}(\varepsilon)^2\rangle=1\ ,\end{aligned} \tag{22}$$

which, itself, follows from Green's second theorem, the Schrödinger equations in the sphere,

$$(-\Delta+v-\varepsilon)|\phi(\varepsilon)\rangle=0 \tag{23a}$$

and

$$(-\Delta+v-\varepsilon)|\dot{\phi}(\varepsilon)\rangle=|\phi(\varepsilon)\rangle\ , \tag{23b}$$

plus the normalization (13). In the language of scattering theory $P^{0}(\varepsilon)$ is proportional to the cotangent of the phase shift η_l, the constant of proportionality being negative so that the potential function is a never decreasing function of energy. Explicitly,

$$\begin{aligned}[P_l^{0}(\varepsilon)]^{-1}&=\alpha_l+[P_l^{\alpha}(\varepsilon)]^{-1}\\&=-\tfrac{1}{2}\lim_{\kappa\rightarrow 0}\kappa w[n_l(\kappa w)]^2\tan(\eta_l)\ .\end{aligned}$$

We see that a change of representation (α) merely corresponds to a shift of the scattering "background." The function

$$\begin{aligned}\left[-\frac{\partial}{\partial\varepsilon}[P^{\alpha}(\varepsilon)]^{-1}\right]^{-1/2}&=P^{\alpha}(\varepsilon)[\dot{P}^{\alpha}(\varepsilon)]^{-1/2}\\&=\sqrt{2/w}\,W\{\phi^{\gamma}(\varepsilon),K^{0}\}\\&=\langle\phi^{\gamma}(\varepsilon)|(\varepsilon-v)|K^{0}\rangle\ ,\end{aligned} \tag{24a}$$

which is representation invariant, is essentially $-\cos(\eta)$, and the function

$$\begin{aligned}[\dot{P}^{\alpha}(\varepsilon)]^{-1/2}&=\sqrt{2/w}\,W\{\phi^{\gamma}(\varepsilon),J^{\alpha}\}\\&=\langle\phi^{\gamma}(\varepsilon)|(\varepsilon-v)|J^{\alpha}\rangle\end{aligned} \tag{24b}$$

is essentially $\sin(\eta)$. Here, again, a particular sign has been chosen for the square roots.

It is customary to parametrize the potential function in terms of the three potential parameters C, Δ, and γ by the usual resonance form for $\tan(\eta)$

$$[P^\alpha(\varepsilon)]^{-1}=\frac{\Delta}{\varepsilon-C}+\gamma-\alpha\ . \tag{25}$$

The parametrization of $-\cos(\eta)$ in (24a) is

$$\left[-\frac{\partial}{\partial\varepsilon}[P^\alpha(\varepsilon)]^{-1}\right]^{-1/2}=\sqrt{2/w}\,W\{\phi^\gamma(\varepsilon),K^0\}=\frac{\varepsilon-C}{\sqrt{\Delta}} \tag{26a}$$

and the parametrization of $\sin(\eta)$ in (24b) is

$$\begin{aligned}[\dot{P}^\alpha(\varepsilon)]^{-1/2}&=\sqrt{w/2}[N^\alpha(\varepsilon)]^{-1}\\ &=\sqrt{2/w}\,W\{\phi^\gamma(\varepsilon),J^\alpha\}=\frac{\varepsilon-V^\alpha}{(\Gamma^\alpha)^{1/2}}\ .\end{aligned} \tag{26b}$$

The latter form corresponds to

$$P^\alpha(\varepsilon)=\frac{\Gamma^\alpha}{V^\alpha-\varepsilon}+\frac{1}{\gamma-\alpha}\ , \tag{27}$$

which is equivalent with (25) because the representation-dependent potential parameters in (26b) are defined by

$$V^\alpha\equiv C-\frac{\Delta}{\gamma-\alpha}\quad\text{and}\quad\Gamma^\alpha\equiv\frac{\Delta}{(\gamma-\alpha)^2}\ . \tag{28}$$

The zero C of the potential function is the energy where $|\phi(\varepsilon)\rangle$ joins onto $|K^0\rangle$ and the pole V^α of the potential function is the energy where $|\phi(\varepsilon)\rangle$ joins onto $|J^\alpha\rangle$.

Expression (25) or (27) solved for ε gives the energy, corresponding to a given potential function (i.e., boundary condition), correct to order $(\varepsilon-\varepsilon_\nu)^2$ where ε_ν is an arbitrary energy, and the values of the potential parameters may be obtained by expanding $|\phi^\gamma(\varepsilon)\rangle$ in a Taylor series

$$|\phi^\gamma(\varepsilon)\rangle=|\phi^\gamma\rangle+|\dot{\phi}^\gamma\rangle(\varepsilon-\varepsilon_\nu)+|\ddot{\phi}^\gamma\rangle(\varepsilon-\varepsilon_\nu)^2/2+\cdots$$

and inserting merely the *first-order expression in (26a) and (26b). If instead one inserts the expansion* to *second* order, the additional terms

$$-\tfrac{3}{2}(\varepsilon_\nu-C)(\varepsilon-\varepsilon_\nu)^2p/\sqrt{\Delta} \tag{29a}$$

and

$$-\tfrac{3}{2}(\varepsilon_\nu-V^\alpha)(\varepsilon-\varepsilon_\nu)^2p/(\Gamma^\alpha)^{1/2} \tag{29b}$$

occur in (26a) and (26b), respectively. Here we have made use of[1]

$$p\equiv\langle(\dot{\phi}^\gamma)^2\rangle=-\frac{\ddot{\phi}^\gamma(s)}{3\phi^\gamma(s)}\quad\text{and}\quad W\{\ddot{\phi}^\gamma,\phi\}=0\ , \tag{30}$$

where p is the fourth potential parameter. A corresponding *third*-order expression for the potential function is obtained by performing the substitution

$$\varepsilon\rightarrow\varepsilon+(\varepsilon-\varepsilon_\nu)^3p \tag{31}$$

in (25) or (27). The fact that there are no second-order terms in (31) proves that (25) is correct to second order. [Note that (31) cannot be derived by insertion of the second-order expressions (26a) plus (29a) and (26b) plus (29b) for the Wronskians in (17), because this would have required the inclusion of third-order terms in (29a) and (29b). The energy derivative of $[P(\varepsilon)]^{-1}$ given by (25) and (31), and the energy derivative of $P(\varepsilon)$ given by (27) and (31) are, however, consistent with, respectively, the sum of (26a) and (29a) and the sum of (26b) and (29b).

From (25) and (31) one may realize that there exists a particular, potential-dependent representation in which $\ddot{P}_{Rl}(\varepsilon_{\nu Rl})=0$ for all Rl. This is the representation where $\alpha_{Rl}=\gamma_{Rl}$ for all Rl. We shall return to this so-called orthonormal representation in Sec. III F.

Having introduced the potential functions and their parameters we now return to the main theme of this section, the definition of the energy-dependent MTO. This is given through the substitution of (15) in the one-center expansion (7) for the envelope function by[17]

$$\begin{aligned}|\chi^\alpha(\varepsilon)\rangle^\infty&\equiv|\phi^\gamma(\varepsilon)\rangle N^\alpha(\varepsilon)+|\tilde{J}^\alpha\rangle[P^\alpha(\varepsilon)-S^\alpha]+|K^\alpha\rangle^i\\ &=|\phi^\alpha(\varepsilon)\rangle N^\alpha(\varepsilon_\nu)+|\tilde{J}^\alpha\rangle[P^\alpha(\varepsilon)-S^\alpha]+|K^\alpha\rangle^i\ .\end{aligned} \tag{32}$$

Here, $N^\alpha(\varepsilon)$ and $P^\alpha(\varepsilon)$ are regarded as diagonal matrices, $|\ \rangle$ denotes a function truncated outside its MT sphere and $|\ \rangle^i$ denotes a function truncated outside the interstitial region, that is, inside all MT spheres.

The energy-dependent MTO's, for any α, are a *complete set* for the MT potential used for their construction, i.e., for the potential $|v\rangle+|\varepsilon\rangle^i$. This is so because if, for given ε, the column vector with components $a^\alpha_{RL}(\varepsilon)$ satisfies the homogeneous, linear equations

$$[P^\alpha(\varepsilon)-S^\alpha]a^\alpha(\varepsilon)=0 \tag{33a}$$

with the normalization

$$\sum_{R,L}(w/2)\dot{P}^\alpha_{RL}(\varepsilon)\,|a^\alpha_{RL}(\varepsilon)|^2=1\ , \tag{33b}$$

then the linear combination

$$|\chi^\alpha(\varepsilon)\rangle^\infty a^\alpha(\varepsilon)=|\phi^\gamma(\varepsilon)\rangle N^\alpha(\varepsilon)a^\alpha(\varepsilon)+|K^\alpha\rangle^i a^\alpha(\varepsilon)\ , \tag{34}$$

by construction, is a solution of Schrödinger's equation for the MT potential.

The so-called Korringa-Kohn-Rostoker (KKR) or tail-cancellation conditions (33) become converged for $(l,l')\le l_\phi$ if $l_\alpha\le l_\phi$ and l_ϕ is defined by the condition that *all* potential functions with $l>l_\phi$ satisfy

$$\begin{aligned}|P^0_l(\varepsilon)|&\gg[(S^0_{ll})^2]^{1/2}\\ &\approx\left[\frac{2l+1}{(2\pi l)^{1/2}}\sum_{\mathbf{R}(\neq 0)}\left[\frac{2w}{|\mathbf{R}-\mathbf{R}'|}\right]^{2(2l+1)}\right]^{1/2}\ .\end{aligned} \tag{35}$$

This limit *will* be reached because, for sufficiently high l's the radial Schrödinger equations are dominated by the centrifugal term and therefore nearly equal the Laplace equations. As a consequence, the higher partial waves are nearly independent of energy and proportional to $J^0_l(r)$, viz.,

$$\phi^{\gamma}_{l}(\varepsilon,r)\approx r^{l}\langle r^{2l}\rangle^{-1/2}=J^{0}_{l}(r)[(2/w)\Gamma^{0}_{l}]^{1/2} . \tag{36}$$

That the constant of proportionality is related to the potential parameter Γ^0 in the way indicated can be checked by insertion of (36) in (24a), using (20) and comparing with (27), or one can use (24b) and (26b). The value of Γ^0 obtained by evaluation of the normalization integral in (36) is

$$\Gamma^{0}_{l}\approx 2(2l+1)^{2}(2l+3)(w/s)^{(2l+1)}s^{-2} , \tag{37}$$

and for the values of the potential parameters V^0 one finds

$$V^{0}_{l}\approx\langle r^{l}\,|\,v(r)\,|\,r^{l}\rangle/\langle r^{2l}\rangle\approx v(s) . \tag{38}$$

As a result, one may for a given maximum value of $|\varepsilon-V^{0}|$ estimate l_{ϕ} by using (35) with $P^{0}_{l}(\varepsilon)\leq\Gamma^{0}_{l}/\max|\varepsilon-V^{0}|$.

Since the high-l components of the MTO tails,

$$-\sum_{R'}\sum_{l'(>l_{\phi})}\sum_{m'}|J^{0}_{R'L'}\rangle S^{\alpha}_{R'L',RL} ,$$

are solutions of the corresponding radial Schrödinger equations, the MTO expansion

$$\sum_{R}\sum_{L}\chi^{\alpha}_{RL}(\varepsilon,\mathbf{r}_{R})a^{\alpha}_{RL}(\varepsilon)=\psi(\varepsilon,\mathbf{r}) \tag{39a}$$

on the left-hand side of (34) is converged when $l\leq l_{\phi}$, and the higher partial waves in the (slowly converging) one-center expansion on the right-hand side of (34)

$$\sum_{L}\phi^{\gamma}_{RL}(\varepsilon,\mathbf{r}_{R})N^{\alpha}_{Rl}(\varepsilon)a^{\alpha}_{RL}(\varepsilon)=\psi(\varepsilon,\mathbf{r}) \tag{39b}$$

are provided by the tails of the lower MTO's.

C. Linear muffin-tin orbitals

It is now possible to define the radial functions $|\tilde{J}^{\alpha}_{Rl}\rangle$ in such a way that the energy dependence of $|\chi^{\alpha}(\varepsilon)\rangle^{\infty}$ vanishes to first order in $\varepsilon-\varepsilon_{\nu}$, where ε_{ν} is an arbitrary, possibly **R** and l dependent, energy chosen at the center of interest. The energy-independent, so-called *linear* MTO's (LMTO's) obtained by neglecting the second- and higher-order terms in (32) therefore yield one-electron energies with errors of order $[(\varepsilon-\varepsilon_{\nu})^{2}]^{2}=(\varepsilon-\varepsilon_{\nu})^{4}$ and higher, that is, one-electron energies correct to order $(\varepsilon-\varepsilon_{\nu})^{3}$, when used as basis functions in connection with the variational principle for the one-electron Hamiltonian.

From (32) it is obvious that $\chi^{\alpha}_{RL}(\varepsilon,\mathbf{r}_{R})$ depends on ε only inside the MT sphere at **R**. The first energy derivative is

$$\begin{aligned}|\dot{\chi}^{\alpha}(\varepsilon)\rangle^{\infty}&=|\phi^{\gamma}(\varepsilon)\rangle\dot{N}^{\alpha}(\varepsilon)+|\dot{\phi}^{\gamma}(\varepsilon)\rangle N^{\alpha}(\varepsilon)+|\tilde{J}^{\alpha}\rangle\dot{P}^{\alpha}(\varepsilon)\\&=|\dot{\phi}^{\alpha}(\varepsilon)\rangle N^{\alpha}(\varepsilon_{\nu})+|\tilde{J}^{\alpha}\rangle\dot{P}^{\alpha}(\varepsilon) .\end{aligned} \tag{40}$$

It has pure RL character and vanishes continuously and with a continuous first derivative at the sphere. $\tilde{J}^{\alpha}_{Rl}(r_{R})$ is now defined by the condition that $\dot{\chi}^{\alpha}_{Rl}(\varepsilon_{\nu},r_{R})$ vanishes throughout, that is

$$\begin{aligned}|\tilde{J}^{\alpha}\rangle&\equiv-|\dot{\phi}^{\alpha}\rangle(w/2)/N^{\alpha}\\&=-|\dot{\phi}^{\alpha}\rangle[(2/w)-|\dot{\phi}^{\alpha}\rangle[(2/w)\dot{P}^{\alpha}]^{-1/2}\end{aligned} \tag{41}$$

with

$$|\dot{\phi}^{\alpha}\rangle\equiv|\dot{\phi}^{\gamma}\rangle+|\phi\rangle o^{\alpha} \tag{42}$$

and

$$o^{\alpha}\equiv\dot{N}^{\alpha}/N^{\alpha} . \tag{43}$$

Here, and in the following, omission of the energy variable means that $\varepsilon\equiv\varepsilon_{\nu}$. The values P^{α}, $(\dot{P}^{\alpha})^{-1/2}$, and o^{α} are thus three potential parameters (diagonal matrices) which are related to the conventional ones by (27)–(31) with $\varepsilon=\varepsilon_{\nu}$. According to (16), $|\phi^{\alpha}\rangle$ is independent of α, and for $|\phi\rangle$ we have therefore dropped the superscript. Since, according to (13), $|\phi\rangle$ and $|\dot{\phi}^{\gamma}\rangle$ are orthogonal in the sphere we have

$$\langle\phi\,|\,\dot{\phi}^{\alpha}\rangle=o^{\alpha}=(V^{\alpha}-\varepsilon_{\nu})^{-1} . \tag{44}$$

In terms of the conventional potential parameters the definition (41) may be reexpressed as

$$|\tilde{J}^{\alpha}\rangle\equiv[\,|\phi\rangle+|\dot{\phi}\rangle(V^{\alpha}-\varepsilon_{\nu})][(2/w)\Gamma^{\alpha}]^{-1/2} . \tag{45}$$

This definition of $|\tilde{J}^{\alpha}\rangle$ is conveniently used also for the energy-dependent MTO (32).

The basic expression for the LMTO, analogous to (7) and (32), is thus seen to be

$$\begin{aligned}|\chi^{\alpha}\rangle^{\infty}&\equiv|\chi^{\alpha}(\varepsilon_{\nu})\rangle^{\infty}N^{\alpha}(\varepsilon_{\nu})^{-1}\\&=|\phi\rangle+|\dot{\phi}^{\alpha}\rangle h^{\alpha}+|K^{\alpha}\rangle^{i}/N^{\alpha} ,\end{aligned} \tag{46}$$

where we have defined the Hermitian matrix

$$\begin{aligned}h^{\alpha}&\equiv-(\dot{P}^{\alpha})^{-1/2}(P^{\alpha}-S^{\alpha})(\dot{P}^{\alpha})^{-1/2}\\&=-P^{\alpha}(\dot{P}^{\alpha})^{-1}+(\dot{P}^{\alpha})^{-1/2}S^{\alpha}(\dot{P}^{\alpha})^{-1/2}\\&\equiv c^{\alpha}+(d^{\alpha})^{1/2}S^{\alpha}(d^{\alpha})^{1/2}-\varepsilon_{\nu} .\end{aligned} \tag{47}$$

In this expression S^{α} is the only *non*diagonal matrix because P^{α} and $\dot{P}^{\alpha}$ are diagonal. h^{α} thus has the form of a two-center tight-binding Hamiltonian and, in fact, it turns out to be the Hamiltonian in the ASA and to first order in $\varepsilon-\varepsilon_{\nu}$ (see Sec. III A). Expression (46) for the LMTO may thus be regarded as the linear term of a Taylor series. Hence the name *linear* MTO.

From (45) one may realize that if $\varepsilon_{\nu}=V^{\alpha}$ for a particular Rl then that partial wave is only described to zeroth rather than to first order by the LMTO set. The corresponding LMTO vanishes and may be deleted from the set. This is a useful way of contracting the basis set for those partial waves which hardly depend on energy and which are therefore described sufficiently well by merely the tails of the remaining LMTO's. This was described for the case of the higher partial waves in the previous section.

The transformation from one LMTO set (46) to another, say from $|\chi^{0}\rangle^{\infty}$ to $|\chi^{\alpha}\rangle^{\infty}$, of course follows the transformations (10) and (17) for, respectively, the structure matrix and the potential functions. Since, however, for any α the set $|\chi^{\alpha}\rangle^{\infty}$ is obtained from the set $|K^{\alpha}\rangle^{\infty}$ by substitution of each two-dimensional $\{\,|K^{0}_{Rl}\rangle,\ |J^{0}_{Rl}\rangle\}$ Hilbert space by the two-dimensional $\{\,|\phi_{Rl}\rangle,|\dot{\phi}^{\gamma}_{Rl}\rangle\}$ Hilbert space, both of which are independent of α, it is obvious that the LMTO's (33) transform like the envelope functions, that is, according to (11). Taking the normalization constants N^{α} into account this linear transformation is

$$|\chi^{\alpha}\rangle^{\infty}=|\chi^{0}\rangle^{\infty}N^{0}(1+\alpha S^{\alpha})/N^{\alpha}\,. \tag{48}$$

LMTO sets of different α thus span the same Hilbert space (provided that $\varepsilon_{\nu}\neq V^{\alpha}$). This is not true for different sets of energy-dependent MTO's.

D. Evaluation of the TB-MTO's and LMTO's in real space

The basic expressions (32) and (46) are not useful for evaluation of the TB-MTO's or TB-LMTO's in real space because they are one-center expansions like (7). Specifically, the products $|\tilde{J}^{\beta}\rangle S^{\beta}$ and $|\dot{\phi}^{\beta}\rangle h^{\beta}$ (remember that β is the α value (12) for the TB representation) involve infinite L' sums which converge slowly for $\mathbf{r}_{R'}$ in the outer part of the MT sphere. We shall now rewrite the MTO and LMTO expressions in such a way that we need not sum over the higher partial waves, i.e., in such a way that the L' convergence is reached for $l'\leq l_{\phi}\approx 2-3$, where l_{ϕ} was defined in connection with (35).

With the notation that $|\ \rangle$ now denotes a function truncated outside the MT sphere, rather than outside the WS cell, we may use (7) to express the envelope function in the interstitial region as the difference between the envelope function in all space and the one-center expansions in the spheres, i.e.,

$$|K^{\beta}\rangle^{i}=|K^{\beta}\rangle^{\infty}-|K^{0}\rangle+|J^{\beta}\rangle S^{\beta}\,.$$

We now separate the irregular part of $|J^{\beta}\rangle$ like in (8) and express $|K^{\beta}\rangle^{\infty}$ by the superposition (11) obtaining

$$|K^{\beta}\rangle^{i}=(|K^{0}\rangle^{\infty}-|K^{0}\rangle)(1+\beta S^{\beta})+|J^{0}\rangle S^{\beta}\,. \tag{49}$$

Here, the first term is simply

$$\begin{aligned}
&[(|K^{0}\rangle^{\infty}-|K^{0}\rangle)(1+\beta S^{\beta})]_{RL}\\
&\quad=(r_{R}/w)_{>}^{-l-1}Y_{L}(\hat{\mathbf{r}}_{R})\\
&\qquad+\sum_{R'}\sum_{l'=0}^{l_{\beta}}(r_{R'}/w)_{>}^{-l'-1}\beta_{R'l'}\sum_{m'}Y_{L'}(\hat{\mathbf{r}}_{R'})S^{\beta}_{R'L',RL}\,.
\end{aligned} \tag{50}$$

The subscript $>$ indicates that the radial function is nonzero only for $\mathbf{r}$ outside the MT sphere in question, i.e., for $r_{R'}>s_{R'}$. Like in (11) the l' sum is finite, and so is the $\mathbf{R}'$ sum. The second term in (49) is regular but contains an infinite L' sum which, however, when $|J^{0}\rangle S^{\beta}$ is combined with the term $-|\tilde{J}^{\beta}\rangle S^{\beta}$ in (32) terminates because we can take

$$\tilde{J}^{\beta}_{l}(r)=J^{0}_{l}(r)\ \text{ when } l>l_{\phi}\geq l_{\beta}\,.$$

The MTO expression, useful for real-space evaluation, is thus

$$\begin{aligned}
|\chi^{\beta}(\varepsilon)\rangle^{\infty}=&\,|\phi^{\gamma}(\varepsilon)\rangle N^{\beta}(\varepsilon)+|\tilde{J}^{\beta}\rangle P^{\beta}(\varepsilon)\\
&+(|J^{0}\rangle-|\tilde{J}^{\beta}\rangle)S^{\beta}\\
&+(|K^{0}\rangle^{\infty}-|K^{0}\rangle)(1+\beta S^{\beta})\,.
\end{aligned} \tag{51}$$

Here the last two, energy-independent terms were discussed above and the first two, energy-dependent terms involve no summations because $N^{\beta}(\varepsilon)$ and $P^{\beta}(\varepsilon)$ are diagonal.

For the TB-LMTO $\chi^{\beta}_{RL}(\mathbf{r}_{R})$ we obtain

$$\begin{aligned}
|\chi^{\beta}\rangle^{\infty}=&(|\phi\rangle-|\dot{\phi}^{\beta}\rangle P^{\beta}/\dot{P}^{\beta})\\
&+(|J^{0}\rangle-|\tilde{J}^{\beta}\rangle)S^{\beta}/N^{\beta}\\
&+(|K^{0}\rangle^{\infty}-|K^{0}\rangle)(1+\beta S^{\beta})/N^{\beta}\,.
\end{aligned} \tag{52}$$

Here, the third term is the canonical multicenter expansion (50) times the potential parameter $(N^{\beta})^{-1}$. It is nonzero for $\mathbf{r}$ in the interstitial region as well as in the MT spheres. As discussed in connection with (11b) this multicenter expansion has typically about 150 terms, namely the tails of the conventional s, p, and d envelopes centered at the site of the TB-LMTO and at the first-, second-, and possibly third-nearest-neighbor sites. The functions involved are rapidly evaluated because they are powers of the relative, Cartesian coordinates, $x_{R'}$, $y_{R'}$, and $z_{R'}$, and inverse powers of $(x^{2}_{R'}+y^{2}_{R'}+z^{2}_{R'})^{1/2}$. The scale constant w is the average WS radius for the sites having $\beta_{Rl}\neq 0$.

The second term in expression (52) for $\chi^{\beta}_{RL}(\mathbf{r}_{R})$ is

$$\sum_{l'}[J^{0}_{l'}(r_{R'})-\tilde{J}^{\beta}_{l}(r_{R'})]\sum_{m'}Y_{L'}(\mathbf{r}_{R'})S^{\beta}_{R'L'RL}/N^{\beta}_{Rl}\,,$$

for $\mathbf{r}$ inside any MT sphere $(\mathbf{R}')$ for which $S^{\beta}_{R'L',RL}$ does not vanish, and zero in the interstitial region. $\tilde{J}^{\beta}$ is given by (45) and the l' summation terminates at $l_{\phi}(\geq l_{\beta})$.

The first line in (52) is simply

$$[\phi_{Rl}(r_{R})-\dot{\phi}^{\beta}_{Rl}(r_{R})P^{\beta}_{Rl}/\dot{P}^{\beta}_{Rl}]Y_{L}(\hat{\mathbf{r}}_{R})$$

for $\mathbf{r}$ in the MT sphere at which the TB-LMTO is centered, and zero outside.

If the first-order accuracy offered by the TB-LMTO is not sufficient it is a simple task to use

$$|\chi^{\beta}(\varepsilon)\rangle^{\infty}/N^{\beta}=|\chi^{\beta}\rangle^{\infty}+|\ddot{\chi}^{\beta}\rangle(\varepsilon-\varepsilon_{\nu})^{2}/2 \tag{53}$$

because the second energy-derivative function has pure RL character and vanishes outside its own sphere. It may be obtained by differentiation of (40) and the result is simply

$$|\ddot{\chi}^{\beta}\rangle\equiv|\ddot{\chi}^{\beta}(\varepsilon_{\nu})\rangle^{\infty}/N^{\beta}=|\phi\rangle 3p+|\ddot{\phi}^{\gamma}\rangle\,, \tag{54}$$

where we have used Eq. (30). This orbital is seen to be independent of the representation.

E. TB-LMTO's for Si using bcc screening

We now plot some of the TB-LMTO's for crystalline silicon using (52). The Si s orbital is shown in the $(1\bar{1}0)$ plane in Fig. 1. The black dots indicate the Si positions and the crosses indicate the tetrahedral interstitial sites. In Fig. 2 we show it along the [001] direction through the second-nearest interstitial site and along the [111] direction through the first-nearest Si site. This TB-LMTO belongs to the "standard basis set"[18] with s, p, and d orbitals on the Si, as well as on the tetrahedral interstitial sites, i.e., with nine Si orbitals on the (000) and (111) positions and nine E (empty-site) orbitals on the $(11\bar{1})$ and (002) positions. The structure matrix is thus the one for

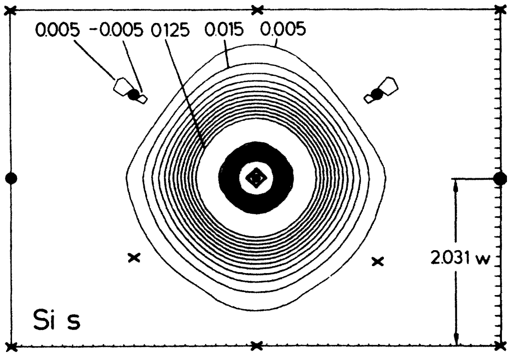

FIG. 1. Si s TB-LMTO in the $(1\bar{1}0)$ plane. Atomic sites are indicated by solid circles, empty sites by crosses. $s_A = s_E = w_{\text{bcc}}$. Screening is on a bcc lattice, i.e., $\alpha_A = \alpha_E = \beta$ and $w = w_{\text{bcc}}$.

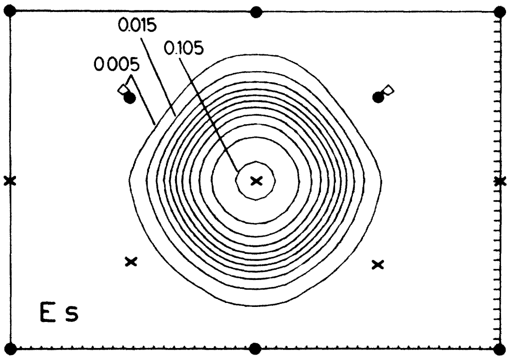

FIG. 3. Interstitial, or empty sphere, s orbital belonging to the same TB-LMTO set as the orbitals shown in Figs. 1 and 4, and in the same plane.

the bcc structure and $w = w_{\text{bcc}}$. The E s orbital is shown in the $(1\bar{1}0)$ plane in Fig. 3 and the Si $p(x+y-z)$ orbital is shown in the same plane in Fig. 4.

The one-electron potential used to define the augmentation of the orbitals was the local-density ASA potential obtained from a standard self-consistent LMTO-ASA calculation using the frozen-core approximation, 36 orbitals per cell and equal sphere radii,[18] i.e., $s_{\text{Si}} = s_E = w_{\text{bcc}} = 2.526$ Bohr radii. (Essentially the same potential would have been obtained without including the E p and d orbitals.[19]) The augmentation was performed inside the WS rather than inside the MT spheres. 95 **k** points were used in $\frac{1}{48}$ of the Brillouin zone. The ε_ν values were chosen at the Rl-projected centers of gravity of the valence band. The potential in the empty sphere is fairly flat and $v_E(r_E) \approx \varepsilon_\nu$, and the E s orbital in Fig. 3 is accordingly nodeless. The l' sums in (52) were truncated at $l_\beta = l_\phi = 2$ and the $\mathbf{R}'$ sum in (50) after the first two bcc shells; this means that the (000) site, the eight (111) sites, and the six (200) sites were included.

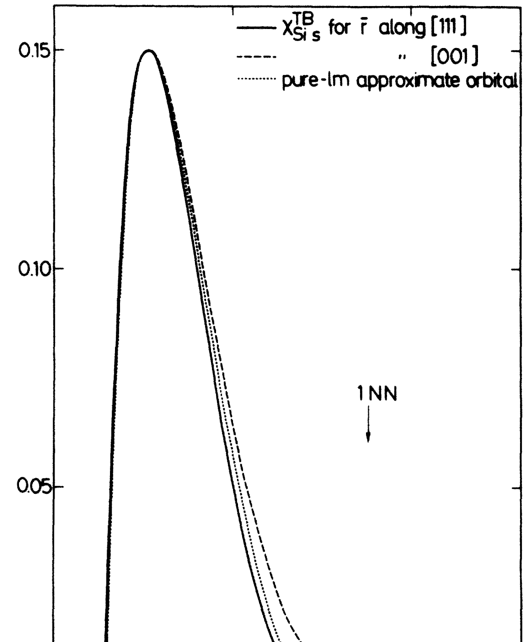

FIG. 2. The same orbital as in Fig. 1 but along the [111] and [001] directions. The dotted curve shows the approximate, pure-s orbital given by Eqs. (56) and (64).

In the contour plots of the TB-LMTO's there is, of course, no trace left over of the WS spheres because the augmentation is continuous and differentiable and because we have used expression (52), rather than (46) plus truncation of the l' sums. Most importantly, the orbitals are seen to be *extremely compact with an effective radius of about* $2w$, that is, 1.0—1.2 times the nearest-neighbor distance. The orbitals do extend into the first- and second-nearest-neighbor spheres, that is why the corresponding elements of the structure matrix are nonvanishing, but the orbitals are confined to a volume much less than that of the one-(000)-, eight-(111)-, and six-(200)-site nearest WS spheres.

A somewhat inconvenient feature is that the s orbital is not round or, in general, that the orbital $\chi^{\beta}_{RL}(\mathbf{r}_R)$ only has pure L character close to its own site, $\mathbf{R}$; further away it

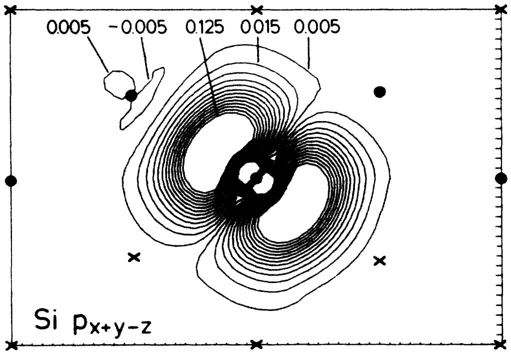

FIG. 4. Si p orbital belonging to the same TB-LMTO set as the orbitals in Figs. 1 and 3, and in the same plane.

merely follows the symmetry of the crystal. In the figures, one sees how the orbitals are confined by the neighboring Si sites and bulge out between them. (This might seem slightly surprising because the *envelope* functions for bcc screening make no difference between Si and E sites.) The Si s orbital along the two extreme directions [111] and [001] is shown in Fig. 2. Even inside its own sphere ($r/w<1$) this orbital is not spherical. In the language of Eq. (46) this is due to the higher partial waves. This fact that the LMTO does not factorize into a *single* product, valid in all space, of a radial function and a spherical or cubic harmonic is what necessitates a representation in terms of many one-center expansions like (46), or in terms of mixed one- and multicenter expansions like (52). (Note that in general the *conventional* LMTO does not have pure L character either, it is only its envelope function and the pseudo-LMTO, used for Fourier sums, which have this property.)

F. Approximate TB-LMTO's

For certain purposes, such as crude charge-density and wave-function plots, the above-mentioned anisotropy may be neglected and the computationally fast approximation

$$\chi^{\beta}_{RL}(\mathbf{r}_R)\approx f_{Rl}(r_R)Y_L(\hat{\mathbf{r}}_R) \tag{55}$$

having pure L character may be used. For the radial function $f(r)$ one would use the proper form inside the sphere, from (46), that is

$$f_{Rl}(r)=\phi_{Rl}(r)+\dot{\phi}^{\beta}_{Rl}(r)h^{\beta}_{RL,RL}\ , \tag{56}$$

and outside the sphere one would take a convenient, rapidly decaying, positive definite function such as an exponential or a Gaussian with parameters determined primarily by the conditions of continuity and differentiability at the sphere. With the amplitude and slope fixed at s_R the detailed form of the tail is not crucial considering the limited accuracy of (55).

For $r\approx s_R$ we obtain from (7), (46), and (5)

$$\begin{aligned} f(r)N^{\beta}&=K(r)-J^{\beta}(r)S^{\beta}_{\text{on}}\\ &=(1+\beta S^{\beta}_{\text{on}})x^{-l-1}-[2(2l+1)]^{-1}S^{\beta}_{\text{on}}x^{l} \end{aligned} \tag{57}$$

with $x\equiv r/w$. We have dropped the subscripts Rl and denoted the on-site element of the structure matrix S^{β}_{on}. The logarithmic derivative at the sphere is thus given by

$$\begin{aligned} D\{f\}+l+1&=(d\ln f/d\ln r)_s+l+1\\ &=\frac{2l+1}{1-2(2l+1)(\beta+1/S^{\beta}_{\text{on}})(s/w)^{-2l-1}} \end{aligned} \tag{58}$$

and the amplitude by

$$f(s)=-\frac{(s/w)^{l}S^{\beta}_{\text{on}}}{2(D\{f\}+l+1)N^{\beta}}\ . \tag{59}$$

The logarithmic derivative only depends on the sphere radius and on the relevant on-site term of the TB structure matrix. The values of these on-site terms may be found in Refs. 8 and 9, and 15, or they may be evaluated from the approximate off-site terms given in Table I using the "Dyson equation" (9) plus the fact that $S^{0}_{\text{on}}=0$. For the bcc structure and with $s=w$ the on-site terms are

$$S^{\beta}_{\text{on}}=\begin{cases}3.093\ (s),\\ 2.787\ (p),\\ 1.299\ (e_g),\\ 2.710\ (t_{2g})\end{cases}, \tag{60}$$

and one finds the following logarithmic derivatives

$$D\{f\}=\begin{cases}-3.910\ (s),\\ -4.039\ (p),\\ -3.735\ (e_g),\\ -4.788\ (t_{2g})\end{cases}. \tag{61}$$

If we approximate the tail by a plain exponential,

$$f(r)=a\exp(-\lambda r/w)\ , \tag{62}$$

we must have

$$D\{f\}=-\lambda s/w \tag{63}$$

and, hence, with $s=w$ and bcc screening $-\lambda$ must equal the values (61). As a check on the consistency of our approach we may compare these λ values with those given in Table I for the decay of the $ss\sigma$-, $sp\sigma$-, and $sd\sigma$-structure constants. The latter were found by least-squares fitting of $A\exp(-\lambda d/w)$ to structure constants computed for a variety of crystal structures. Within the accuracy of the pure-L approximation the agreement is satisfactory.

For the pure-L approximate orbital shown by the dotted line in Fig. 2 and by the contour plot in Fig. 5 we used, for $r\geq s$, the slightly more sophisticated form

$$f(r)=a(r/w)^{l}\exp[-(\sigma r/w)^{2}-(\tau r/w)^{4}]\ , \tag{64}$$

where the third parameter was determined such that not only the amplitude and slope but also the curvature at the sphere was matched. This curvature is given by the Laplace equation, i.e., by

$$(rf)''=[l(l+1)/r^{2}](rf)$$

or, equivalently, by

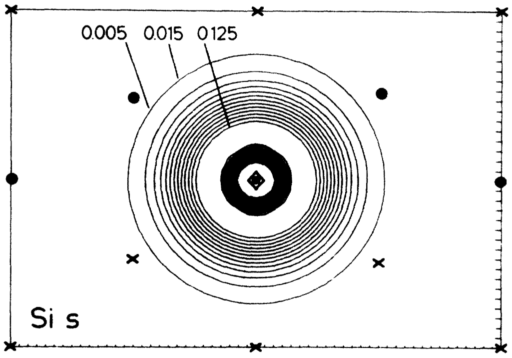

FIG. 5. The pure-s approximation to the TB-LMTO shown in Fig. 1.

$$(d\ln D\{f\}/d\ln r)_s = -(D\{f\}+l+1)(D\{f\}-l)\ . \tag{65}$$

Matching of slope and curvature thus gives, respectively,

$$D\{f\} = l - 2(\sigma s/w)^2 - 4(\tau s/w)^4 \tag{66}$$

and

$$(D\{f\}+l+1)(D\{f\}-l) = 4(\sigma s/w)^2 + 16(\tau s/w)^4\ . \tag{67}$$

Together with (58) this determines σ and τ. For $l=2$ and bcc screening it was not possible with the signs chosen in (64) to fit both slope and curvature [Eqs. (66) and (67) gave a negative $(\tau s/w)^4$] so in this case we took $\tau=0$ and neglected (67).

G. TB-LMTO's for Si using diamond screening

In some cases it is preferable to have screening multipoles *exclusively on the atomic sites* and not on interstitial sites, even though the structure is open and the TB-LMTO's thereby become less well localized. An example could be an investigation of silicon in which one wishes to go continuously from the diamond to a more closely packed structure. In that case one would let the radius of the interstitial spheres go continuously to zero and at some stage delete the LMTO's at the interstitial sites. This is only possible when the envelope functions do not diverge at these sites, that is, when $\alpha_E=0$. For the diamond structure one would thus use that TB-LMTO representation for which the screening constants for the diamond-lattice sites are those given by (12) and $w=w_{\text{dia}}=2^{1/3}w_{\text{bcc}}$. This representation was mentioned in Sec. II A. As long as the empty-sphere orbitals are kept in the basis set this "diamond LMTO set" spans the same Hilbert space as the bcc set considered in Sec. II E.

The Si s orbital is shown in Fig. 6. It is, of course, more diffuse and anisotropic than the Si bcc s orbital in Fig. 1. Nevertheless, the "rule" that the effective radius of a TB LMTO is about $2w$ still holds. The spillover into the interstitial region is considerable. In this region the potential is fairly flat and close to ε_ν and this means that the empty-sphere potential parameters approximately satisfy $V_{El}^0 \approx \varepsilon_\nu$ and Eq. (37) for Γ_{El}^0. The tails of the Si LMTO's are therefore nearly solutions of Schrödinger's equation in the interstitial region at the energy ε_ν.

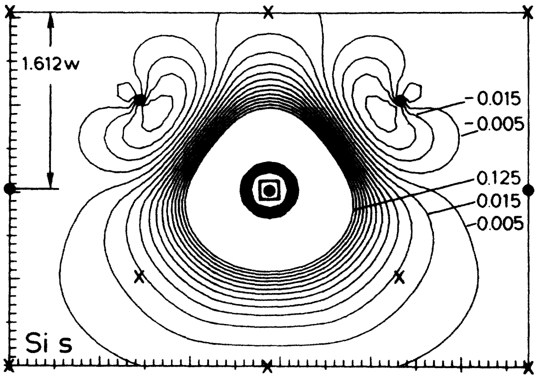

FIG. 6. Si s TB-LMTO in the same plane as Fig. 1. The sphere sizes are as in Fig. 1, but the screening is for the diamond lattice, i.e., $\alpha_A=\beta$ and $\alpha_E=0$. Moreover, $w=w_{\text{dia}}=2^{1/3}w_{\text{bcc}}$.

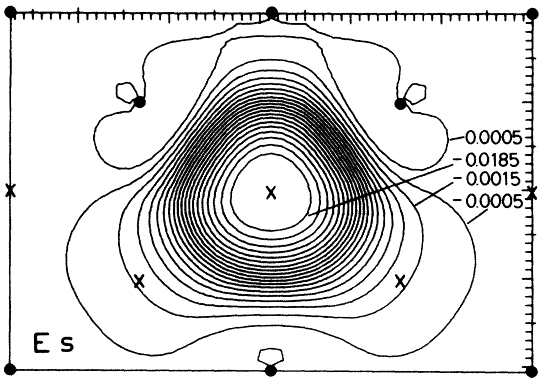

FIG. 7. Interstitial-site s orbital belonging to the same TB-LMTO set as the orbital shown in Fig. 6.

If the energy dependence of the empty-sphere partial waves can be neglected over the energy range of interest, then they are effectively higher partial waves and the LMTO's centered at the interstitial sites can be deleted from the basis set. It turns out that the empty-sphere p and d LMTO's may indeed be deleted but that the empty-sphere s LMTO must be retained.[19] This is because for $s_E=w/2^{1/3}=2.53$ Eq. (37) gives only 1.2 Ry for the width parameter Γ_{Es}^0, but 28 and 174 Ry for Γ_{Ep}^0 and Γ_{Ed}^0, respectively. Γ_{Es}^0 is, however, proportional to s_E^{-3} so that for more closely packed structures the empty-sphere s LMTO can be deleted as well.

[For the bcc LMTO set the tails of the Si-centered LMTO's approximately satisfy the radial Schrödinger equations for the empty spheres at energies V^β which, according to (28), lie lower than V^0 by the amounts $\Gamma^0(\beta^{-1}-\gamma^{-1})^{-1}$, which are of order rydbergs. The energies V^β are thus too far away from the energies of interest that the empty-sphere s and p LMTO's can be deleted from the bcc set.[19]]

In conclusion, the spillover of the Si orbital in Fig. 6 may be viewed as a natural consequence of the orbitals enhanced capability for describing the wave function in the intersitial region.

The interstitial-site s orbital for the diamond set is shown in Fig. 7. It has the same degree of localization and type of anisotropy as the Si-centered orbital. The amplitude of the E orbital is, however, very small because ε_ν is close to V^0.

III. CHARGE DENSITY

The charge density may be computed from

$$n(\mathbf{r}) = \sum_{R',L'}\sum_{R,L} \chi_{R'L'}^{\beta}(\mathbf{r}_{R'})\, n_{R'L',RL}^{\beta}\, \chi_{RL}^{\beta *}(\mathbf{r}_R) \tag{68}$$

using the TB-LMTO's and the corresponding density matrix

$$n^\beta \equiv \int^{\varepsilon_F} d\varepsilon\, D^\beta(\varepsilon) = \int^{\varepsilon_F} d\varepsilon \sum_j b_j^\beta \delta(\varepsilon-\varepsilon_j)(b_j^\beta)^\dagger\ . \tag{69}$$

Here, $D^\beta(\varepsilon)$ are the projected density-of-states functions [not to be confused with the logarithmic derivative function used in (21)], b_j^β the coefficient vector of the LMTO expansion of the wave function, and ε_j the energy. For a given **r**, **R** and **R**′ only run over those few sites which are within the orbital radius of approximately $2w$ from **r**. For each such site, **R**, the values of the TB LMTO's are obtained from expression (52) whose most involved (third) term requires summation over the 15–30 sites closest to **R** (not to **r**). This last summation is not needed if the TB LMTO's can be substituted by their pure-L approximations described in Sec. II F.

Expression (68) is of course only correct to first order in $\varepsilon-\varepsilon_\nu$ (for the MT part of the potential) because so are the LMTO's. If the appropriate projected density-of-states functions,

$$\frac{2}{w}\frac{1}{\pi}\mathrm{Im}[g^\beta(\varepsilon)] \equiv \sum_j a_j^\beta(\varepsilon)\delta(\varepsilon-\varepsilon_j)[a_j^\beta(\varepsilon)]^\dagger , \tag{70}$$

are known then it is more accurate, and just slightly more involved, to evaluate the charge density from

$$n(\mathbf{r}) = \int^{\varepsilon_F} d\varepsilon\, |\chi^\beta(\varepsilon)\rangle^\infty \frac{2}{w}\frac{1}{\pi}\mathrm{Im}[g^\beta(\varepsilon)]^\infty\langle\chi^\beta(\varepsilon)| \tag{71}$$

using the energy-dependent TB MTO's. The reason why it is only slightly more involved to use $\chi_{RL}^\beta(\varepsilon,\mathbf{r}_R)$ is that its energy dependence is confined to the sphere **R** and the angular momentum L. This was explained in Secs. II C and II D. Within the second-order expansion (54) of the MTO, the energy integral in (71) may even be performed explicitly, and in Sect. II G we shall devise a most simple way of including the second-order terms in (68) too.

In Secs. III B–III G we will explain how the density matrix may be obtained in various cases, and in Sec. H we shall apply the simplest procedure to silicon. However, before doing so, we need to write down the LMTO Hamiltonian and overlap matrices.

A. Overlap and Hamiltonian matrices in a general LMTO representation

The contribution to the overlap matrix from the sum over the integrals in the spheres and the lower partial waves is easily obtained from (46), (44), (42), and (22) as

$$O_{\mathrm{MT}}^\alpha \equiv {}^\infty\langle\chi^\alpha|\chi^\alpha\rangle_{\mathrm{MT}}^\infty = (1+h^\alpha o^\alpha)(o^\alpha h^\alpha+1)+h^\alpha p h^\alpha . \tag{72}$$

Here the elements of the diagonal matrix p are the fourth potential parameters (30). If α refers to the TB representation the matrix products may be evaluated by direct summations in **R** space, otherwise not. For a crystal with Bloch vectors **k** and lattice translations **T** one would use $h_{R'L',RL}^\alpha(\mathbf{k})$ as obtained from (47) with

$$S_{R'L',RL}^\alpha(\mathbf{k}) \equiv \sum_T e^{i\mathbf{k}\cdot\mathbf{T}} S_{R'L',(R+T)L}^\alpha , \tag{73}$$

such that **R** runs only over the sites in the primitive cell. The l dimension of S^α and h^α is l_ϕ. The remaining contribution to the overlap matrix from the higher partial waves, and from the integral over the interstitial region, is the so-called combined correction term. This term may be obtained from analytical expressions for ${}^\infty\langle K^0|K^0\rangle^\infty$ and is given in Refs. 1, 4, and 5 for the crystalline case and in Refs. 8 and 15 for the general case.

The contribution to the Hamiltonian matrix from the sum over the integrals in the spheres and the lower partial waves, and for the MT potential used to define the LMTO's, is

$$\begin{aligned} H_{\mathrm{MT}}^\alpha &\equiv {}^\infty\langle\chi^\alpha|-\Delta+v|\chi^\alpha\rangle_{\mathrm{MT}}^\infty \\ &= h^\alpha(1+o^\alpha h^\alpha)+(1+h^\alpha o^\alpha)\varepsilon_\nu(o^\alpha h^\alpha+1)+h^\alpha\varepsilon_\nu p h^\alpha \end{aligned} \tag{74}$$

as obtained from (22), (23), (44), and (46). In (74) only the first term is important because if ε_ν is independent of **R** and l this value may be taken as the zero of energy whereby the last two terms drop out.

The atomic spheres approximation (ASA) *for the potential* now consists of using only (72) and (74) for the overlap and Hamiltonian matrices but substituting the MT spheres by overlapping WS spheres. This is the same approximation as the one used in deriving the simple KKR or tail-cancellation condition (33)–(34). We now return to the question of how to determine the density matrix.

B. TB-LMTO band calculation

This is the trivial case. Let $O_{R'L',RL}^\beta(\mathbf{k})$ and $H_{R'L',RL}^\beta(\mathbf{k})$ be the overlap and Hamiltonian matrices including non-MT contributions (in the ASA there is a simpler procedure described in Secs. III E and III F) and in the TB-LMTO representation. The one-electron energies $\varepsilon_j(\mathbf{k})$ and eigenvectors $b_{RL,j}^\beta(\mathbf{k})$ obtained from the band calculation satisfy

$$[b_{j'}^\beta(\mathbf{k})]^\dagger O^\beta(\mathbf{k}) b_j^\beta(\mathbf{k}) = \delta_{j'j} \tag{75a}$$

and

$$[b_{j'}^\beta(\mathbf{k})]^\dagger H^\beta(\mathbf{k}) b_j^\beta(\mathbf{k}) = \delta_{j'j}\varepsilon_j(\mathbf{k}) . \tag{75b}$$

The orbital projected density of states in (69) are then

$$\begin{aligned} D_{R'L',(R+T)L}^\beta(\varepsilon) \equiv \sum_j \frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}} d^3k e^{-i\mathbf{k}\cdot\mathbf{T}} b_{R'L',j}^\beta(\mathbf{k}) \\ \times\delta(\varepsilon-\varepsilon_j(\mathbf{k}))b_{RL,j}^{\beta *}(\mathbf{k}) . \end{aligned} \tag{76}$$

Using (75a) and (76) we can check that the total density of states is

$$\mathrm{Tr} O^\beta D^\beta(\varepsilon) = \sum_j \frac{\Omega}{(2\pi)^3}\int_{\mathrm{BZ}} d^3k\,\delta(\varepsilon-\varepsilon_j(\mathbf{k})) .$$

C. General LMTO band calculation

In this case the band calculation was performed in a general LMTO representation α and it yielded the eigenvectors $b_j^\alpha(\mathbf{k})$.

The transformation from the β to the α LMTO's is

$$|\chi^\alpha\rangle^\infty = |\chi^\beta\rangle^\infty(\dot{P}^\beta)^{1/2}[1+(\alpha-\beta)S^\alpha](\dot{P}^\alpha)^{-1/2} . \tag{77}$$

This is analogous to (48) and is easily proved using (5) and

(7): According to (9), $\alpha+(S^\alpha)^{-1}$ is representation invariant and the structure matrix therefore transforms according to

$$S^\alpha = S^\beta[1+(\alpha-\beta)S^\alpha] \ . \tag{78}$$

The transformations of the potential functions (17) and (18) are similarly

$$\frac{P^\alpha(\varepsilon)}{P^\beta(\varepsilon)} = \frac{N^\alpha(\varepsilon)}{N^\beta(\varepsilon)} = 1+(\alpha-\beta)P^\alpha(\varepsilon) \ . \tag{79}$$

The transformation to the eigenvectors $b_j^\beta(\mathbf{k})$ to be used in (76) is therefore

$$b_j^\beta(\mathbf{k}) = (\dot{P}^\beta)^{1/2}[1+(\alpha-\beta)S^\alpha(\mathbf{k})](\dot{P}^\alpha)^{-1/2} b_j^\alpha(\mathbf{k}) \ . \tag{80}$$

Here the only matrix (with dimension equal to the number of orbitals per primitive cell) is the structure matrix $S^\alpha(\mathbf{k})$. The latter is usually known because it has been used to construct the Hamiltonian and overlap matrices (see Sec. III A). If it is not known one may first construct the TB structure matrix (73) using the R-space tables in Refs. 8 or 15, and then, through inversion of the Hermitian matrix $(\alpha-\beta)^{-1}-S^\beta(\mathbf{k})$, find

$$1+(\alpha-\beta)S^\alpha = [(\alpha-\beta)^{-1}-S^\beta]^{-1}(\alpha-\beta)^{-1} \tag{81}$$

for use in (80). Equation (81) follows from (78).

D. Conventional LMTO band calculation

Here α is equal to zero and complications merely arise because conventional computer programs[1,4] use potential parameters and LMTO normalizations which may differ from the ones used in the present paper.

With conventional notation the three basic potential parameters used in (25) are

$$C \equiv \varepsilon_\nu + \omega(-l-1) \ , \tag{82}$$

$$\Delta^{1/2} \equiv (s/w)^{l+1}(w/2)^{1/2}\Phi(-l-1,s) \ , \tag{83}$$

and

$$\gamma \equiv \frac{(s/w)^{2l+1}}{2(2l+1)} \frac{\Phi(-l-1,s)}{\Phi(l,s)} \ . \tag{84}$$

In terms of these, the potential parameters that we use may be obtained by setting $\varepsilon=\varepsilon_\nu$ in (25)—(27).

Whereas the conventional LMTO $|\chi^c\rangle^\infty$ is normalized to have the value $\phi(-l-1,s)$ at its own sphere $|\chi^0\rangle^\infty$ has the value $K^0(s)N^0$. Therefore,

$$|\chi^c\rangle^\infty = |\chi^0\rangle^\infty[(w/2)\dot{P}^0]^{1/2}(s/w)^{l+1}\phi(-l-1,s) \tag{85}$$

and, since $|\chi^c\rangle^\infty b^c = |\chi^0\rangle^\infty b^0$, the transformation (80) from the conventional to the TB eigenvector is

$$b_j^\beta(\mathbf{k}) = (\dot{P}^\beta)^{1/2}[1-\beta S^0(\mathbf{k})]\Delta^{1/2} b_j^c(\mathbf{k}) \ . \tag{86}$$

E. Green's-function calculations in the ASA

The case of the ASA is extremely simple because, as we shall show, transformation between different representations requires no matrix multiplication as in (80) but merely energy-dependent scalings. The ASA technique is also highly convenient for Green's-function calculations on perturbed crystals[7,20] because the matrix entering the Dysons equations is the one derived from the KKR equations (33), i.e.,

$$g^\alpha(\varepsilon) = \left[P^\alpha(\varepsilon) - i0^+ - S^\alpha \right]^{-1} \tag{87}$$

which has the canonical, two-center (and TB, if $\alpha=\beta$), form.

The imaginary part of this Green's-function matrix may, in principle, be obtained by transforming (87) into the usual, Hamiltonian form,

$$(\dot{P}^\alpha)^{-1/2}[\varepsilon - i0^+ - (\varepsilon_\nu + h^\alpha)]^{-1}(\dot{P}^\alpha)^{-1/2} \ ,$$

through linearization of the potential function, and by subsequent diagonalization of the first-order Hamiltonian, $\varepsilon_\nu + h^\alpha$, into ε_j with the unitary matrix $u^\alpha_{RL,j}$. This should be done at each energy, i.e., $\varepsilon_\nu \equiv \varepsilon$, and as a result

$$\begin{aligned}\frac{1}{\pi}\mathrm{Im}[g^\alpha(\varepsilon)] &= [\dot{P}^\alpha(\varepsilon)]^{-1/2}\sum_j u_j^\alpha(\varepsilon)\delta(\varepsilon-\varepsilon_j(\varepsilon)) \\ &\qquad \times [u_j^\alpha(\varepsilon)]^\dagger[\dot{P}^\alpha(\varepsilon)]^{-1/2} \\ &= \frac{w}{2}\sum_j a_j^\alpha(\varepsilon)\delta(\varepsilon-\varepsilon_j(\varepsilon))[a_j^\alpha(\varepsilon)]^\dagger \ . \end{aligned} \tag{88}$$

In the third equation we have expressed the imaginary part of the Green's-function matrix in terms of the KKR eigenvectors and energies defined in (33) noting that $N^\alpha_{Rl}(\varepsilon)a^\alpha_{Rl,j}(\varepsilon) = u^\alpha_{Rl,j}(\varepsilon)$ is unitary for each ε. Since $a_j^\alpha(\varepsilon)$ is the coefficient vector in the MTO expansion of the wave function $\psi_j(\mathbf{r})$, as seen in (34) or (39a), $2w^{-1}\pi^{-1}\mathrm{Im}[g^\alpha(\varepsilon)]$ are the projected density of states defined in (70). Similarly, since the coefficients in the expansion of the wave function in terms of the representation-independent partial waves on the right-hand side of (34) or in (39b) are $N^\alpha(\varepsilon)a_j^\alpha(\varepsilon)$, one realizes that the one-center expansion of the charge density is

$$n(\mathbf{r}) = \int^{\varepsilon_F} d\varepsilon\, |\phi^\gamma(\varepsilon)\rangle \mathscr{D}(\varepsilon) \langle \phi^\gamma(\varepsilon)| \tag{89}$$

with

$$\begin{aligned}\mathscr{D}(\varepsilon) &\equiv \sum_j u_j^\alpha(\varepsilon)\delta(\varepsilon-\varepsilon_j(\varepsilon))[u_j^\alpha(\varepsilon)]^\dagger \\ &= [\dot{P}^\alpha(\varepsilon)]^{1/2}\frac{1}{\pi}\mathrm{Im}[g^\alpha(\varepsilon)][\dot{P}^\alpha(\varepsilon)]^{1/2} \\ &= N^\alpha(\varepsilon)\frac{2}{w}\frac{1}{\pi}\mathrm{Im}[g^\alpha(\varepsilon)]N^\alpha(\varepsilon) \ . \end{aligned} \tag{90}$$

The projected density-of-states functions, $\mathscr{D}(\varepsilon)$, are representation invariant, and so is $N^\alpha(\varepsilon)a_j^\alpha(\varepsilon)$. This means that the MTO eigenvectors $a_j^\alpha(\varepsilon)$ transform simply by scaling.

More generally, the transformation of the Green's-function matrix (87) may be obtained from (78) and (79) as

$$
\begin{aligned}
g^{\beta}(\varepsilon) &= (P^{\beta}-S^{\beta})^{-1} = \{P^{\beta}-S^{\alpha}[1+(\alpha-\beta)S^{\alpha}]^{-1}\}^{-1} \\
&= (\{P^{\beta}[1+(\alpha-\beta)S^{\alpha}]-S^{\alpha}\}[1+(\alpha-\beta)S^{\alpha}]^{-1})^{-1} \\
&= [1+(\alpha-\beta)S^{\alpha}]\{P^{\beta}-[1-(\alpha-\beta)P^{\beta}]S^{\alpha}\}^{-1} \\
&= [1+(\alpha-\beta)S^{\alpha}][P^{\alpha}-S^{\alpha}]^{-1}P^{\alpha}/P^{\beta} \\
&= [1+(\alpha-\beta)P^{\alpha}+(\alpha-\beta)(S^{\alpha}-P^{\alpha})]g^{\alpha}P^{\alpha}/P^{\beta} \\
&= [P^{\alpha}/P^{\beta}-(\alpha-\beta)(P^{\alpha}-S^{\alpha})]g^{\alpha}P^{\alpha}/P^{\beta} \\
&= \frac{P^{\alpha}(\varepsilon)}{P^{\beta}(\varepsilon)} g^{\alpha}(\varepsilon) \frac{P^{\alpha}(\varepsilon)}{P^{\beta}(\varepsilon)} - (\alpha-\beta)\frac{P^{\alpha}(\varepsilon)}{P^{\beta}(\varepsilon)} \ . \qquad (91)
\end{aligned}
$$

During these manipulations we have dropped the ε. In (91) the poles, V^{α}, of $P^{\alpha}(\varepsilon)$ merely cancels the zeros of $g^{\alpha}(\varepsilon)$; they do not propagate into $g^{\beta}(\varepsilon)$. For comparison with the result (90), i.e., that $\mathscr{D}(\varepsilon)$ is transformation invariant, one should remember that, according to (79), $N^{\alpha}(\varepsilon)/N^{\beta}(\varepsilon)=P^{\alpha}(\varepsilon)/P^{\beta}(\varepsilon)$. In this connection we point out that if one uses the parametrization (25) or (27) plus (31), the latter form is correct to third order but the former merely to second order.

F. Band calculation using the orthogonal LMTO representation

In order to calculate the unperturbed, crystalline Green's function to start off with, it is convenient to have the energy bands and eigenvectors obtained by diagonalizations rather than through the solution of a secular problem like (33). This is also the way in which the general band-structure problem was solved in Secs. III B–III D. The first-order approach used in deriving (88), for just one value of ε_{ν} though, usually gives reasonable energy bands in a range of half a rydberg around ε_{ν}. A wider range may be covered by the same approach *provided* that one chooses the representation given by $\alpha_{Rl}=\gamma_{Rl}$ for all Rl, because then, according to (25), *all potential functions are linear to second order in* $\varepsilon-\varepsilon_{\nu}$. In other words, $\ddot{P}^{\gamma}=0$, all radial overlaps (44) vanish,

$$o^{\gamma}=0 \ , \qquad (92)$$

and *the LMTO's are orthonormal,* apart from the combined correction term and the small term $h^{\gamma}ph^{\gamma}$ in (72).

In the ASA the KKR equations with

$$P^{\gamma}(\varepsilon)=(\varepsilon-C)/\Delta$$

and

$$N^{\gamma}(\varepsilon)\equiv\left[\frac{w}{2}\dot{P}^{\gamma}(\varepsilon)\right]^{1/2}=\left[\frac{w}{2\Delta}\right]^{1/2} \qquad (93)$$

reduce to pure eigenvalue equations with the overlap and Hamiltonian matrices

$$\widetilde{O}^{\gamma}(\mathbf{k})=1 \ , \qquad (94a)$$

$$\widetilde{H}^{\gamma}(\mathbf{k})\equiv C+\sqrt{\Delta}S^{\gamma}(\mathbf{k})\sqrt{\Delta}=\varepsilon_{\nu}+h^{\gamma}(\mathbf{k}) \ . \qquad (94b)$$

These are identical with the MT expressions (72) and (74), apart from the terms proportional to p. The structure matrix, which depends on the potential through γ, has exponentially damped oscillations in real space and it may be obtained from the TB structure matrix, or from the conventional, unscreened structure matrix, through inversion in each $\mathbf{k}$ point using, respectively, (81) or (10) with $\alpha=\gamma$. The band structure is now obtained by diagonalization of (94), i.e.,

$$[u_{j'}^{\gamma}(\mathbf{k})]^{\dagger}[C+\sqrt{\Delta}S^{\gamma}(\mathbf{k})\sqrt{\Delta}]u_{j}^{\gamma}(\mathbf{k})=\delta_{j'j}\varepsilon_{j}(\mathbf{k}) \qquad (95a)$$

and

$$[u_{j'}^{\gamma}(\mathbf{k})]^{\dagger}u_{j}^{\gamma}(\mathbf{k})=\delta_{j'j} \ . \qquad (95b)$$

The projected density of states $\widetilde{D}^{\gamma}(\varepsilon)$ calculated by inserting these eigenvectors and eigenvalues in (76) or (69) are seen to equal $\mathscr{D}(\varepsilon)$ in (90) within the approximations (25)–(27). These approximations are of second order for the potential functions and of first order for their derivatives. The real part of the Green's-function matrix may now be calculated from the imaginary part by Hilbert transformation and in this way one obtains

$$
\begin{aligned}
\widetilde{G}^{\gamma}(\varepsilon) &= \sum_{j} u_{j}^{\gamma}[\varepsilon-i0^{+}-\varepsilon_{j}]^{-1}[u_{j}^{\gamma}]^{\dagger} \\
&= [\varepsilon-i0^{+}-(C+\sqrt{\Delta}S^{\gamma}\sqrt{\Delta})]^{-1} \\
&= \Delta^{-1/2}\widetilde{g}^{\gamma}(\varepsilon)\Delta^{-1/2} \ . \qquad (96)
\end{aligned}
$$

Here, j is short hand for $j\mathbf{k}$, and $\widetilde{g}^{\gamma}(\varepsilon)$ is $g^{\gamma}(\varepsilon)$ as defined in (87), but with the second-order expression (93) for the potential functions.

In order to transform to the TB representation using (91) one needs

$$P^{\gamma}(\varepsilon)/P^{\beta}(\varepsilon)=(\varepsilon-V^{\beta})(\gamma-\beta)/\Delta \ , \qquad (97)$$

as obtained from (25) and (28). Consequently,

$$
\begin{aligned}
\widetilde{g}^{\beta}(\varepsilon) &= \frac{\varepsilon-V^{\beta}}{(\Delta\Gamma^{\beta})^{1/2}}\widetilde{g}^{\gamma}(\varepsilon)\frac{\varepsilon-V^{\beta}}{(\Delta\Gamma^{\beta})^{1/2}}-\frac{\varepsilon-V^{\beta}}{\Delta\Gamma^{\beta}} \\
&= \frac{\varepsilon-V^{\beta}}{(\Gamma^{\beta})^{1/2}}\widetilde{G}^{\gamma}(\varepsilon)\frac{\varepsilon-V^{\beta}}{(\Gamma^{\beta})^{1/2}}-\frac{\varepsilon-V^{\beta}}{\Gamma^{\beta}} \ . \qquad (98a)
\end{aligned}
$$

This can be used in Dyson's equation to treat extended perturbations. The densities of states $\widetilde{D}^{\beta}(\varepsilon)$ needed in (69) to calculate the charge density equals

$$N^{\beta}2w^{-1}\pi^{-1}\mathrm{Im}[\widetilde{g}^{\beta}(\varepsilon)]N^{\beta} \ ,$$

as seen by substituting $|\chi^{\beta}\rangle^{\infty}N^{\beta}$ for $|\chi^{\beta}(\varepsilon)\rangle^{\infty}$ in (71). Using now (88) and (98a), plus the facts that

$$N^{\beta}=(\Gamma^{\beta})^{1/2}(\varepsilon_{\nu}-V^{\beta})^{-1}(w/2)^{1/2}$$

and that $o^{\beta}=(V^{\beta}-\varepsilon_{\nu})^{-1}$, one finds

$$\widetilde{D}^{\beta}(\varepsilon)=[1-(\varepsilon-\varepsilon_{\nu})o^{\beta}]\widetilde{D}^{\gamma}(\varepsilon)[1-(\varepsilon-\varepsilon_{\nu})o^{\beta}] \ . \qquad (98b)$$

The density matrix in (68),

$$\widetilde{n}^{\beta}\equiv\widetilde{n}^{\gamma}-[o^{\beta}\widetilde{n}^{\gamma}(10)+\mathrm{H.c.}]+o^{\beta}\widetilde{n}^{\gamma}(11)o^{\beta} \ , \qquad (99)$$

is thus expressed in terms of zeroth, n^{γ}, first, $n^{\gamma}(10)$, and second, $n^{\gamma}(11)$, energy moments of the projected densities of states for the orthogonal representation. This is the simplest possible way of computing the charge density and it was used for the silicon calculation to be described in Sec. III H.

Expression (98b) could also have been obtained without excursion to the KKR Green's functions directly from the LMTO transformation (77) putting $\alpha=\gamma$. This transformation may be written in the form

$$|\chi^{\gamma}\rangle^{\infty}=|\chi^{\beta}\rangle^{\infty}(1-o^{\beta}h^{\gamma})=|\chi^{\beta}\rangle^{\infty}(1+o^{\beta}h^{\beta})^{-1} \qquad (100)$$

as seen by manipulations with the potential parameters or, more directly, by insertion of (42) in (46). Since u^{γ} diagonalizes $\varepsilon_{\nu}+h^{\gamma}$, one immediately obtains expression (98b). Another point worth noting is that the transformation (100) is, in fact, a Löwdin orthogonalization. This is seen by comparison of the second form (100) with expression (72) for the overlap matrix.

Although the γ representation is strictly orthonormal only in the ASA and to second order, the general formulas given in Secs. III A–III C of course remain valid for $\alpha=\gamma$. This representation in which the potential parameters o vanish is normally the most convenient one to use for band calculations and the remaining nonorthogonality terms may usually be treated by first-order perturbation theory.

G. Second-order expressions for the charge density and the KKR-ASA Green's function

It is somewhat unsatisfactory to have energies correct to third (Secs. III B–III D) or second (Sec. III F) order and then obtain a charge density (68) whose radial part is correct to only first order because the LMTO's are no better. The cure is simply to substitute the LMTO's by the second-order MTO's given in (53) Sec. II D. This operation conserves continuity and differentiability of the wave functions because $|\ddot{\chi}\rangle^{\infty}$, which is representation independent, goes smoothly to zero at and outside its own sphere. The normalization of each orbital is, however, affected and renormalization is therefore necessary.

In order to calculate the new overlap matrix we need the integrals

$$\begin{aligned}{}^{\infty}\langle\ddot{\chi}\,|\,\chi^{\alpha}\rangle^{\infty}&=\langle\ddot{\phi}^{\gamma}\,|\,\chi^{\alpha}\rangle^{\infty}+3p\langle\phi\,|\,\chi^{\alpha}\rangle^{\infty}\\&=\langle\ddot{\phi}^{\gamma}\,|\,\phi\rangle+[\langle\ddot{\phi}^{\gamma}\,|\,\dot{\phi}^{\gamma}\rangle+\langle\ddot{\phi}^{\gamma}\,|\,\phi\rangle o^{\alpha}]h^{\alpha}\\&\quad+3p[1+o^{\alpha}h^{\alpha}]\\&=2p+[\langle\ddot{\phi}^{\gamma}\,|\,\dot{\phi}^{\gamma}\rangle+2po^{\alpha}]h^{\alpha}\simeq 2p\ ,\end{aligned} \qquad (101)$$

which only have contributions from inside the spheres. In deriving (101) we have used that

$$\langle(\dot{\phi}^{\gamma})^{2}\rangle+\langle\phi\,|\,\ddot{\phi}^{\gamma}\rangle=0\ , \qquad (102)$$

as follows from the normalization $\langle\phi^{\gamma}(\varepsilon)^{2}\rangle=1$ (13). The last approximation in (101) consists of keeping only terms of leading (zeroth) order in h^{α}. The change in the overlap matrix upon going from the LMTO to the second-order MTO is thus a simple MT contribution, and the total MT part is

$$\begin{aligned}&{}^{\infty}\langle\chi^{\alpha}+(\varepsilon-\varepsilon_{\nu})^{2}\ddot{\chi}/2\,|\,\chi^{\alpha}+(\varepsilon-\varepsilon_{\nu})^{2}\ddot{\chi}/2\rangle^{\infty}\\&\quad=(h^{\alpha}o^{\alpha}+1)(1+o^{\alpha}h^{\alpha})+h^{\alpha}ph^{\alpha}+2(\varepsilon-\varepsilon_{\nu})^{2}p\\&\quad\simeq[(\varepsilon-\varepsilon_{\nu})^{2}p+1]^{\infty}\langle\chi^{\alpha}\,|\,\chi^{\alpha}\rangle^{\infty}[1+(\varepsilon-\varepsilon_{\nu})^{2}p]\ ,\end{aligned} \qquad (103)$$

to second order. The last approximation holds when, as is usually the case, the combined correction term is considerably less than unity.

The renormalization may now be performed as follows. In (76) each eigenvector is substituted by

$$\hat{b}^{\beta}_{RL,j}(\mathbf{k})=[1+(\varepsilon-\varepsilon_{\nu Rl})^{2}p_{Rl}]^{-1}b^{\beta}_{RL,j}(\mathbf{k})\ , \qquad (104)$$

and since the prefactor only depends on the state $j\mathbf{k}$ through the energy the corresponding modification of the projected density of states simply consists of the energy-dependent scalings

$$\hat{D}^{\beta}(\varepsilon)=[1+(\varepsilon-\varepsilon_{\nu})^{2}p]^{-1}D^{\beta}(\varepsilon)[1+(\varepsilon-\varepsilon_{\nu})^{2}p]^{-1}\ . \qquad (105)$$

The charge density is then

$$\begin{aligned}n(\mathbf{r})=&\,|\chi^{\beta}\rangle^{\infty}\hat{n}^{\beta\infty}\langle\chi^{\beta}|\\&+\tfrac{1}{2}[\{\,|\phi\rangle 3p+|\ddot{\phi}^{\gamma}\rangle\}\hat{n}^{\beta}(20)\langle\phi|+\text{H.c.}]\end{aligned} \qquad (106)$$

to second order and in terms of the zeroth and second moments of $\hat{D}^{\beta}(\varepsilon)$. Often it suffices to take the spherical average of the second-order term in (106) so that only the diagonal elements of the second moments $\hat{n}^{\beta}(20)$ are required.

In a second-order, orthogonal calculation employing the ASA as described in Sec. III F, also the term $h^{\gamma}ph^{\gamma}$ in the overlap matrix must be corrected for. This is most easily done like in (104) by substitution of $u^{\gamma}_{RL,j}$ by

$$\hat{u}^{\gamma}_{RL,j}(\mathbf{k})=[1+\tfrac{3}{2}(\varepsilon-\varepsilon_{\nu Rl})^{2}p_{Rl}]^{-1}u^{\gamma}_{RL,j}(\mathbf{k})\ . \qquad (107)$$

Here the prefactor is however nothing but $\dot{P}^{\gamma}(\varepsilon)^{-1/2}$ to second order, divided by $(\dot{p}^{\gamma})^{-}1/2$. This can be seen by performing the substitution (31): $\varepsilon\rightarrow\varepsilon+(\varepsilon-\varepsilon_{\nu})^{3}p$ in the second-order expression $P^{\gamma}(\varepsilon)=(\varepsilon-C)/\Delta$, and differentiating. As a result, from the projected density of states, $\tilde{D}^{\gamma}(\varepsilon)$, calculated using the orthonormal eigenvectors u^{γ}_{j}, one may obtain

$$\begin{aligned}\hat{D}^{\gamma}(\varepsilon)&=[1+\tfrac{3}{2}(\varepsilon-\varepsilon_{\nu})^{2}p]^{-1}\tilde{D}^{\gamma}(\varepsilon)[1+\tfrac{3}{2}(\varepsilon-\varepsilon_{\nu})^{2}p]^{-1}\\&=\Delta^{-1/2}\frac{1}{\pi}\text{Im}[\hat{g}^{\gamma}(\varepsilon)]\Delta^{-1/2}\ ,\end{aligned} \qquad (108)$$

which is correct to second order, for the energies as well as for the eigenvectors. A Hilbert transform will give a Green's function $\hat{G}^{\gamma}(\varepsilon)$, which is better than $\tilde{G}^{\gamma}(\varepsilon)$ in (96). The former may be transformed to the TB representation using (98a), plainly with $\hat{G}^{\gamma}(\varepsilon)$ replacing $\tilde{G}^{\gamma}(\varepsilon)$ and $\hat{g}^{\beta}(\varepsilon)$ replacing $\tilde{g}^{\beta}(\varepsilon)$, because the substitution (31) in (97) is irrelevant to second order. Similarly, in (98b) and (99) the tildes can be replaced by carets, and the charge density is obtained from (106) with $\hat{n}^{\beta}$ given by the careted version of (99) and with $\hat{n}^{\beta}(20)$ given by $\hat{n}^{\gamma}(20)$.

This approach is simpler than the one described in (104)–(106) because it uses plain diagonalizations, without treating an overlap matrix, and it uses energy-dependent scalings of matrix elements instead of matrix multiplications in the LMTO transformations. On the other hand, it needs the ASA and the energies are only correct to second, rather than to third order. Third-order energies and the combined correction term may of course be calcu-

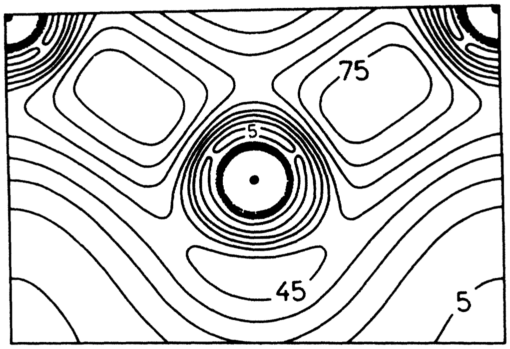

FIG. 8. Self-consistent valence-charge density of Si calculated without shape approximations for the potential and using the LAPW method (Ref. 14). The plane is the same as in Fig. 1.

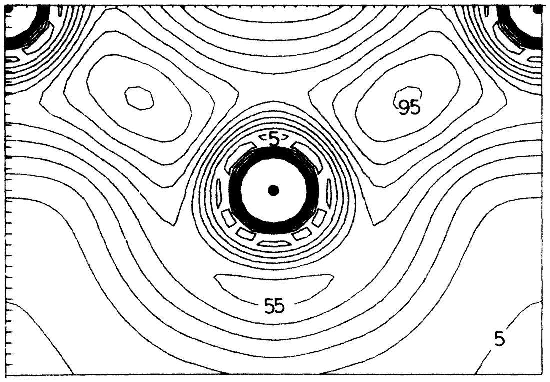

FIG. 10. Same as Fig. 9, but using, instead of the TB-LMTO's for bcc screening, the approximate, pure-*lm* orbitals (see Figs. 1, 2, and 5).

lated via first-order perturbation theory as was mentioned at the end of Sec. III F. The second-order energies must, however, be kept as the intermediate argument of all functions, otherwise the basis-set transformation cannot be performed plainly through energy scalings.

H. Charge density in Si

In Fig. 8 we show the Si valence charge density calculated by Hamann[14] using the LAPW method and no shape approximations for the potential. Among the established charge densities for Si obtained from density-functional theory this is presumably the most accurate. Our valence charge density obtained from the self-consistent LMTO-ASA calculation described in Sec. II E is shown in Fig. 9. This calculation simply used the orthonormal representation (94), the second-order expression (99) for the density matrix and the first-order TB-LMTO's described in Sec. II E.

The surprising, almost perfect agreement suggests that the atomic-sphere approximation for the self-consistent potential is a very good one. We suspect that the ASA would suffice also for calculations involving symmetry-lowering deformations, the only important point being that the total-energy functional or force is evaluated using the full charge density. In view of the ease and speed with which self-consistent LMTO-ASA band- and Green's-function calculations can be performed, this is a most important observation.

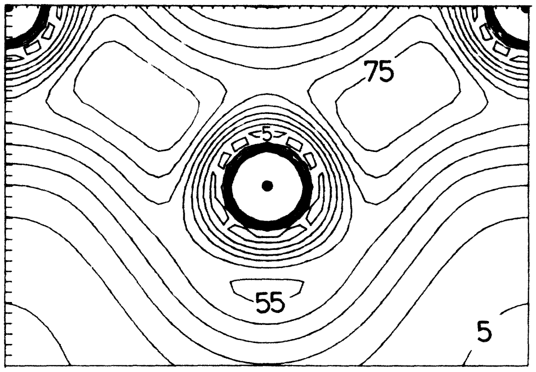

FIG. 9. Same as Fig. 8, but calculated using the LMTO method with *s*, *p*, and *d* orbitals on the atomic and interstitial sites, as explained in the text, and using the ASA for the potential.

The only notable difference between Figs. 8 and 9 is that the charge density obtained from the AS potential is slightly higher in the backbond. Such an effect of the ASA is conceivable although it is not clear whether this small discrepancy does not result from differences in the exchange-correlation potentials, the **k**-space samplings, the treatment of the core etc. (*En passant,* we mention that outside the core region our charge density looks exactly like the one obtained by Hamann for a local, hard-core pseudopotential.[21]) It should be noted that the slight discrepancy between our ASA result and Hamanns full-potential result cannot be due to the neglected energy dependence of the basis functions, i.e., to the fact that we did not use the technique in Sec. III G, because also Hamann used a straightly linear method, without involving $\ddot{\phi}^{\gamma}(r)$ etc.

The most speedy way of obtaining a charge density is to use the pure-*lm* approximation for the TB-LMTO's. This was explained in Sec. II F and at the beginning of Sec. III. The corresponding result for Si, using bcc screening, is shown in Fig. 10, and in Fig. 11 it is compared with the proper LMTO density of Fig. 9 along a nearest-neighbor

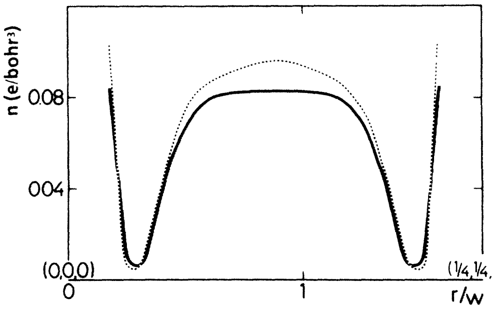

FIG. 11. Comparison of the charge densities shown in Figs. 9 and 10 along the Si-Si nearest-neighbor direction. Solid curve: TB-LMTO. Dotted curve: pure-*lm* approximation.

Si-Si direction. The effect of the pure-*lm* approximation is seen to be rather large in the bond region, although it is smaller than the effect seen in Hamanns paper of using a soft-core pseudopotential.[22] It is certainly also smaller than the effect of spheridizing the charge density as done in conventional LMTO-ASA calculations. Another measure of accuracy is provided by the fact that the "experimental" valence charge density synthesized from x-ray data[23] resembles Fig. 10 more closely than Figs. 9 and 8.

IV. SUMMARY

In this paper we have demonstrated that solid-state LMTO's constitute a highly accurate, minimal basis set which is not restricted by shape approximations for the one-electron potential. By the example of crytalline silicon we have furthermore demonstrated that even the charge density obtained from the simplest self-consistent LMTO-ASA calculation is as accurate as those obtained from the best state-of-the-art full-potential or first-principles pseudopotential calculations.

The new technique that has allowed us to make full use of the LMTO's is a recently developed formalism for linear transformations in the Hilbert space spanned by the LMTO's. This gives access to short-ranged, so-called TB-LMTO's and to nearly orthonormal LMTO's. In Secs. II A, II B, and II C, and in Sec. III F we have given a self-contained account of this formalism. A useful way of evaluating the TB-LMTO's has been given in Sec. II D, and extremely simple, approximate orbitals, the so-called pure-*lm* orbitals, were introduced in Sec. II F. Two different sets of silicon TB-LMTO's (both spanning the same Hilbert space, of course) were presented in Secs. II E and II G. It was mentioned, that for the purpose of describing the valence band, the latter set could be truncated so that merely five orbitals per atom remain. This is demonstrated in Ref. 19. The evaluation of the (non-spherically-averaged) charge density from the LMTO-TB representations has been discussed in Sec. III, and the transformations to the TB representation from the various other representations used in LMTO band- or Green's-function calculations have been given in Secs. III B—III F. For highly accurate calculations we have, in Sec. III G, shown how to go beyond the linear approximation for the MTO's and the charge density.

This paper has been dealing with the LMTO transformation theory, the TB-LMTO's, and the charge density. These techniques have recently been used[24] in a first-principles study of the bonding in a large number of semiconductors, not only by plotting charge densities, but also by calculating quantities such as bond-orders, metallicities, etc. A silicon Wannier function has been obtained as well.[25] Other papers discuss the real-space construction of the TB structure matrix,[15] i.e., of the canonical hopping integrals, the contraction to minimal LMTO basis sets,[19] a Green's-function TB-LMTO method for extended defects like surfaces and interfaces,[20] and the application of the recursion method to amorphous systems.[26] The evaluation of interatomic forces and the total energy using the full, non-spherically-averaged charge density will be the subject of a future paper.

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[16] In the present paper we adopt the notation of Ref. 9. This means that the relation to the notation in Ref. 8 is as follows: $\varepsilon=E$, $\alpha=\bar{Q}$, $K^0=K$, $K^\alpha=\bar{K}$, $\chi^\alpha=\bar{\chi}$, $S^0=S$, $S^\alpha=\bar{S}$, $P^\alpha(\varepsilon)=\bar{P}(E)$, etc. The potential parameter γ_l is $(s/w)^{2l+1}$ times the γ_l defined in Refs. 1—4 and, hence, equal to Q^{-1} of Refs. 5 and 7, and equal to Q of Ref. 8. When $\alpha=\gamma$ the corresponding LMTO representation is nearly orthonormal. Therefore $\dot{\phi}^\gamma$ and χ^γ in the present notation equal, respectively, $\dot{\phi}$ and Θ in Refs. 5 and 7, and $\dot{\phi}$ and χ in Ref. 8. We stress that if a superscript has been dropped in the present notation then the quantity is in a *general* representation. In previous

notations this was different, e.g., $\dot{\phi}$ would refer to the nearly orthonormal representation while, K, J, S, and P would refer to the conventional, unscreened representation, and χ was sometimes referring to the orthonormal and sometimes to the unscreened representation. In the present paper the basic potential parameters are C, Δ, γ, and $p=\langle(\dot{\phi}^{\gamma})^2\rangle$, as usual. Moreover, $V^0=V$ and $\Gamma^0=\Gamma$. The first-order potential parameters used in the definition of the first-order Hamiltonians h^{α} are $c^{\alpha}-\varepsilon_{\nu}=-P^{\alpha}/\dot{P}^{\alpha}=(C-\varepsilon_{\nu})[1\ -(\gamma-\alpha)(C-\varepsilon_{\nu})/\Delta]=\bar{C}-E_{\nu}$ and $d^{\alpha}=1/\dot{P}^{\alpha}=\Delta[1-(\gamma-\alpha)(C-\varepsilon_{\nu})/\Delta]^2=\bar{\Delta}$, so that $C=c^{\gamma}$ and $\Delta=d^{\gamma}$. Finally, $1/N^{\alpha}=(2d^{\alpha}/w)^{1/2}=(2\bar{\Delta}/w)^{1/2}$, $N^{\alpha}/\dot{N}^{\alpha}=1/o^{\alpha}=V^{\alpha}-\varepsilon_{\nu}=\omega(P^0=1/\alpha)$, and $|\dot{\phi}^{\alpha}\rangle\omega(P^0=1/\alpha)=|\phi(P^0=1/\alpha)\rangle$.

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