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Two-center approximation in the quantum theory of solids*

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A study is presented of the two-center approximation to the multicentered integrals which appear in the Hartree-Fock theory of solids when a localized set of basis functions is employed. A model potential is introduced to simulate the complicated self-consistent field of real crystals. This permits a simple separation of multicentered contributions to energy integrals and at the same time provides a system for which accurate solutions can be obtained easily. Crystal potentials are constructed for LiF, a typical ionic insulator, and silicon, a typical covalent semiconductor. All integrals with the model potentials are accurately evaluated, and the exact energy-band structures are compared to the results obtained in the two-center approximation. Two types of errors are found, and the orbital ranges are identified for which the two-center approximation is especially bad. For both crystals it is concluded that the two-center approximation is accurate for core orbitals only, semiqualitative for the valence orbitals, and completely inappropriate for orbitals which describe conduction bands. Generalization of these results is made to other systems, and it is concluded that neglect of multicentered integrals must always be done with special care if even qualitatively meaningful results are to be obtained.

I. INTRODUCTION

When solving the Hartree-Fock equations in the quantum theory of molecules or solids using a variational basis set composed of localized or atomic-like functions, large numbers of multicentered integrals are encountered. The difficulty of evaluating these multicentered integrals has frequently necessitated approximation to, or complete neglect of, certain types of integrals. While multicentered integrals are usually much smaller than corresponding single-centered integrals, there are vastly more of them which contribute. Although neglect of multicentered terms has often been necessary because of their near intractability, such approximations must be regarded with suspicion. As a matter of fact, the linear-combination-of-atomic-orbitals method (LCAO) was made comparable in accuracy with other methods of energy-band theory only after accurate methods of evaluating these multicentered integrals were introduced.[1,2]

The near intractability of these calculations, especially when dealing with heavier atoms, has caused some reluctance to abandon the various approximations in molecular or solid-state problems. A review of approximations used in molecular studies has been given by Nicholson.[3] In solid-state studies three or more centered integrals are often completely neglected,[4] or the LCAO formalism is simply used as an interpolative or pseudopotential method.[5-7]

It is possible to evaluate analytically all the multicentered integrals which are encountered in the Hartree-Fock equations if the LCAO basis functions are expanded first in a set of Gaussian orbitals. This procedure has been used for a number of years by quantum chemists to treat molecular systems. Analytic expressions for integrals involved are given by Clementi.[8] While attempts have been made to use Gaussian expansions in Hartree-Fock studies of solids,[9-11] the enormity of effort required in infinite periodic systems has forced systematic approximations to, or neglect of certain integrals.[12] Such studies have been limited to solids composed of atoms with *s* and *p* valence electrons only. Euwema *et al.*[12] have made extensive studies of the various approximations needed to make these calculations tractable, but did not compare approximate answers to answers obtained by straightforward convergence of the exact expressions: They compared one approximation to another better approximation. While significant differences were found among their various approximations, it is difficult to sort out the sources of error because their effort was a very complicated self-consistent Hartree-Fock calculation.

Among earlier studies, several should be mentioned here.[13-16] Kunz[13] has estimated the errors introduced by the two-center approximation in the band structure of NaCl by computing three-centered integrals in a spherical approximation. His conclusion was that bandwidths and band shapes were rather sensitive to the approximation, with 75% changes occuring in both.

Bartling[14] made a similar study in a band-structure calculation for α-MnS, but carried out more terms in the expansion of the crystal potential in cubic harmonics. He used the ξ-function method of evaluating multicentered integrals and had difficulty with convergence.

In a much simpler, but informative study, Wohlfarth[15] has considered neglect of three-centered integrals in a model calculation consisting of a linear chain of hydrogen atoms with a rather large lattice constant, introduced to minimize overlap. He found errors of the order of 30% in band widths. While the model was not physical, it did permit some exact statements about errors in the approximation.

In another, even simpler calculation, Lapidus[16] constructed a one-dimensional model for a molecule of butadiene which consisted of δ-function potentials. In this case, exact results could be compared to two-centered approximate values, and he found reasonable agreement only in the limit of atomic separations which were large compared to the size of the atoms (as measured by the range of atomic wave functions). Energy eigenvalues did not agree even qualitatively at closer spacings.

While the last two studies offered the advantage of direct comparison of approximate solutions to exact solutions, the models which were employed to make this possible did not have much resemblance to any real physical system. It is the purpose of this paper to examine a much more realistic model of a solid-state system in which it is still possible to obtain essentially exact eigenvalues, which can be compared with eigenvalues from the two-center approximation.

Two studies have been made here with similar conclusions, one a model potential band calculation for LiF and the other a model potential study of the band structure of silicon. In both cases two- and three-centered contributions were easily separated, and both were accurately computed. Parameters in the model potentials were not highly refined, but gave energy-band structures which are comparable to much more intricate self-consistent-field (SCF) band structures. The model potential is discussed in Sec. II. In Sec. III a comparison of various two- and three-centered integrals is made, and the band structures are compared. Section IV concludes this paper with an analysis of the two-center errors and a discussion of a related problem, the possible linear dependence of LCAO basis functions.

II. MODEL POTENTIAL

In order to obtain a simple separation of two- and three-centered integrals, achieve a realistic energy band structure, and avoid the very time consuming requirements of a first-principles self-consistent-field treatment, a crystal potential was constructed as a superposition of model atomic potentials. For LiF,

$$V(\vec{r}) = \sum_l [V_{\mathrm{Li}}(\vec{r} - \vec{R}_l) + V_{\mathrm{F}}(\vec{r} - \vec{R}_l - \vec{\tau})], \qquad (1)$$

where $\vec{R}_l$ is a lattice vector, $\vec{\tau}$ is the vector from the lithium atom at the origin to the fluorine atom at $(a/2)(1, 0, 0)$, and the sum is over all lattice vectors in the face-centered-cubic Bravais lattice. The lattice constant a was taken to be 4.0173 Å. The model potentials for each atom were given the Yukawa form

$$V_{\mathrm{Li}}(\vec{r}) = Z_{\mathrm{Li}} \exp(-\alpha_{\mathrm{Li}} r)/r, \qquad (2)$$

and similarly for the fluorine atoms. The parameter Z was assigned to be the charge on the nucleus, 3 for lithium and 9 for fluorine, while the parameter α was fixed as 2.0 reciprocal atomic units for both atoms (for calculational convenience).

A similar potential was also constructed for crystalline silicon, but the parameters in the Yukawa potentials were adjusted. First the energy levels from an atomic Hartree-Fock calculation were fit by varying the parameters Z and α. Parameters were chosen which gave a good fit to the $2s$, $3s$, and $3p$ levels. This occurred for $Z = 22$ and $\alpha = 1.04$. After the band calculation was completed, the parameter Z was adjusted to improve agreement with the observed (indirect) band gap for silicon, and refinements were made on the nonlinear parameter α. The lattice constant used for silicon was 5.4307 angstroms. Additional details about the silicon-model potential calculation are given elsewhere.[17] The best parameter values were $Z = 22$, $\alpha = 1.23$.

Since the goal of this paper was to examine carefully the approximations and not the band structures, no more elaborate parameter adjustments were made here. In spite of the fact that no parameter adjustments were made for LiF, and only partial adjustment of the silicon model was made, both band structures show qualitative features similar to the more complicated self-consistent-field[18] (SCF) or elaborate pseudopotential calculations.[19] A discussion of these band structures is given in Sec. III. Additional details are given by Desai.[20]

III. TWO-CENTER APPROXIMATION

The modern LCAO-SCF method has been developed over the last ten years by a number of authors. A review of the formalism is presented in the text by Callaway.[21] A typical integral needed to compute matrix elements of the Hamiltonian is

$$E_{ij}(\vec{R}_{AB}) = \int \phi_i(\vec{r} - \vec{A}) V(\vec{r}) \phi_j(\vec{r} - \vec{B})\, d\vec{r}, \qquad (3)$$

where $V(\vec{r})$ is the crystal potential given in this case by Eq. (1), and ϕ_i and ϕ_j are localized orbitals centered about $\vec{A}$ and $\vec{B}$, respectively. Inserting Eq. (1) into Eq. (3) produces sums of the three-centered integrals, which, for arbitrary ϕ and V, are extremely tedious to compute. With Gaussian basis functions ϕ and Yukawa model potentials, analytic expressions for the integrals are available[22] which can be coded for computer calculation and summed to the desired degree of accuracy. For an appropriate choice of Yukawa parameters the direct lattice sum converges readily. This is in strong contrast to an unscreened Coulomb potential which must be handled with the Ewald procedure.[22]

The two-center approximation has been made in previous LCAO studies because of the difficulty in evaluating and summing all the integrals in Eq. (3). For arbitrary wave functions and potential of interaction the three-center integrals are extremely tedious to obtain with any accuracy. In the following discussions the two-center approximation is defined as complete neglect of all terms involving more than two atomic sites. Thus, if both wave functions are on the same site in Eq. (3), all potential sites were summed, but if the wave functions were on different sites, $\vec{A}$ and $\vec{B}$, only the potential contributions at sites A and B were summed. It is the purpose of this paper to examine this approximation in two crystal systems: LiF, which is typical ionic insulator; and silicon, which is a typical covalent semiconductor.

A. LiF integrals

In this study several complete band-structure determinations have been made for LiF. Two different sets of Gaussian orbital basis functions were employed. The first used a set of atomic wave functions from an earlier SCF study, while the second used an expanded basis set. Table II gives the expanded basis set. Reference 18 contains a table of the atomic wave functions. The expanded set was constructed in a fashion similar to that of Euwema *et al.*[12] Core orbitals were represented by contractions, but valence orbitals were allowed complete variational freedom. The Gaussians with very small exponents which appear in the atomic set were discarded to avoid convergence problems and possible linear dependence of basis functions. These very-long-ranged orbitals are not needed in periodic structures. In atomic or molecular structures they are required to satisfy boundary conditions at infinity. The nonlinear parameters in individual Gaussian orbitals were not optimized in this study, but a check of convergence of the basis set has been performed by repeating the calculations with varying numbers of Gaussians. This point is discussed further in Sec. IV.

Table I shows some of the integrals obtained with the atomic basis set for the model potential. The three-center integrals (labeled 3C) were converged to eight significant figures by carrying out the sums directly. The integrals labeled SCF were obtained from the complete self-consistent-field calculation, excluding exchange,[18] and the integrals labeled 2C used the approximation defined in the preceeding paragraph. The table includes wave functions of s and p symmetry on each of the two sublattices of LiF for first neighbors and representative other neighbors. The general agreement between 3C model and SCF crystalline potential integrals suggests that the model band structure should resemble the SCF band structure, as it does. At first glance the 2C model integrals appear to be roughly the same, also, leading one to expect at least qualitative agreement between all three band structures. This turns out not to be the case. The 2C integrals display average errors of

TABLE I. Representative potential integrals with the atomic Gaussian basis for LiF. Energies are in Ry. SCF labels the self-consistent-field potential integrals, and the integrals labeled 3C and 2C are the exact and the two-center approximation to model-potential integrals. Each integral in a row is to be multiplied by the power of 10 given in the last column labeled "Expt." Integrals are labeled in column 1 by a notation which should be clear. The vector in column 1 is R_{AB} of Eq. (3) in units of $\frac{1}{2}a$.

Integral type	SCF	3C	2C	Expt.
Li-Li 1*s*-1*s* (1,1,0)	−0.3910	−0.3608	−0.3368	−3
(2,0,0)	−0.1235	−0.1203	−0.0855	−4
2*s*-2*s* (1,1,0)	−0.2835	−0.3157	+0.0224	0
(2,0,0)	−0.1784	−0.1962	+0.0069	0
(7,3,2)	−0.2278	−0.2435	0.0000	−5
2*s*-2*x* (1,1,0)	−0.2113	−0.2349	−0.0137	0
(7,3,2)	−0.1454	−0.1555	−0.0000	−4
1*s*-2*x* (1,1,0)	−0.2382	−0.2239	−0.2183	0
(7,3,2)	−0.6041	−0.6426	−0.0193	−8
2*s*-2*x* (1,1,0)	−0.1445	−0.1564	+0.0021	0
(7,3,2)	0.8505	0.9089	0.0000	−4
F-F 1*s*-1*s* (1,1,0)	−0.1447	−0.1592	−0.1592	−4
(2,0,0)	−0.1928	−0.2105	−0.2032	−7
2*s*-2*s* (1,1,0)	−0.1949	−0.2428	−0.2176	−2
(2,0,0)	−0.5483	−0.4724	−0.0645	−4
2*s*-2*x* (1,1,0)	−0.7551	−0.8547	−0.8891	−2
(1,1,2)	−0.5997	−0.6138	−0.1057	−5
1*s*-2*x* (1,1,0)	−0.1699	−0.1891	−0.1891	−1
(1,1,2)	−0.9064	−0.1011	−0.0989	−6
2*x*-2*x* (1,1,0)	0.7899	0.9763	0.9139	−2
(2,0,0)	−0.1044	−0.1107	−0.0253	−3
(2,1,1)	0.6777	0.6887	0.9866	−6
Li-F 1*s*-1*s* (0,0,1)	−0.6128	−0.6728	−0.6726	−2
1*s*-2*s* (0,0,1)	−0.2109	−0.2045	−0.2021	−1
2*s*-2*s* (0,0,1)	−0.2707	−0.3560	−0.3467	0
1*s*-2*z* (0,0,1)	−0.8782	−0.8250	−0.8157	−1
2*s*-2*z* (0,0,1)	−0.7142	−0.8972	−0.8198	−1
2*z*-2*z* (0,0,1)	−0.0957	−0.1136	−0.0923	0
(1,1,5)	−0.3462	−0.4396	−0.1884	−5

TABLE II. Expanded Gaussian basis for LiF. The contraction coefficients C multiply the normalized Gaussian orbitals, $\exp(-\alpha r^2)$, where α is the orbital exponent (in reciprocal atomic units) given in column 2.

Orbital type	Orbital exponent	$C1$	$C2$	$C3$	$C4$	$C5$
Li s	3184.467 10	0.001 482				
	480.512 66	0.011 447				
	108.863 25	0.059 942				
	30.289 479	0.245 798				
	9.641 514	0.758 958				
	3.391 556	0.0	1.0			
	1.272 029	0.0		1.0		
	0.5	0.0			1.0	
	0.2	0.0				1.0
Li p	2.0	1.0				
	1.0		1.0			
	0.5			1.0		
	0.2				1.0	
F s	37 736.000	0.000 221	−0.000 140			
	5 867.0791	0.001 640	−0.001 065			
	1 332.4679	0.008 735	−0.005 719			
	369.858 66	0.036 662	−0.023 829			
	117.129 69	0.123 661	−0.086 204			
	40.302 86	0.311 407	−0.233 185			
	14.898 01	0.443 441	−0.477 358			
	5.877 74	0.222 868	−0.303 661			
	1.626 76	0.0	0.0	1.0		
	0.61	0.0	0.0		1.0	
	0.23	0.0	0.0			1.0
F p	1024.0802	0.011 242				
	23.794 387	0.080 741				
	7.495 459	0.311 642				
	2.763 871	0.706 619				
	1.099 056	0.0	1.0			
	0.45	0.0		1.0		
	0.20	0.0			1.0	

the order of 10%, but larger errors in certain critical integrals are enormously magnified during the band calculation (e.g., the integral Li-Li $2p_x$-$2p_x$ for the 110 neighbor). Resulting errors in the $2C$ band structure are not $\frac{1}{10}$ Ry, but over 100 Ry in the worst case. The band structures are discussed in more detail below, where this extreme sensitivity is traced to the use of atomic basis functions with long-ranged Gaussian orbital components.

In order to examine the two-center approximation more carefully, the atomic basis set was replaced with the larger set given in Table II. Some typical integrals for this set are given in Table III, where a a clear distinction between corelike and valencelike orbitals appears when the two-center approximation is made. Once again the individual integrals differ by only a few per cent in most cases, and, with the long-ranged terms which appear in the atomic basis set eliminated, discrepancies are not so large for the extended states. Still, the band structure in the two-center approximation contains very large errors in some of the energy bands.

TABLE III. Representative potential integrals for the expanded Gaussian basis for LiF. Notation is the same as Table I. The symbol 1s now means $C1$ s contraction, 1x means $C1$ px contraction, etc. Similar results hold for F-F and Li-F integrals with comparable orbital exponents.

Li-Li integrals	SCF	3C	2C	Expt.
4s-4s (1, 1, 0)	−0.0872	−0.1704	−0.0416	−3
5s-5s (1, 1, 0)	−0.1923	−0.2888	−0.0688	−2
1s-5s (1, 1, 0)	−0.6408	−0.6512	−0.6504	−2
4s-4s (2, 0, 0)	−0.1941	−0.2726	−0.0002	−5
5s-5s (2, 0, 0)	−0.3577	−0.5618	−0.0051	−2
1s-5s (2, 0, 0)	−0.2115	−0.2149	−0.2146	−4
4s-3x (1, 1, 0)	0.2341	0.4573	0.1116	−3
5s-4x (1, 1, 0)	0.2364	0.4902	0.1169	−1
1s-4x (1, 1, 0)	0.2157	0.2192	0.2189	−1
5s-1x (1, 1, 0)	0.3005	0.2459	0.2382	−2
3x-3x (1, 1, 0)	0.4058	0.8686	0.2111	−3
4x-4x (1, 1, 0)	0.1532	0.2827	0.0664	−1
1x-4x (1, 1, 0)	0.7851	0.6574	0.6290	−2

TABLE IV. Modified atomic Gaussian basis for silicon. Notation is the same as Table II.

Orbital type	Orbital exponent	$C1$	$C2$	$C3$
Silicon s	69 989.30	0.000 18	−0.000 06	0.000 02
	10 380.20	0.001 40	−0.000 46	0.000 17
	2330.010	0.007 37	−0.002 41	0.000 87
	657.4660	0.030 37	−0.010 23	0.003 95
	214.0040	0.099 95	−0.034 60	0.012 26
	77.60640	0.254 28	−0.100 88	0.040 92
	30.63950	0.405 20	−0.202 65	0.071 61
	12.81560	0.315 09	−0.230 77	0.116 61
	3.927 140	0.038 93	0.536 51	−0.377 14
	1.452 210	−0.007 10	0.648 44	−0.366 89
	0.257 644	0.001 05	0.009 74	1.116 73
Silicon p	337.4950	0.002 45	−0.000 88	
	78.6871	0.021 40	−0.006 93	
	24.9351	0.105 84	−0.040 06	
	9.215 15	0.326 18	−0.114 08	
	3.615 260	0.495 75	−0.231 97	
	1.451 990	0.221 66	0.148 59	
	0.503 992	0.007 27	0.352 80	
	0.186 040	0.000 38	0.655 73	

B. Silicon integrals

Energy bands for the model potential for silicon have also been obtained to study the two-center errors. In this case, two different sets of basis functions were employed also, but neither was as elaborate as the extended LiF basis. All Hamiltonian and overlap integrals were obtained first using the atomic wave functions of Veillard.[23] Numerical difficulties which were encountered with the overlap matrix for this set were resolved by recomputing the atomic Gaussian expansion coefficients in the presence of the silicon crystalline field after first eliminating the long ranged s and p orbitals.[17] This second atomic set of basis functions is listed in Table IV.

A comparison of $3C$ and $2C$ integrals obtained with these two sets of atomic wave functions is given in Table V. The errors which occurred were similar to the errors in the LiF integrals when the basis functions were comparable. The atomic silicon wave functions were longer ranged and displayed larger errors in the $2C$ approximation for the $3s$-$3s$, $3s$-$3p$, and $3p$-$3p$ integrals than did the corresponding wave functions in Table IV. Because these latter valence wave functions were considerably shorter in range than the atomic silicon or the LiF valence wave functions, the $2C$ approximation was more accurate. Nonetheless, important qualitative features of the silicon band structure were not obtained in the $2C$ approximation.

C. Energy bands for LiF

Although no adjustment of the model potential for LiF was made, a clear resemblance to the SCF band structure of LiF appeared as shown in Fig. 1. The SCF band structure is from Ref. 18. Both band structures include exchange interactions in the $X\alpha$ approximation with $\alpha = 1.0$ (without exchange both valence bands are unbound). By altering the model parameters for fluorine, the model potential for LiF could be adjusted to give better agreement between the fluorine bands of the two calculations.

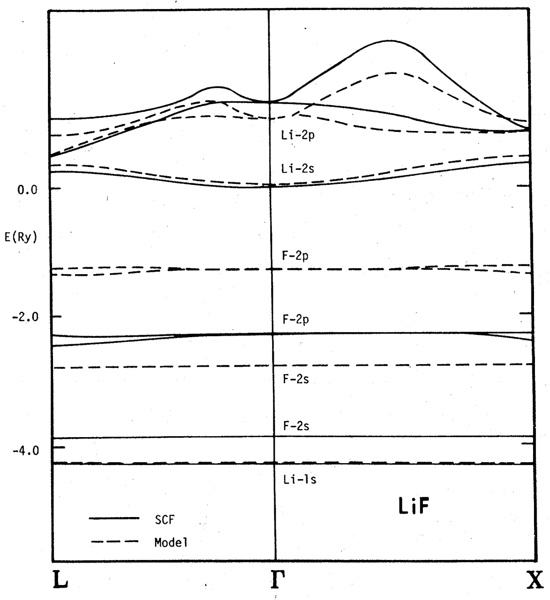

FIG. 1. Energy bands for LiF. The solid curves are the SCF results of Ref. 18. The broken curves were obtained from the model potential for LiF using the same basis functions as Ref. 18. Exchange was included in both results using a local exchange potential.

However the qualitative agreement between the band structures suggests that the parameters used here give potentials of appropriate range to test the two-center approximation, as it would be encountered in much more complex calculations with the SCF potentials.

At this point the two-center approximation was tested for the atomic basis functions and the model crystal potential for LiF. The Hamiltonian matrix (10×10) was reconstructed with the two-center integrals and the secular equation was solved again. Results for the core levels were unaltered and the valence bands changed by very small amounts throughout most of the Brillouin zone. On the other hand, the conduction bands were radically altered. The predominantly Li-$2p$ conduction bands collapsed through the valence and core levels to values below -100 Ry. General chaos appeared in the conduction bands and also in the core levels below -10 Ry; a graph would only be confusing, and space is not wasted with one here.

While there had been no indication of difficulty with the atomic basis functions in the SCF calculations (aside from expected inadequacies in the higher conduction bands), this extreme sensitivity to rather small changes, which occurred in the potential integrals as the two-center approximation was made, suggested that the basis functions might be suffering from a near linear dependence.[12,24,25] This behavior may be detected if some overlap eigenvalues get very small, or if off-diagonal elements get large. As the overlap eigenvalues approach zero, the overlap matrix becomes very sensitive to numerical inaccuracies, and negative overlap eigenvalues may be produced by round-off and precision errors. In the LCAO method this usually happens when two orbital exponents are close in magnitude and both small, so that the Bloch functions which are constructed from them are nearly constant over all the crystal. The practice has been simply to eliminate those functions which are too long ranged, sometimes only at selected points in the Brillouin zone.

To check out the basis functions for this problem and to test convergence with respect to basis, the entire calculation was repeated with the expanded set given in Table II, being careful to converge all integrals to eight significant figures and all matrix elements to at least six significant figures. Figure 2 compares the atomic basis (10×10 matrix) energy bands with the expanded basis (34×34). There were small improvements in the top valence bands, moderate changes in the lowest conduction band, and as expected, substantial revision of the higher conduction bands. With the expanded set of basis functions the smallest orbital exponents still were sensitive to errors in the Hamiltonian matrix, as can be seen from the two-center approximations in Table VI. In all cases, the small overlap eigenvalues associated with the long-ranged basis functions were found to cause extreme sensitivity to errors in the Hamiltonian matrix. The 2C errors are just as drastic with the more accurate basis set as they were with the atomic set, and are not produced by errors of convergence, but are properties of the approximation and the long-range nature of some of the basis functions.

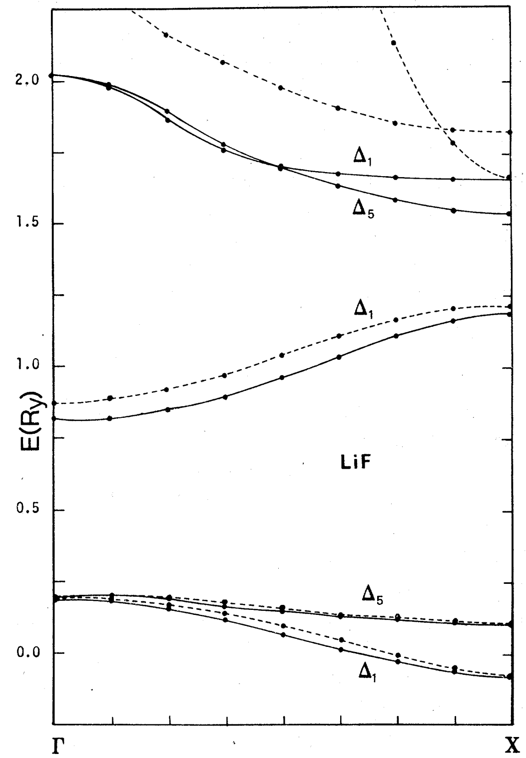

FIG. 2. Model energy bands of LiF. The solid curves were obtained from a basis of 34 orbitals and the broken curves from a basis of 10 orbitals. The LiF model potential with no exchange was used in both cases.

D. Energy bands for silicon

The band structure of silicon was first computed with the atomic basis given in Ref. 23. In the calculation a near linear dependence similar to that discussed for LiF in the preceding paragraphs became even more troublesome. Although all overlap integrals and the overlap matrix elements were computed in IBM 370/155 double precision, and a double precision diagonalization routine was employed, some overlap eigenvalues were so small that numerical instabilities were encountered which resulted in negative overlap eigenvalues at some points in the Brillouin zone. This problem, as it occurs in silicon, is discussed by Ciraci.[26] To eliminate this problem, it was necessary to modify the basis set. This was done by deleting the small orbital exponents from the atomic basis and performing a crystal-field calculation for the atomic set.[17] This new basis is listed in Table IV.

Energy bands from the atomic set, in addition to exhibiting negative overlap at some points in the Brillouin zone, were sensitive to the two-center approximation. Although no conduction bands fell into the core, there was an overlap and mixing of valence and conduction bands. After the new basis set was obtained, the energy bands were well behaved. A comparison of the $3C$ and $2C$ energy bands for the basis set of Table IV is given in Fig. 3. While the $2C$ approximation is better here than in either LiF calculation, it does not give qualitatively correct predictions (for this model potential) for the shape of the conduction bands. The errors in Table V appear small, but are large enough to affect the band structure. It should be pointed out that the longest-ranged basis function in the silicon set has a range in lattice constants which is only half the range of the corresponding function in the extended basis set for LiF.

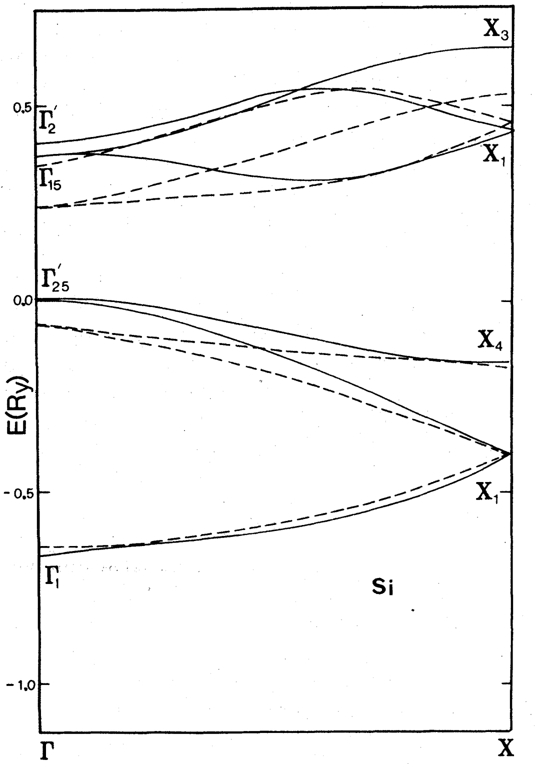

FIG. 3. Model energy bands of silicon. The model potential included no exchange. The basis set is given in Table IV. The solid curves include all $3C$ integrals; the broken curves use the $2C$ approximation.

TABLE V. Representative potential integrals for silicon. Notation is the same as Table I. The lattice vector is given in units of $\frac{1}{8}a$.

Integral type		3C	2C	Expt.
Atomic basis	$1s$-$1s$ (2,2,2)	0.1231	0.1229	−3
	(4,4,0)	0.6878	0.6867	−5
	$3s$-$3s$ (2,2,2)	−0.4327	−0.3591	0
	(4,4,0)	−0.6513	−0.2468	−1
	$1s$-$2x$ (2,2,2)	0.3446	0.3441	−3
	(4,4,0)	0.4223	0.4216	−3
	$3s$-$3x$ (2,2,2)	0.3952	0.3220	0
	(4,4,0)	0.1332	0.0547	0
	$2x$-$2x$ (2,2,2)	−0.2915	−0.2870	−3
	(4,4,0)	0.1498	0.1455	−3
	$3x$-$3x$ (2,2,2)	−0.6717	0.3928	−1
	(4,4,0)	0.1256	0.0428	0
Crystal basis	$1s$-$1s$ (2,2,2)	−0.1482	−0.1481	−3
	(4,4,0)	−0.3299	−0.3295	−7
	$3s$-$3s$ (2,2,2)	−0.1457	−0.1393	0
	(4,4,0)	−0.1711	−0.0460	−2
	$1s$-$2x$ (2,2,2)	0.2464	0.2460	−3
	(4,4,0)	0.8721	0.8671	−6
	$3s$-$3x$ (2,2,2)	0.1774	0.1679	0
	(4,4,0)	0.7770	0.2928	−2
	$2x$-$2x$ (2,2,2)	0.1242	0.1236	−3
	(4,4,0)	0.1122	0.1091	−5
	$3z$-$3z$ (2,2,2)	0.9057	0.9300	−1
	(4,4,0)	−0.7762	−0.8520	−3

IV. ANALYSIS OF ERRORS AND CONCLUSIONS

There are two related phenomena responsible for errors in the $2C$ energy levels. The first obvious source is error in evaluation of the integrals. If overlap between the potential function on one site with wave functions on two other sites is small enough, $3C$ contributions should be negligible compared to contributions in which all three functions are on one or two sites. The amount of overlap is, in turn, determined by the range of the three functions and the lattice constant. For the LiF model potential used here, the range was a few lattice constants; but for silicon it was more. The product αa was about 11 for silicon and 16 for the LiF model potential. On the other hand, the wave-function ranges could be quite large. Orbital exponents in Tables II and IV vary from rather large to rather small. For the long-ranged orbitals, the sum over potential sites in the integral converged to eight significant figures only after more than a thousand atomic potential sites had been summed, despite the fact that potential functions were short ranged. Integrals of this type had the largest contribution from $3C$ terms, not the $2C$ terms, so that the $2C$ approximation sometimes produced not only the wrong magnitude for the integral, but even the wrong sign.

This behavior was not observed when one of the wave functions was localized (e.g., Li 1*s* or F 1*s* in Tables I and III): then the 2*C* integral approximation was much better. If both wave functions were localized, even the 2*C* integral was negligible. Examination of many integrals for this calculation (where it should be remembered that the range of the model potential functions was of the order of one lattice constant) yielded the following error criterion:

$$|E(3C)-E(2C)|/|E(3C)|<0.1 \quad \text{for } \alpha_i a>20. \qquad (4)$$

For $\alpha_i a \gg 20$ the accuracy of this approximation improved rapidly. For potentials of shorter range, this criterion could be relaxed, but for longer-ranged potentials it would be difficult to satisfy this criterion for any of the α_i. In these cases neglect of any multicentered integrals must be done with great care to ensure physically meaningful results for the approximation.[12]

The other source of error in the energy levels concerns the type of orbitals employed. While small errors in valence-type and core-type orbital integrals produced small errors in the core and valence eigenvalues, small errors in the conductionlike orbitals were greatly magnified by the band calculation, as discussed in the previous section. If orbital exponents in the Gaussian basis set were too small, the overlap matrix had eigenvalues which were extremely small, sometimes causing numerical instabilities. In the limit that two Bloch functions are linearly dependent, one of the corresponding overlap eigenvalues is exactly zero, so the magnitude of the smallest overlap eigenvalue is a measure of a near linear dependence. For $\alpha_i a < 2$ this behavior was clearly demonstrated here. For α_i all distinct, and if all computations were carried out to sufficient accuracy, there should have been no problems. But with the finite precision of a digital computer, or with approximations to some of the integrals, this near linear dependence caused catastrophic effects, as shown in Table VI.

For LiF, the smallest overlap eigenvalue for the 34×34 matrix at the points Γ and X were 0.000 579 and 0.000 013, showing a strong *k* dependence. The spurious core levels in Table VI were strongly related to these eigenvalues and the associated basis functions. To examine this relationship more closely, the Bloch functions composed of Gaussians with the smallest orbital exponents were dropped from the basis set for each symmetry type, leaving a basis set of 26 Bloch functions. The lowest energies for this set are given in Table VI, labeled 2*C* (26). The lowest overlap eigenvalues for this matrix (26×26) were larger, 0.003 60 and 0.003 65 at Γ and X, and spurious core-energy eigenvalues disappeared. Also, the strong *k* dependence of the overlap eigenvalues was removed. It should be noted that significant differences exist between the 2*C* (26) and 3*C* (34) energy levels: 0.5 eV in the top valence band, and more than 1.4 Ry in the lowest conduction band at Γ. With the smaller basis set, semiquantitative valence-band structures may be obtained, but the absence of longer-ranged basis functions precludes even qualitative description of the conduction bands with the 2*C* approximation. This is also true for the 3*C* (26) eigenvalues. These agree with the 2*C* (26) eigenvalues to within 0.000 8 Ry in the valence bands and 0.009 Ry in the conduction bands, so it is not the two-center ap-

TABLE VI. Energy levels of the LiF model potential at three symmetry points. Energies are in Ry. The row labeled 3*C* (34) gives energies computed exactly with the expanded basis set (34×34 matrix). The row labeled 2*C* (34) gives the 2*C* approximation with the same set, while the row labeled 2*C* (26) gives the two-center results for a 26×26 matrix obtained by deleting the lowest orbital exponent from the set for each type wave function in Table II. Energy values in parentheses are out of order energetically, or correspond to conduction bands which have collapsed through the core.

	Γ_{15}(Li *p*)	Γ_1(Li *s*)	Γ_{15}(F 2*p*)	Γ_1(F 2*s*)	Γ_1(Li 1*s*)	Γ_{15}(Cond.)	Γ_1(F 1*s*)	Γ_{15}(Cond.)
3*C*(34)	2.020	0.813	0.183	−1.189	−1.584	···	−50.310	···
2*C*(34)	2.102	0.924	0.187	−1.186	−1.578	(−13.449)	−50.310	(−125.681)
2*C*(26)	2.067	(2.242)	0.183	−1.145	−1.550	···	−50.310	···
	Δ_1(*s p*)	Δ_5(F 2*p*)	Δ_1(F 2*p*)	Δ_1(F 2*s*)	Δ_1(Li 1*s*)	Δ_1(Cond.)	Δ_5(Cond.)	Γ_1(F 1*s*)
3*C*(34)	0.963	0.140	0.066	−1.203	−1.544	···	···	−50.310
2*C*(34)	1.083	0.117	0.075	−1.192	−1.535	(−5.261)	(−26.766)	−50.315
2*C*(26)	1.602	0.149	0.112	−1.164	−1.526	···	···	−50.310
	X_4'(*p*)	X_5'(F 2*p*)	X_4'(F 2*p*)	X_1(F 2*s*)	X_1(Li 1*s*)	X_1(F 1*s*)	X_5'(Cond.)	X_4'(Cond.)
3*C*(34)	1.185	0.098	−0.083	−1.197	−1.509	−50.310	···	···
2*C*(34)	(1.242)	0.091	−0.065	−1.199	−1.511	−50.310	(−137.06)	(−6592.3)
2*C*(26)	1.572	0.111	−0.016	−1.153	−1.502	−50.310	···	···

proximation causing the largest errors here, but an inadequate basis set.

In the silicon calculations the basis sets were not as large as the LiF expanded set. None of the long-ranged silicon orbitals were given complete variational freedom, and it is expected that *d*-symmetry orbitals, which were not included in either case, would be more important in the silicon conduction bands. For these reasons, the silicon model potential band structures probably are not as accurate as the LiF ones. This may account for the failure to obtain the exact band gap by variation of the parameter Z in the model potential.[17] The extreme sensitivity of the silicon overlap eigenvalues to errors in the overlap integrals or matrix elements may be traced to the form of the overlap matrix and the use of extended Gaussian orbitals. In construction of the overlap matrix, bonding and antibonding combinations of orbitals on each of the two silicon atoms in the primitive cell are used. The orbitals in each of the atoms are the same, and for small α_i overlap eigenvalues are especially troublesome, as clearly indicated in the paper by Ciraci.[26]

When the overlap problem was eliminated for silicon, the 2*C* approximation appeared to be slightly better than it was in LiF, as indicated by the integrals of Table V and the energy bands of Fig. 3. This last fact is primarily a consequence of the modified basis set for silicon. The range of the most diffuse orbital for silicon was only half the range of the most diffuse orbital in LiF (measured in lattice constants). The improved 2*C* approximation for the modified atomic silicon basis should be expected from the results of eliminating basis functions in LiF. This was discussed in the paragraphs above, where very close agreement between 3*C* and 2*C* energy bands was obtained for shorter-ranged orbitals. (It should be remembered that neither of these agreed with the larger more complete, basis set for LiF.) Although the 2*C* approximation appears less radical in silicon, there are still important qualitative differences in the band structures.

Considering the results for both LiF and silicon, one is faced with a dilemma: to avoid exaggerated errors which can occur with long-ranged functions it is necessary to eliminate basis functions which are important to the description of the lower conduction band. There is no way to obtain even a qualitative description of conduction bands using the two-center approximation to the model potentials for LiF and silicon.

These conclusions hold for the basis sets described in this paper and for the model potentials constructed here. If the self-consistent potential of a real crystal were employed, the approximation would be worse. If the basis is modified to exclude long-ranged orbitals, the approximation is improved. Depending upon the crystal, this may or may not be possible. In these studies it is found not to be possible if quantitative valence and conduction bands are required: the long-ranged orbitals are needed in the Gaussian basis. Use of other types of basis functions, truncation of orbitals at the Wigner-Seitz cell boundaries, or replacing long-ranged orbitals with off-atomic-center short-ranged orbitals are methods which might be employed to eliminate these otherwise important multicentered integrals. The local orbital procedure of Kunz,[27] which uses a localizing operator in the Hartree-Fock equations, is another possibility which could be employed in appropriate crystal systems.

For the usual LCAO procedures, and for crystal systems which must be described by long-ranged orbitals, the two-center approximation is not likely to yield even qualitative results. If the orbital range is too great, it is not advisable to use any approximations to the multicentered integrals because of the extreme numerical sensitivity which can greatly exaggerate small errors.

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