PHYSICAL REVIEW B VOLUME 24, NUMBER 10 15 NOVEMBER 1981

Localized orbitals for band-structure calculations in complex semiconductors

J. Hugel and C. Carabatos
Laboratoire de Physique des Milieux Condensés, Université de Metz, France

F. Bassani*
Department of Physics, University of Illinois, Urbana, Illinois

F. Casula†
Istituto di Fisica, Università di Cagliari, Italy

(Received 22 December 1980; revised manuscript received 11 August 1981)

A modified version of the tight-binding method of band-structure calculations, based on well-defined localized orbitals, is proposed. The localized orbitals are obtained as the self-consistent eigenstates of a local Hamiltonian defined in a unit cell at each atomic site, with an arbitrary localizing potential about each cell. The crystal eigenstates are computed by expanding the Bloch functions in localized orbitals and diagonalizing a crystal Hamiltonian which compensates for the arbitrary localizing potential. A general discussion of this method and a comparison with similar approaches is given. Specific results are reported and discussed for the case of NiO.

I. INTRODUCTION

The oldest approach to the study of the electronic band structure of crystalline solids is the tight-binding method, based on expanding Bloch functions in atomic orbitals centered on lattice sites.[1] A similar approach was introduced by Hückel for molecular systems, where no translational symmetry exists. The calculations are simplified in this case by assuming atomic orbitals on different sites to be orthogonal.[2] The orthogonality condition can be rigorously imposed in the case of crystals by using Wannier functions centered at each unit cell, instead of atomic orbitals.[1]

While the above approaches have been very useful for a general understanding of the atomic structure of solids, they have encountered considerable difficulties as computational methods because of slow convergence in the number of atomic functions to be used and in the number of interacting lattice cells. This is the reason why the tight-binding method was not applied with confidence in spite of its general validity and of its usefulness in establishing connections between atomic and crystal properties. Following Mooser and Pearson,[3] ideas based on atomic states are currently used to explain the very existence of complex semiconductors and to justify the variation trends of optical properties in crystal families.[4]

The difficulties with the calculations reside essentially in the inadequacy of the initial localized functions used in constructing the Bloch functions. One may state that the problem of the band structure of solids can be reduced to that of determining "appropriate localized functions." They should be similar to atomic functions near the nuclei and should not extend very far from the nucleus to which they refer, so as to have interactions only between neighboring cells. Atomic orbitals are not "appropriate localized functions" in the overlap region between cells, where the crystal potential does not coincide with the atomic potential. Wannier functions are not satisfactory either, because of the difficulties of their *a priori* determination.[5] Different sets of localized functions are equally valid in principle, because the same Bloch function can be expanded in different types of localized functions.

Because of its advantages, the use of the tight-binding approach has been revived in recent years along this line of thought by using different points of view. The first one is semiempirical in nature and consists in developing formally the method and in finding ways to estimate the relevant parameters (one-center and two-center energy integrals). The first attempt was suggested by Slater and Koster,[6] and amounts to choosing the disposable parameters by fitting results to experimental data or to results obtained at a few $\vec{k}$ points by a more accurate calculation. A modification of this method was adopted by Bassani and Pastori-Parravicini in studying the band structure of graphite and layer compounds.[7] They computed the overlap and energy integrals from the atomic functions, but introduced scaling factors to reduce them to more acceptable values. Interesting results for complex semiconductors have been obtained in this way by many authors, who have semiempirically modified the overlap and the energy integrals[8] or the atomic functions (distorted atomic orbitals).[9] In some cases the integrals computed from atomic orbitals are found to be appropriate for reproducing valence bands,[10] eventually taking into account three-center integrals[11] in covalent materials.

A second point of view is to search for the best localized functions to be used in the expansion of the Bloch functions. They do not have to coincide with the Wannier functions nor with the functions of isolated atoms or ions, but should rather represent as closely as possible the electron density in the crystal. Two ways have been suggested to obtain them. One is to determine the localized functions from the variational principle by minimizing the total energy. The other is to set up an appropriate local potential and to solve the corresponding Schrödinger equation.

The theoretical basis for the first approach has been given by Kohn,[5] but it has been used only in a test case for metallic hydrogen.[12] The same idea has been followed by Ellis *et al.* for semiconductors,[13] but their starting functions have to be chosen somewhat arbitrarily.

The theoretical basis for the second approach has been given by Adams[14] and by Gilbert.[15] They have shown that one can set up a localizing potential, defined as the projector of an arbitrary potential on the manifold of occupied states, without changing the physical results. Following similar physical ideas, Anderson has formulated a "chemical pseudopotential method,"[16] which has been very useful in studying valence states in semiconductors.[17] More recently Doni *et al.*[18] have clarified the theoretical grounds of the semiempirical tight-binding method, by establishing a direct relationship between the integrals to be computed in a Hartree-Fock approach and the semiempirical tight-binding parameters.

The general formulation of Adams and Gilbert has been used by Kunz for obtaining local orbitals to be used in band-structure calculations.[19] He found the solutions of a local Hartree-Fock equation without introducing the Slater approximation for the exchange term. Many interesting and accurate results have been obtained by Kunz and coworkers by using these local orbitals in actual solid-state calculations.[20]

While all this confirms the validity of a localized orbital approach, we think that it is possible to obtain a simplified formulation of Gilbert's theory, which still gives definite prescriptions on the choice of the local Hamiltonian, but is more related to the physical situation in the crystal. We are interested in the electronic structure of compound semiconductors with *d*- or *f*-like states, in particular, transition-metal and rare-earth oxides. In these cases the ionicity must be taken into account. Physical intuition suggests that one can find localized functions to be used for the lowest conduction bands as well as for the valence bands. In this paper, following the general ideas of Gilbert,[15] we suggest a practical prescription for obtaining localized functions in ionic crystals. Such localized functions are self-consistent solutions of the Schrödinger equation for a potential which coincides with the crystal potential inside an ionic cell and is an arbitrary localizing potential outside it. By using our method, particularly suitable local functions for crystal calculations can be determined. They can be obtained also in cases where the free ions do not have bound states by choosing an appropriate localizing potential outside the atomic cell. The novelty of this approach, besides the specific definition of the potential inside the unit cell, is in fact the use of the arbitrary potential.

Recently Zunger and Freeman[21] have developed a self-consistent LCAO method in the local density formalism, and have obtained very accurate results for a number of crystals. While the philosophy underlying our method is quite close to theirs, we give a mathematically and computationally less involved procedure, focusing our attention on the modification of the original atomic functions due to the presence of neighboring atoms and to the localizing potential. Our procedure takes into account self-consistently the contributions to the potential inside a local cell due to the electrons belonging to other cells, though it does not attempt full self-consistency in solving the crystal secular problem. Our goal will be reached, as we will discuss later, if we can really obtain "good" localized functions to be used in the expression of the Bloch functions.

Finally, we note that other self-consistent calculations have been performed by Ciraci and Batra,[22] but their method gives no emphasis on the localization of the wave functions and, therefore, does not avoid problems related with multicenter integrals and distant-neighbor interactions.

We apply the procedure outlined above to the case of NiO and we plan to extend the calculations to the other transition-metal oxides. In Sec. II we define the local Hamiltonian and discuss the choice of the local potential. In Sec. III we give the procedure for the coupled self-consistent solutions of the local Hamiltonians.

In Sec. IV we discuss aspects of energy-band calculations using our localized functions. In Sec. V we give the results for the localized functions of NiO and compare them with the functions of the isolated ions. The band structure of NiO is given as a first example and the role of the localizing potential is discussed. Finally, in Sec. VI we summarize the results and suggest applications of the method.

II. DEFINITION OF THE LOCAL HAMILTONIAN

We define a local Hamiltonian, which is particularly suitable for complex semiconductors with ionic character, and which satisfies as closely as possible the theoretical requirements discussed in the Introduction for the definition of the localized orbitals.

The first condition is to subdivide the crystal in cells, in order to determine functions which are localized at each cell. There are many possible ways to affect this subdivision, depending on the type of crystals. For molecular crystals like H_2 a cell should preferably contain the molecule, so that the localized function is not too different from a molecular function near the nuclei. Similarly, for strongly covalent crystals a cell should be centered about a bond. On the contrary, in the case of ionic crystals it seems appropriate to consider cells centered around each nucleus. The shape and size of the cells is determined so that the lattice is completely filled and the translational and rotational symmetries are preserved.

The localized functions to be used in constructing the Bloch functions are obtained by solving a local Schrödinger equation with a local potential equal to the crystal potential inside the cell and with a constant arbitrary potential V_0 outside it. This constant potential does not appear in the crystal potential and its role is just that of localizing the orbitals so as to make the crystal secular equation more rapidly covergent. This corresponds to the localizing potential well introduced by Gilbert.[15] Obviously, the value of V_0 influences some of the wave functions, mostly in their tails. A careful choice is required since we want to be able to consider only a limited number of localized functions. On the other hand, once the localized functions have been obtained, the band structure should be ultimately independent of V_0 once full self-consistency is achieved.

The Schrödinger equation at site l for the localized orbitals about a nucleus of charge $Z^{(l)}e$, is written as follows:

$$H^{(l)}(\vec{r})\phi_n^{(l)}(\vec{r})=E_n^{(l)}\phi_n^{(l)}(\vec{r}) , \tag{1}$$

where the local Hamiltonian is defined as

$$H^{(l)}(\vec{r})=\frac{p^2}{2m}-\frac{Z^{(l)}e^2}{r}+V_{\text{Coul}}^{(l)}(\vec{r}) + V_{\text{exch}}^{(l)}(\vec{r})+V_{\text{intercell}}^{(l)}(\vec{r}) \tag{2a}$$

inside the cell, and

$$H^{(l)}(\vec{r})=\frac{p^2}{2m}+V_0 \tag{2b}$$

outside the cell. The Coulomb potential in (2a) is expressed through the spherically averaged electron densities in the usual way, i.e.,

$$V_{\text{Coul}}(r)=\frac{e^2}{r}\int_0^r dr'r'^2 4\pi\rho_{\text{tot}}^{(l)}(r') + e^2\int_r^\infty \frac{4\pi\rho_{\text{tot}}^{(l)}(r')r'^2}{r'}dr' . \tag{3}$$

The exchange-correlation (exch) potential is taken as the averaged Slater exchange, corrected by a correlation factor $\alpha(r)$, which should be density dependent[23,24]:

$$V_{\text{exch}}(r)=-3e^2\left[\left[\frac{3}{8\pi}\right]\rho_{\text{tot}}^{(l)}(r)\right]^{1/3}\alpha(r) . \tag{4}$$

In actual calculations, we adopt a constant averaged value of α, as is frequently done in band-structure calculations.[25]

The density $\rho_{\text{tot}}^{(l)}(r)$ is computed from the localized wave functions of the occupied electronic states, taking into account both the ones centered on the lth crystal site and the tails of the ones centered on the other sites l' which extend in the lth cell:

$$\rho_{\mathrm{tot}}^{(l)}(r)=\frac{1}{4\pi}\sum_{n}|R_n^{(l)}(r)|^2+\frac{1}{4\pi}\sum_{n,l'}|R_n^{(l')}(r)|^2\,, \tag{5}$$

where $R_n^{(l)}$ denotes the radial part of the nth wave function. It should be observed that the number of occupied states to be considered in the first summation on the right-hand side of Eq. (5) is smaller by one than the number of valence electrons when we compute valence bands. This results because the averaged exchange potential (4) does not cancel the corresponding Coulombic interaction of the electron with itself. In practical calculations one uses the total number of valence electrons, since the difference is very small inside the cell. This procedure has the advantage of using the same potential for both valence and conduction states,[18] but in many cases is not sufficiently accurate to give the correct valence-conduction band gap.

The remaining potential due to the other cells is the long-range contribution due to the ionic charges

$$V_{\mathrm{intercell}}^{(l)}(r)=\sum_{l'\neq l}\frac{q_{l'}e^2}{|\vec{r}-\vec{r}_{l'}|}\,, \tag{6}$$

where $q_{l'}$ gives the value and sign of the ionic charge in units of e. This summation can be performed over all types of crystals. The result can be separated into a spherically symmetric contribution, i.e., the Madelung potential, plus other contributions which can be expanded in crystal harmonics adapted to the lattice symmetry. In NaCl-type crystals, with lattice distance r_0, one obtains an expansion in terms of spherical harmonics Y_1^m as [26]

$$V_{\mathrm{intercell}}^{(l)}(r)=q_l'\,\alpha_M\left[\frac{e^2}{r_0}\right]+\left[\frac{4\pi}{9}\right]^{1/2}q_l'\,S_{40}\left[\frac{e^2}{r_0^5}\right]r^4\times[Y_4^{0*}+\sqrt{15/4}(Y_4^{4*}+Y_4^{-4*})]+\cdots\,, \tag{7}$$

where the constants depend on the lattice structure (for instance, $\alpha_M=-1.747\,56$ and $S_{40}=-3.5789$ for the NaCl structure). The Madelung term α_M only contributes a shift to the potential inside the cell, while the other terms in (7) give a much smaller contribution, which removes the degeneracy of some levels. The splitting of the d- or f-like levels produced by the higher-order terms of Eq. (7) is computed by perturbation theory.

For crystals which have atoms with a permanent magnetic moment, the exchange potential is different for spin-up and spin-down electrons, since the total density in (4) and (5) must be referred only to electrons with the same spin. Consequently $(\rho_{\mathrm{tot}}/2)$ in Eq. (4) must be replaced by $\rho_{\sigma,\mathrm{tot}}$ which is obtained by summing in (5) only on the occupied states of the electrons with spin up $(\sigma=1)$ or with spin down $(\sigma=-1)$ respectively.[27] Of course, this will separate the spin-up and spin-down states and will also give slightly different energies in the ferromagnetic and paramagnetic cases.[28]

As mentioned before, in addition to the above described potential inside the lattice cell, we introduce an arbitrary uniform potential V_0 outside the lattice cell. This does not modify the physics of the problem because the potential outside the lattice cell does not appear in the total crystal potential. However, the introduction of the potential well V_0 specifies the local functions which are used as bases in the construction of the Bloch functions. The freedom in the choice of V_0 is due to the fact that some freedom is allowed in the choice of these local functions. Local functions can be obtained also when the potential inside the cell would not localize orbitals.

III. SELF-CONSISTENT SOLUTIONS FOR THE LOCALIZED WAVE FUNCTIONS

The localized wave functions are obtained by solving numerically the Schrödinger equation (1) using a self-consistent procedure. This is done by using the classical Herman-Skillmann computer program[29] and inserting the contributions to the potentials due to the electron densities of atoms belonging to other cells, as contained in the expressions (3), (4), and (5), and the potential V_0.

Since we consider, in general, semiconductors with different atoms in the unit cell, we have to consider coupled solutions of the equations for different cells and to impose self-consistency on all of them. Furthermore, computational simplicity can be achieved only by approximating the elementary cells around atoms with spheres.

The relevant parameters on which the localized eigenstates depend are, for each elementary cell, its volume, the value of the localizing potential V_0, and finally, the value adopted in expression (4) for the α parameter in order to take properly into account exchange and correlation effects. We adopt the value $\alpha=\frac{2}{3}$ which has been used in many calculations, though a better choice would come from a detailed analysis of correlation screening.[23,24]

The volume of the elementary cell at an atomic site is limited by the condition that the sums of the volumes at different atoms must be equal to the volume of the translational unit cell. In a binary lattice, one is left with only one parameter, the volume of one subcell.

The value of the localizing potential V_0 should not influence the crystal eigenstates since it does not appear in the crystal potential

$$V_{\mathrm{crys}}(\vec{r})=\sum_l V^{(l)}(\vec{r}) , \tag{8}$$

where each local potential $V^{(l)}$ is defined as in Eq. (2a) and $V^{(l)}\equiv 0$ outside the lth cell. Its role is just to define the basic set of functions used for expansion of Bloch functions. Of course, the choice of V_0 modifies the localized functions and, therefore, affects the band structure since the expansion of the Bloch function is not taken on a complete set. However, when the calculation is done self-consistently, the resulting band structure should be independent of V_0 because it is the self-consistent solution of a well-defined crystal potential independent of V_0.

In practice, of course, it is useful to make a choice of V_0 so that the method is rapidly convergent, which happens only when the localized functions are very close to the exact crystal eigenfunctions.

There are two practical ways to achieve this goal. One, rather cumbersome but theoretically appealing, consists in repeating the calculation with computed sets of functions until self-consistency is achieved. The rate of convergence depends on V_0, and a good choice would give a band structure nearly self-consistent from the beginning. This can be verified by computing the electron density from the Bloch states and comparing it with the initial density.

A second way is to compare from the beginning the electron density with the experimental results, as can be obtained, for instance, from x-ray scattering experiments.[30] The densities can be made to agree because the local Hamiltonian discussed in Sec. II can be constructed to give the correct electron density in each cell. The two approaches should be equivalent. Unfortunately, at present, x-ray diffraction experiments may not be sufficiently accurate to give electron densities which can be used to define the goodness of crystal states.

Another possibility is to treat V_0 and the potential sphere radius in a semiempirical way as disposable parameters, which can be fixed so as to give good results for the band structure. Though less satisfactory then the fully self-consistent approach, this procedure still has advantages over the current tight-binding semiempirical energy-band schemes, which use as parameters the basic Hamiltonian matrix elements[8,9] (13 parameters needed in zinc-blende semiconductors[8]). The advantage is due to the fact that, once V_0 and the volume of the lattice cell is fixed, everything can be computed from first principles.

IV. PROCEDURE FOR OBTAINING CRYSTAL EIGENSTATES

Once the localized functions have been obtained at each atomic site, the procedures of the tight-binding method can be used to obtain the crystal eigenstates. The secular equation to be solved is

$$\| H_{ij}(\vec{k})-E(\vec{k})S_{ij}(\vec{k}) \| =0 , \tag{9}$$

where the indices i and j refer to all different Bloch functions constructed from the available localized functions. The overlap matrix S_{ij}, obtained in the usual way, is not diagonal because we have preferred to concentrate on the localization of the functions rather than impose the condition of orthogonality at different lattice sites.

The Hamiltonian matrix elements can be written as

$$H_{ij}(\vec{k})=\sum_n \left\langle \phi_i^{(0)}(\vec{r}) \left| \frac{p^2}{2m}+\sum_l V^{(l)}(r) \right| e^{i\vec{k}\cdot\vec{r}_n}\phi_j^{(n)}(\vec{r}) \right\rangle . \tag{10}$$

Owing to the localization of the orbitals $\phi^{(n)}(\vec{r})$ and to the finite radius of each $V^{(l)}(r)$, we are, in general, justified in neglecting the contributions of three-center integrals ($l\neq n\neq 0$). This, however, is not a general rule but has to be verified case by case, because it depends critically on the type of localized functions which are used.[11,31,32] The finite radius of the local potential $V^{(l)}(r)$ does not eliminate the influence of a cell on the functions localized on another cell, because they extend on the entire space, as shown in Sec. III. However, their high degree of localization allows us to consider only the interactions with a small number of neighboring cells.

All the matrix elements can be expressed as a linear combination of a smaller number of independent integrals in the usual way.[6,33] These have to be computed by direct numerical integration. We can write typical formulas for the matrix elements of H, making explicit use of the eigenvalue $E_n^{(l)}$ of Eq. (1) with the local Hamiltonian $H^{(l)}$, as given by Eq. (2). We have for the diagonal matrix elements:

$$\begin{aligned} H_{ij}(\vec{k}) = {} & E_i^{(0)} - V_0^{(0)} \langle \phi_i^{(0)}(\vec{r}) \,|\, \phi_i^{(0)}(\vec{r}) \rangle_{r>r_0} + \sum_{n\neq 0} \langle \phi_{i(r)}^{(0)} \,|\, V^{(n)}(\vec{r}) \,|\, \phi_i^{(0)}(\vec{r}) \rangle \\ & + \sum_{l} e^{i\vec{k}\cdot\vec{r}_l} [E_i^{(0)} \langle \phi_i^{(0)}(\vec{r}) \rangle - V_0^{(0)} \langle \phi_i^{(0)}(\vec{r}) \,|\, \phi_i^{(l)}(\vec{r}) \rangle_{r>r_0} + \langle \phi_i^{(0)}(\vec{r}) \,|\, V^{(l)}(\vec{r}) \,|\, \phi_i^{(l)}(\vec{r}) \rangle] \\ & + \sum_{l\neq 0} \sum_{n\neq l} e^{i\vec{k}\cdot\vec{r}_l} \langle \phi_i^{(0)}(\vec{r}) \,|\, V^{(n)}(\vec{r}) \,|\, \phi_i^{(l)}(\vec{r}) \rangle \; . \end{aligned} \tag{11}$$

The expression for the off-diagonal elements is

$$\begin{aligned} H_{ij}(\vec{k}) = {} & \sum_{l\neq 0} e^{i\vec{k}\cdot\vec{r}_l} [E_i^{(0)} \langle \phi_i^{(0)}(\vec{r}) \,|\, \phi_j^{(l)}(\vec{r}) \rangle - V_0^{(0)} \langle \phi_i^{(0)}(\vec{r}) \,|\, \phi_j^{(l)}(\vec{r}) \rangle_{r>r_0} + \langle \phi_i^{(0)}(\vec{r}) \,|\, V^{(l)}(\vec{r}) \,|\, \phi_j^{(l)}(\vec{r}) \rangle] \\ & + \sum_{l} \sum_{n\neq l} e^{i\vec{k}\cdot\vec{r}_l} \langle \phi_i^{(0)}(\vec{r}) \,|\, V^{(n)}(\vec{r}) \,|\, \phi_j^{(l)}(\vec{r}) \rangle \; , \end{aligned} \tag{12}$$

where $V_0^{(0)}$ is the constant potential outside the zeroth cell, which localizes the wave functions centered on that site, and the notation $r > r_l$ means that the corresponding integral must be performed outside the lth cell. We remark that $V_0^{(l)}$ appears formulas (11) and (12) in such a way as to compensate its effect on the eigenvalues of the local Hamiltonian $E_i^{(l)}$. Its introduction has the only effect of specifying the localized orbitals so that the expansion set is reduced and the two-center approximation is justified.

V. EXAMPLES TO THE CASE OF NiO

We wish now to discuss the localized orbitals for an application of this method to NiO. This is a typical case in which the method we propose may be useful because the crystal is ionic and intercell potential contributions are important; furthermore, the presence of localized d states suggests that a tight-binding approach should be used.

We want then to obtain localized functions for the O^{2-} ions and for the Ni^{2+} ions. In particular, since we are interested in the highest valence bands and the lowest conduction bands, we are looking for $2s$- and $2p$-like oxygen functions and for $3d$- and $4s$-like functions of nickel. We expect that lower localized states will not be different from atomic states, with the correction due to the Madelung term.

We present in Fig. 1 the self-consistent potential of the local cell of Ni^{2+} in NiO, and for comparison the self-consistent potential of isolated Ni^{2+}.

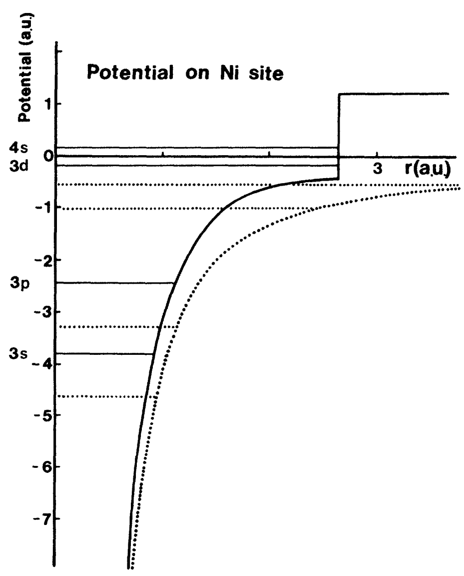

FIG. 1. Self-consistent potential on Ni site in NiO with $V_0 = 1.2$ a.u. outside the cell (full line), and with $R_{Ni} = 2.65$ a.u., compared with the self-consistent potential for the Ni^{2+} ion (dotted line).

It can be observed that the contributions of the neighboring cells modify the shape of the potential. The positions of the relevant energy levels are also indicated. One can see that the core levels are shifted upwards just by the Madelung term, while the energy positions of the valence states ($3d$,$4s$) depend also on the contributions of the neighboring cells and on the choice of V_0. The values of V_0 (1.2 a.u.) and $R_{\mathrm{Ni}}=2.65$ have been chosen so as to localize the $4s$ function of Ni^{2+}, which could barely exist as a bound state without the V_0 well because of the repulsive Madelung term. The choice is not unique, and we have verified that band-structure results obtained with different values of V_0 are about the same, provided the $4s$ state is localized.

We show in Fig. 2. the radial $3d$-like wave function of NiO computed from Eq. (1), obtained with the potential about Ni^{2+} shown in Fig. 1, and, for comparison, the wave function obtained without the V_0 well and the wave function of the free ion. In Fig. 3 we show the radial $4s$-like function about Ni^{2+} with the V_0 well, without it, and, for comparison, the $4s$ orbital of the free ion. The wave functions display clearly the localizing effect of the V_0 potential added to the self-consistent potential. Inside the cell the functions are little different from atomic orbitals. Near the cell boundaries important differences occur. Without the V_0 potential the local orbitals are slightly expanded with respect to the corresponding orbitals of the free ion because of the repulsive intercell ionic potential (6); with the V_0 potential added, the tails of the orbitals are shortened and the orbitals are strongly localized. This effect is much more relevant on the $4s$ function, which would be barely bound without the V_0 potential, than on the $3d$ function, which is already well localized in the free ion and remains localized also without the V_0 potential. The main effect of the V_0 potential is then to localize the $4s$-like function about the Ni^{2+} site.

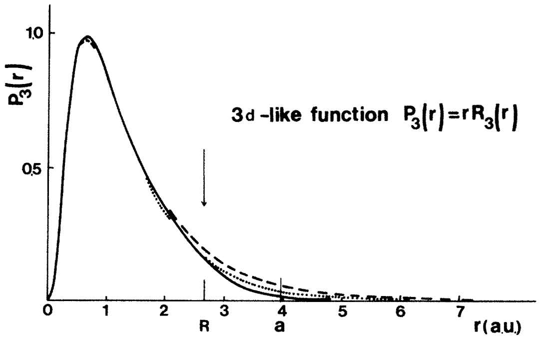

FIG. 2. Radial part $P_3(r)$ of the $3d$-like wave function on Ni site in NiO obtained for $V_0=1.2$ a.u. (full line) compared with the $3d$-like wave function on Ni site in NiO obtained for $V_0=0$ (dashed line) and compared with the $3d$ wave function for the Ni^{2+} ion (dotted line). The first-neighbor distance a and the radius of the Ni^{2+} well R are indicated.

We also report in Fig. 4 the self-consistent potential for O^{2-} with $V_0=0.15$ and $R_0=2.8$ a.u. and the self-consistent potential which would result with $V_0=0$. The comparison with the free-ion potential is not possible in this case because the free ion is not stable. We present in Fig. 5 the $2p$-like functions obtained from the above potential; the function with $V_0=0$ is also reported and for comparison also the function obtained with the method proposed by Watson[34] is given. It may be observed that the effect of V_0 here is very small because the localization is already obtained with intercell potential interaction (6). It can be observed that our $2p$ wave functions are more localized than those obtained by Watson putting the ion at the center of a charged hollow sphere to compensate for the ionicity. The choice of the well radii have been made to conserve volume and the relative size of the two ions. Slightly different choices have a very small effect on the results.

We wish to point out that the shapes of the localized orbitals inside the atomic cell depend strongly on the self-consistent potential inside the cell and, in particular, on the choice of the exchange-correlation term. A better estimate of the correlation-screening factor $\alpha(r)$ of formula (4) and the exclusion of the potential of the electron on itself in formula (5) would indeed modify the function $2p$ much more than a change of the V_0 poten-

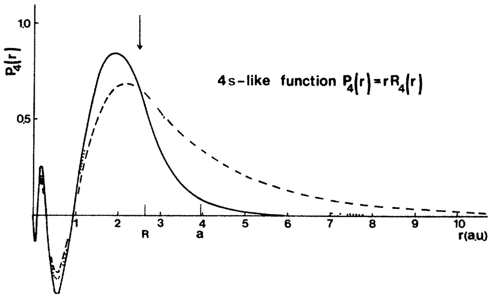

FIG. 3. Radial part $P_4(r)$ of the $4s$-like wave function on Ni site in NiO obtained for $V_0=1.2$ a.u. (full line) compared with the $4s$-like wave function on Ni site in NiO obtained for $V_0=0.0$ (dashed line) and compared with the $4s$ wave function for the free Ni^{2+} ion (dotted line).

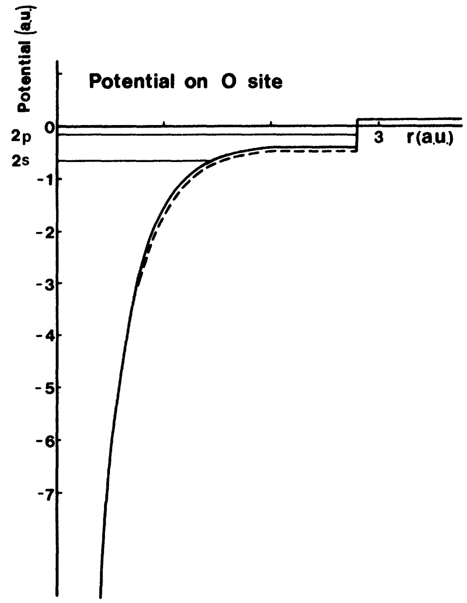

FIG. 4. Self-consistent potential on O site in NiO and $V_0=0.13$ a.u. and $R_0=2.8$ (full line) compared with the self-consistent potential on O site in NiO and $V_0=0$ (dashed line).

tial. An approach of this type is being carried out by Kunz on alkali halide crystals.[35]

A related question which we wish to raise is how the localized wave functions obtained here represent the true electron density in the crystal. A direct comparison could be made by computing the x-ray scattering factors, as done in a recent paper[36] for the alkali halides, with the Watson sphere model. The present model should give systematically larger deviations from scattering factors of free ions than the Watson model, as indicated by Fig. 5. This seems in line with measurements of γ-ray diffraction intensities in alkali halides.[30] The comparison with the electronic crystal density should also be a sensitive way of estimating the accuracy of the self-consistent potential, particularly its exchange-correlation contribution. Preliminary x-ray scattering experiments have been performed in cubic oxides by Sasaki *et al.*[37] We have not attempted a detailed comparison of atomic scattering factors because the results do not appear sufficiently accurate to give a test for the individual wave functions and their discrepancies from atomic values. Such a detailed comparison should involve very large reciprocal lattice vectors and γ rays should be used.[30] We hope that this will be possible in the near future. As mentioned before, the correspondence between experimental and computed electron densities with a given V_0 can be taken as a test for the goodness of the initial localized basis functions. The final self-consistent densities should agree with diffraction data independent of the choice of V_0.

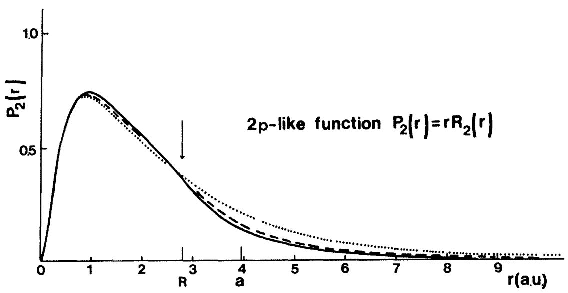

FIG. 5. Radial part $P_2(r)$ of the 2p-like wave function on O site in NiO obtained for $V_0=0.13$ a.u. (full line) compared with the 2p-like wave function on O site in NiO obtained for $V_0=0.0$ (dashed line) and compared with the 2p-like wave function for the O^{2-} ion as obtained by Watson (Ref. 34) (dotted line).

Using the potentials and the wave functions described above, we have performed a calculation of the electronic band structure of NiO. The detailed description of the calculation of NiO and other transition-metal oxides will be reported elsewhere.[40] We give here in Fig. 6 the valence bands and the lowest conduction bands at the center of the Brillouin zone and in the Δ and Λ directions. The band structure shows an s-like conduction band with the maximum at Γ, and p- and d-like valence bands, with maxima along the Λ and Δ directions, as obtained with more involved computational methods.[38,39] Our results on the valence-band structure, and particularly the splittings between d bands and the p bands, agree more closely with the results of Collins, Kunz, and Ivey[39] than with the results of Mattheis.[38]

To show the influence of the constant potential wells and of the choice of the radii we also plot in Fig. 7 the band structure obtained by interchanging the values of the two cell radii (2.8 for Ni and 2.65 for O) and by changing the value of the potential V_0 on oxygen to 0.025. It can be observed that the band structure is practically the same as that of Fig. 6. In particular, the decrease in the radius R_0 would increase the value of the p levels of O, but this is compensated by the decrease in the potential well V_0, so that the separation $\Gamma_{15}-\Gamma_{25'}$ of p and d edges remains about the same. The shape of the bands is even less sensitive to changes in R_0 and V_0.

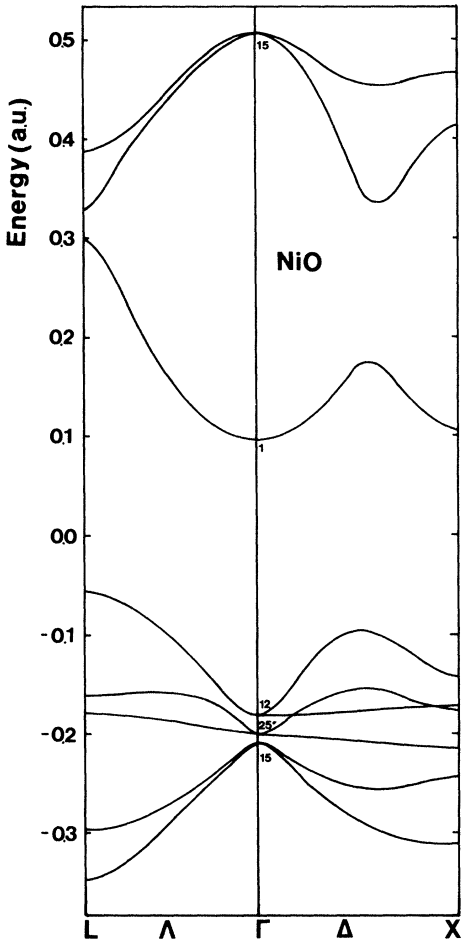

FIG. 6. Energy-band structure of NiO along the Λ and Δ directions of the Brillouin zone with the values of the potential given in the previous figures. Also the 4p higher conduction band is included.

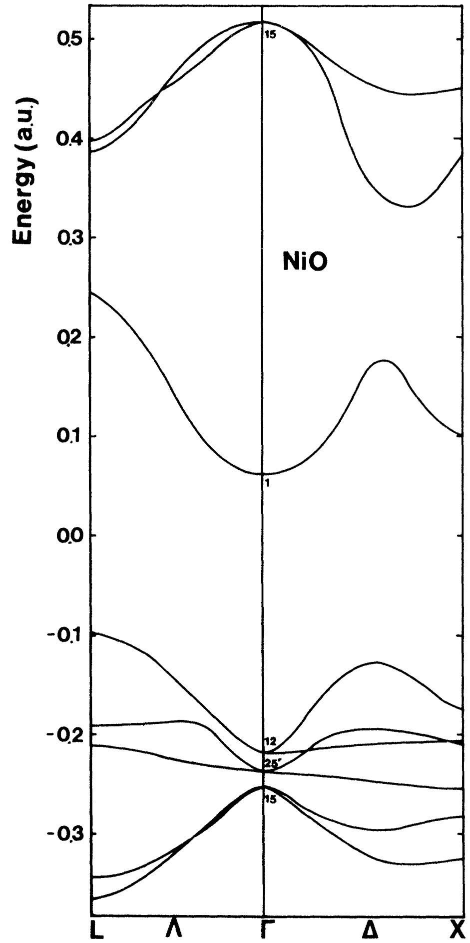

FIG. 7. Energy-band structure of NiO along the Λ and Δ directions of the Brillouin zone with different values of the potential wells and inverted cell radii ($R_0=2.65, R_{\mathrm{Ni}}=2.8, V_0=0.025, V_{\mathrm{Ni}}=1.2$).

A more detailed description of the NiO band structure with a discussion of the electron densities and of the rate of convergence towards self-consistency will be reported separately.[40] We do not wish to give here a detailed discussion of the band structure of NiO in comparison with experimental data. We can refer for that to previous papers[39] and to a general review article.[41] We only wish to point out that the results we obtain with the present method are generally encouraging, and suggest further applications to oxides[40] and other ionic crystals.

VI. CONCLUSIONS

The main results of this paper can be briefly summarized as follows. A prescription has been given to generate self-consistent localized functions in crystals, making use of an arbitrary localizing potential. The localized functions can be used as the basis set for energy-band calculations in ionic semiconductors or insulators with a complex unit cell. They can also be used to compute electron densities and atomic scattering factors in crystals.

The advantage of this prescription with respect to other procedures is twofold. First of all, the functions obtained in this way satisfy the self-consistent equation appropriate to the crystal density inside a lattice cell. Second, they are sufficiently localized to ensure rapid convergence with respect to the number of neighbors and to justify the validity of the two-center approximation.

Localized functions have been obtained for NiO and have been compared with the corresponding ones for isolated ions. A detailed calculation of the band structure of NiO with the above localized functions gives valence and conduction bands of comparably quality to those of other band-structure approaches.

We think that this method can be easily applied to a large number of compounds, particularly to transition-metal oxides or to rare-earth oxides, and to other ionic semiconductors. Our aim will be to couple the simplicity and the physical insight granted by the tight-binding approach to a satisfactory degree of accuracy.

ACKNOWLEDGMENTS

One of the authors (F. B.) is indebted to the staff of the University of Illinois and of Purdue University for support and technical assistance. Illuminating discussions with A. B. Kunz on the role of exchange and correlation effects and with J. M. Honig on the electronic transport properties of transition-metal oxides are gratefully acknowledged. This work was partially supported by Consiglio Nazionale delle Richerche through Gruppo Nazionale de Struttura della Materia.

---

[*] Present address: Scuola Normale Superiore, Pisa, Italy.

[†] Present address: IBM Research Center, San Jose, California 95193.

[1] See, for instance, F. Bassani and G. Pastori-Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, 1975), Chap. 3.

[2] See, for instance, R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry* (Interscience, New York, 1959).

[3] E. Mooser and W. B. Pearson, Prog. Semicond. 5, 103 (1960).

[4] W. A. Harrison, Phys. Rev. B 8, 4487 (1973); S. T. Pantelides and W. A. Harrison, *ibid.* 11, 3006 (1975); D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975); P. Manca, Nuovo Cimento Suppl. 6, 759 (1968).

[5] W. Kohn, Phys. Rev. B 7, 4388 (1973).

[6] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[7] F. Bassani and G. Pastori-Parravicini, Nuovo Cimento B50, 95 (1967).

[8] See, for instance, R. A. Broomley and R. B. Murray, J. Phys. C 5, 738 (1972); R. A. Broomley, R. B. Murray, and A. D. Yoffe, *ibid.* 5, 746 (1972); 5, 759 (1972); P. G. Harper and D. R. Edmondson, Phys. Status Solidi B 44, 59 (1971); D. R. Edmondson, Solid State Commun. 10, 1085 (1972); E. Doni, G. Grosso, and G. Spavieri, *ibid.* 11, 493 (1972), E. Doni, R. Girlanda, V. Grasso, A. Balzarotti, and M. Piacentini, Nuovo Cimento B51, 154 (1979); H. P. Hjalmarson, Ph. D. thesis, University of Illinois, Urbana, Illinois (unpublished).

[9] J. E. Simmons, C. C. Lin, D. F. Fouquet, E. E. Lafon, and R. C. Chaney, J. Phys. C 8, 1549 (1975); F. Casula and A. Kisiel, Nuovo Cimento B39, 470 (1977).

[10] N. Daude, C. Gout, and C. Jouanin, Phys. Rev. B 15, 3229 (1977).

[11] R. C. Chaney, C. C. Lin, and E. E. Lafon, Phys. Rev. B 3, 459 (1971).

[12] W. Andreoni, Phys. Rev. B 14 4247 (1976).

[13] D. E. Ellis and G. S. Painter, Phys. Rev. B 2, 2887 (1970); 1, 4747 (1970); G. S. Painter, D. E. Ellis, and A. R. Lubinsky, *ibid.* 4, 3610 (1971).

[14] W. H. Adams, J. Chem. Phys. 34, 89 (1961); 37, 2009 (1962).

[15] T. Gilbert, in *Molecular Orbitals in Chemistry, Physics, and Biology,* edited by P. O. Löwdin and B. Pullman (Academic, New York, 1964), p. 405.

[16] P. W. Anderson, Phys. Rev. 181, 25 (1969); J. D. Weeks, P. W. Anderson, and A. G. H. Davidson, J. Chem. Phys. 58, 1388 (1973).

[17] D. W. Bullett, J. Phys. C 8, 2695 (1975); 8, 2707 (1975); 8, 3108 (1975); D. W. Bullett and M. L. Cohen, *ibid.* 10, 2083 (1977); F. Casula, S. Ossicini, and A. Selloni, Solid State Commun. 28, 141 (1978); 30, 309 (1979).

[18] E. Doni, L. Resca, R. Resta, and R. Girlanda, Solid State Commun. 34, 461 (1980); Proceedings of the XVth International Conference on the Physics of Semiconductors (Kyoto, 1980, in press).

[19] A. B. Kunz, Phys. Status Solidi 36, 301 (1969); Phys. Rev. B 7, 5369 (1973); 8, 1690 (1973).

[20] A. B. Kunz, Phys. Rev. B 2, 5015 (1970); A. B. Kunz and N. O. Lipari, J. Phys. Chem. Solids 32, 1141 (1971); Phys. Rev. B 3, 491 (1971); 4, 1374 (1971); 4, 4639 (1971).

[21] A. Zunger and A. J. Freeman, Phys. Rev. B 15, 4716 (1977); 15, 5049 (1977); 17, 1839 (1978); 17, 2030 (1978); 17, 4850 (1978).

[22] S. Ciraci and I. P. Batra, Phys. Rev. B 15, 4923 (1977); I. P. Batra, S. Ciraci, and W. E. Rudge, *ibid.* 15, 5858 (1977).

[23] J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Lett. 9, 215 (1962).

[24] W. Kohn and L.-J. Sham, Phys. Rev. 140A, 1133 (1965).

[25] See, for instance, J. C. Slater, in *Computational Method in Band Theory,* edited by P. O. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971), p. 447.

[26] F. W. De Wette and B. R. A. Nijoboer, Physica (Utrecht) 24, 1105 (1958).

[27] G. W. Pratt, Phys. Rev. 88, 1217 (1952).

[28] Spin-polarized energy bands have been obtained with the same approximation for exchange potential, for instance, by S. J. Cho, Phys. Rev. B 1, 4589 (1970); K. Lendi, Phys. Condens. Matter 17, 215 (1974).

[29] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, New Jersey, 1963).

[30] R. Colella (private communication). One of the authors is indebted to R. Colella for a discussion of new atomic scattering factors in ionic crystals and their discrepancies from values expected from free atoms.

[31] A. B. Kunz, Phys. Rev. 162, 789 (1967).

[32] J. L. Fry, N. E. Breuer, F. C. Case, and A. L. Desai, Phys. Rev. B 15, 5811 (1977).

[33] W. Andreoni and F. Casula, J. Phys. C 8, 1371 (1975); F. Casula, Nuovo Cimento B32, 94 (1975).

[34] R. E. Watson, Phys. Rev. 111, 1108 (1958).

[35] A. B. Kunz (private communication).

[36] P. C. Schmidt and A. Weiss, Z. Naturforsch. Teil A 34, 1471 (1980).

[37] S. Sasaki, K. Fujino, and Y. Takeuchi, Proc. Jpn. Acad. 55B, 43 (1979).

[38] L. F. Mattheis, Phys. Rev. B 5, 290 (1972); 5, 306 (1972).

[39] G. T. Surratt and A. B. Kunz, Solid State Commun. 23, 555 (1977); 25, 9 (1978). See also T. C. Collins, A. B. Kunz, and J. L Ivey, Int. J. Quantum Chem. Symp. 9, 519 (1975).

[40] J. Hugel and C. Carabatos (unpublished).

[41] For a general discussion of electron behavior in transition-metal oxides see D. Adler, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrereich (Academic, New York, 1968), Vol. 21, p. 1.