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Self-consistent calculation of the electronic structure of silicon and germanium using the intersecting-spheres model*

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The intersecting-spheres model is a general approach to the calculation of the electronic structure of molecules and solids which adopts a one-electron local potential, an energy-independent trial function, and a cellular partition of space. It has been used with satisfactory results to determine the total energy and the ionization spectra of simple molecules. We report now results concerning the self-consistent band structure of Si and Ge, and we show that these results compare favorably with band structures calculated by the orthogonalized-plane-wave method, under the same assumption for the exchange and correlation potential.

I. INTRODUCTION

When we consider the various existing methods for the calculation of the electronic structure of solids, limiting our attention to the approaches of nonempirical character which make use of a local self-consistent potential, we can observe that the methods which have met with more success in the past either contain a systematic approximation of the self-consistent potential, like the APW[1] and the KKR[2] methods, or introduce a special treatment of the core region, like the OPW method[3]; these approximations in some way limit the applicability of the above-mentioned approaches to specific crystals. In particular, methods which use a muffin-tin potential cannot work well for covalent systems and their generalization to include non-muffin-tin terms, although possible, is rather difficult to perform,[4] while the OPW method fails to converge when the valence and conduction levels which are investigated have no counterpart in the atomic core.[5]

Among the other approaches, the cellular method,[6] which allows a more accurate description of the one-electron potential than the original APW and KKR methods, suffers from problems of convergence, since it requires a large number of matching points on the surface of the cells and consequently needs large l expansions of the trial function.[7]

The LCAO method, finally, can be considered as the most general approach, since in principle it does not introduce systematic approximations to the potential, nor requires separate treatment for the core levels; its generality has been underestimated in the past, when it was erroneously considered useful only in the case of tight binding; this is not true[8,9]; however, since more or less slowly decaying functions centered on different nuclei usually overlap at a distance of various neighbors, the computational effort implied by the evaluation of two and three center integrals can become unwieldy even with efficient Gaussian-based programs if a variational calculation with a very flexible trial function is desired.[10]

It is evident that a method with the quick convergence of the direct lattice sums typical of the cellular method and with the general form of the self-consistent potential typical of the LCAO approach is desirable; such a cellular LCAO method is in our view provided by the intersecting-spheres model. This approach has been satisfactorily tested in the case of simple molecules[11] and a preliminary computation of the band structure of diamond[12] has given encouraging results.

In the first part of this article we give a description of the intersecting-spheres model for solids; in the second part we report on self-consistent calculations of the electronic structure of silicon and germanium and compare the resulting band structures with those obtained by a long-established method like OPW under the same assumptions for the exchange and correlations potential.

II. INTERSECTING-SPHERES MODEL

The formulation of the intersecting-spheres model for solids closely parallels that given for molecules.[11] Therefore, we report here only the main points of the model and make reference to previous works whenever useful. The basic idea for the intersecting-spheres model is the introduction of an energy-independent trial function, constituted by atomiclike functions centered at the various nuclei and mutually overlapping as little as possible, while still remaining continuous and with continuous gradient. To build up such a basis set, a partition of the volume occupied by the solid into cells closely related to that occurring in the cellular method is very useful. These cells are obtained in the following way: we surround each atom in the unit cell of the direct lattice (one, two, or three dimensional) with a sphere of given radius. For a three-dimensional lattice the radii are chosen in such a way that the whole space is filled by overlapping spheres. At each intersection between spheres we insert a cylinder of given height which connects the surfaces of the intersecting spheres. From these geometrical objects a partition into nonoverlapping cells can be derived in a way which is illustrated in Fig. 1 for a simple one-dimensional structure. The cells derived from the atomic spheres are called atomic cells; those derived from the cylinders are called spline regions for a reason explained in the following. In the case of a three-dimensional structure the atomic cells are polyhedra, while the spline regions can be partitioned into prisms associated with couples of neighboring atoms. Each atomic cell is coated by spline regions which join the atom with its neighbors.

For a given wave vector $\vec{k}$ we assume that the trial function is a linear combination of Bloch sums defined as

$$\Psi_{inlm,\vec{k}} = \frac{1}{\sqrt{N}} \sum_{a} e^{i\vec{k}\cdot\vec{R}_a} \Phi_{inlm}(\vec{r} - \vec{R}_a) \; . \tag{1}$$

In Eq. (1) N is the number of unit cells in the lattice and a runs over all direct lattice translations, while Φ_{inlm} is a localized function centered at the position of the ith atom in the unit cell with translation vector $\vec{R}_a$. In the intersecting-spheres model Φ_{inlm} is chosen in the following way: within the atomic cell i, it is the solution of the self-consistent atomic problem corresponding to quantum numbers n, l, m and with the outer boundary condition not at infinity, as it occurs for a free atom, but at the radius of the atomic sphere; elsewhere Φ_{inlm} is zero, except in the spline regions attached to cell i, where the atomic function is continued and sent to zero at the outer surface of each region. This behavior can be obtained through the use of spline functions. In fact the atomic solutions

$$\varphi_{inlm}(r_i, \vartheta_i, \varphi_i) = \mathcal{R}_{inl}(r_i)\, Y_{lm}(\vartheta_i, \varphi_i) \tag{2}$$

can be expressed with respect to a rotated reference frame with the polar axis joining two atomic centers as

$$D(\alpha,\beta,\gamma)\varphi_{inlm}(r_i,\vartheta_i,\varphi_i) = \mathcal{R}_{inl}(r_i) \sum_{m'=-l}^{l} \mathfrak{D}^{l}_{m'm}(\alpha,\beta,\gamma) Y_{lm'}(\vartheta_i', \varphi_i'), \tag{3}$$

where α, β, γ are the Euler angles which define the rotation of the reference frame.[13] The single terms in the sum of Eq. (3) can be matched with continuity of the function and of its gradient at the plane boundary between the atomic cell i and the spline region by the function

$$\chi_{m'}(\zeta, \rho, \varphi) = e^{im'\varphi} \sum_{p=1}^{4} a_p(\rho) \zeta^{p-1} \; . \tag{4}$$

Cylindrical coordinates are used; the exponential ensures matching along φ, and the four coefficients a_p ensure that the function and its gradient are continuous at one end of the spline region and vanish at the other end. We stress the fact that the atomic solution is retained only within the atomic cell and that the spline functions are retained only within the spline regions (prisms) and not over the full cylinders from which the spline regions are derived.

Using the above defined Φ_{inlm} functions in the Bloch sums a secular equation can be derived for the problem of the electronic structure of solids in exactly the same way as for a conventional LCAO treatment; the only pleasant difference is that functions Φ_{inlm} centered on different atomic sites overlap only if two atomic cells are in contact with the same spline region; therefore the lattice sums involved in the evaluation of the various matrix elements are as short as possible.

The mathematical techniques for the computation of the individual contributions to the matrix elements between Bloch sums are exactly the same as those used for molecules and need not to be reported here; the interested reader is referred to Ref. 11, where a detailed account of the formalism is given. We only recall some relevant points: the mathematical representation of the self-consistent potential and of the charge density adopted by the intersecting-spheres model is an expansion in spherical harmonics around the various atomic centers; the self-consistent Hamil-

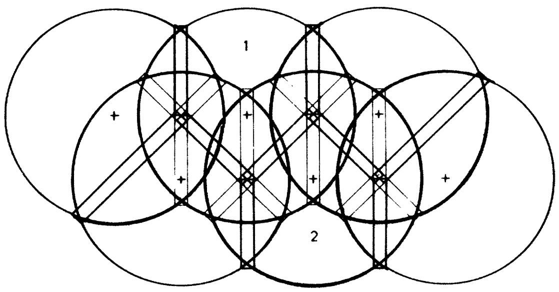

FIG. 1. Cellular partition for a linear chain according to the intersecting-spheres model. Heavy lines define the atomic cells and the spline regions; the light lines show the atomic spheres and the cylinders used to derive the partition. 1 and 2 denote the atomic cells within the unit cell of the infinite chain.

tonian is broken into a fixed term, containing the kinetic operator and nonoverlapping atomic potentials (for which the Φ_{inlm} functions are solutions within the atomic cells) and a self-consistent correction which includes all the modifications to the starting potential due to the self-consistent charge distribution of the crystal. The matrix elements contain contributions arising from the atomic cells and contributions coming from the spline regions, which are evaluated separately. Contributions deriving from the fixed term of the Hamiltonian are evaluated exactly; for what concerns the self-consistent corrections the following approximation is used: the self-consistent charge density is defined by the proper sum of products of atomic functions not only within the atomic cells, where such a representation is exact, but also within the spline regions up to the planes of intersection of each atomic sphere with the neighboring spheres, as if the spline regions had actually zero thickness; the same approximation is used for calculating the matrix elements of the self-consistent correction to the potential. This approximation, which is exact for spline regions of zero thickness, is not used for the matrix elements of the fixed part of the potential, nor for the overlap matrix elements, in order to obtain a good accuracy even when the spline regions are not thin.

In the intersecting-spheres model integrals like

$$\int Y^*_{lm} Y_{l'm'} \sin\vartheta_i \, d\vartheta_i \, d\varphi_i \tag{5}$$

are not in general extended to 4π, but to the solid angle $\Omega(r_i)$ which is subtended by the atomic cell i at the radius r_i; therefore we first calculate the spherical harmonics expansion of a θ function equal to 1 in the atomic cell and zero elsewhere[11,14]

$$\vartheta(\vec{r}_i) = \sum_{lm} \vartheta_{lm}(r_i) Y_{lm}(\vartheta_i, \varphi_i) \; . \tag{6}$$

Consequently

$$\int_{\Omega(r_i)} Y^*_{lm} Y_{l'm'} \sin\vartheta_i \, d\vartheta_i \, d\varphi_i = \sum_{l''m''} \vartheta_{l''m''}(r_i) \int_{4\pi} Y^*_{lm} Y_{l''m''} Y_{l'm'} \times \sin\vartheta_i \, d\vartheta_i \, d\varphi_i \; . \tag{7}$$

In Eq. (7) the well-known Gaunt integrals appear.

For crystals the self-consistent charge density is determined through integration over the Brillouin zone; in the case of the intersecting-spheres model symmetry arguments and the rotation properties of spherical harmonics[15] easily allow us to limit the integration to the irreducible segment of the Brillouin zone.

III. COMPUTATIONS

In order to provide evidence concerning the accuracy of the intersecting-spheres model for solids we have performed self-consistent band-structure calculations for silicon and germanium. We have done the calculations in a self-consistent way to obtain informations not only about the convergence properties of the method with respect to the basis set, but also to verify the accuracy of the whole model and to establish its practical usefulness for computations of physical interest.

For silicon and germanium the direct lattice is face centered cubic with two atoms per unit cell, located at the origin and at $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The atomic cells are truncated tetrahedra with four hexagonal faces toward the nearest neighbors and 12 triangular faces toward the next-nearest neighbors.[7] Both the potential and the charge density can be expanded in tetrahedral harmonics around each atomic center.[14] We have truncated these expansions in spherical harmonics at $l = 4$ after having verified that on going from $l = 3$ to $l = 4$ only changes of at most 0.1 eV occurred for the valence and lower conduction levels. The θ-function expansion of Eqs. (6) and (7) was consequently truncated at $l = 8$.

For each atomic center we have assumed a basis set constituted by the atomiclike functions needed by a minimal basis set plus two s, two p, and two d extra radial functions (the two lowest virtual orbitals for each l). In this way the basis set was constituted by 54 and 72 functions for silicon and germanium, respectively. We have used the radii of the spheres and the thickness of the spline regions as nonlinear variational parameters to obtain the lowest possible eigenvalues for the valence and lower conduction levels at the first cycle of the iteration process. We have noted that the dependence of these levels on the nonlinear parameters is not critical for the above-mentioned basis sets, being typically less than 0.2 eV for a 0.5 a.u. variation of the radius of the spheres from the optimal value, and less than 0.3 eV for a 0.4 a.u. variation of the thickness of the splines from the optimum thickness.

For what concerns the determination of the charge density, we have substituted the integration over the irreducible segment of the Brillouin zone by a weighted sum over a six point cubic mesh; points and weights were chosen as given in Ref. 16, where it is shown that such a choice provides satisfactory convergence for the self-consistent eigenvalues. We have separately verified that halving the mesh size did not introduce significant changes to the band structure.

We have found satisfactory convergence for the direct lattice sums needed to evaluate the self-consistent potential when six shells of neighbors were considered for each atom. This quick convergence is motivated by the fact that when the potential is expanded in spherical harmonics around an atomic center in the diamond lattice the dipole and quadrupole terms of the expansion are zero for symmetry reasons.[14] Thus, when performing the reexpansion of the potential of a given atomic cell with respect to another atomic center,[11] beyond the distance at which the atomic spheres no longer intersect only octupole and higher terms are to be reexpanded and convergence is very fast. Such a behavior is further enhanced by the very shape of the atomic cells, which extend farther from the nuclei in the nonbonding directions. In this way the tetrahedral distortion of the charge density due to the covalent bond is to some extent compensated by the shape of the cell, thus giving a small value to the octupole potential term.

For what concerns the accuracy of the approximation to the charge density in the spline regions, we have verified that the above-mentioned substitution of the spline functions with the atomiclike orbitals leads to errors for the total charge of the unit cell not larger than 0.02 electronic charges in the range of spline thicknesses explored in the computations. The charge densities were consequently renormalized to preserve the neutrality of the unit cell.

In Fig. 2 the self-consistent band structure of silicon along the Λ and Δ symmetry lines is reported. Slater exchange approximation[17] and the experimental lattice constant $a = 5.431$ Å were used. The variationally determined values for the radius of the atomic spheres and for the thickness of the spline regions resulted to be 5.0 and 1.2 a.u., respectively. In Table I we report the energy positions of the valence and conduction levels at the six high-symmetry points Γ, X, L, W, $\Delta(\frac{1}{2},0,0)$, and $\Sigma(\frac{1}{2},\frac{1}{2},0)$ of the irreducible segment of the Brillouin zone, together with the values obtained with a self-consistent OPW calculation[16] using about 259 plane waves. The $\Gamma_{25'}$ level was assumed as our zero since the values reported in Ref. 16 are given in such a way. The agreement between the two computations is quite satisfactory for the valence bands; the average disagreement between the valence levels at the six points is in fact 0.17 eV. We believe this to be a remarkable result, since such an agreement has been obtained between self-consistent calculations using a completely different approach. The disagreement concerning the conduction levels probably indicates that the convergence properties of the finite basis set adopted by us are significantly better for the occupied than for the empty levels.

In Fig. 3 we report the self-consistent band structure of germanium along the Λ and Δ lines. Slater exchange[17] and the experimental lattice

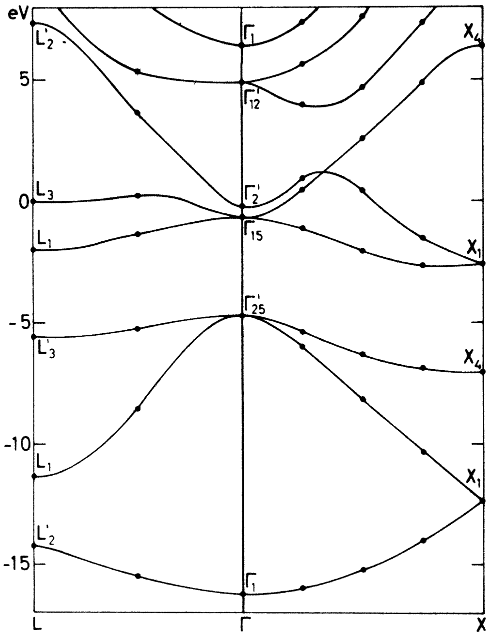

FIG. 2. Self-consistent band structure of Si along the Λ and Δ symmetry lines. Energies are in eV. Slater exchange approximation was used.

TABLE I. Self-consistent energy eigenvalues for Si at the high-symmetry points Γ, X, L, W, $\Delta(\frac{1}{2},0,0)$, and $\Sigma(\frac{1}{2},\frac{1}{2},0)$ according to the OPW method (Ref. 16) and to the intersecting-spheres model (ISM). The same zone sampling and exchange approximation were used in the two calculations. Energies are in eV.

Level	OPW	ISM	Level	OPW	ISM
Γ_{15c}	2.79	4.07	W_{2c}	10.80	11.75
$\Gamma_{2'c}$	2.75	4.50	W_{1c}	5.15	6.93
$\Gamma_{25'v}$	0.0	0.0	W_{2c}	4.83	6.24
Γ_{1v}	−11.74	−11.49	W_{2v}	−3.57	−3.39
X_{4c}	9.79	11.14	W_{1v}	−7.61	−7.49
X_{1c}	1.28	2.11	$W_{2c}-W_{2v}$	8.40	9.63
X_{4v}	−2.72	−2.34	Δ_{5c}	5.89	7.30
X_{1v}	−7.75	−7.64	$\Delta_{2'c}$	3.62	5.13
$X_{1c}-X_{4v}$	4.00	4.45	Δ_{1c}	1.55	2.68
L_{3c}	3.83	4.75	Δ_{5v}	−1.78	−1.59
L_{1c}	1.60	2.74	$\Delta_{2'v}$	−3.58	−3.46
$L_{3'v}$	−1.18	−0.82	Δ_{1v}	−10.69	−10.51
L_{1v}	−6.75	−6.64	$\Delta_{1c}-\Delta_{5v}$	3.33	4.27
$L_{2'v}$	−9.53	−9.54	Σ_{1c}	5.54	6.59
$L_{3c}-L_{3'v}$	5.01	5.57	Σ_{4c}	5.02	6.41
$L_{1c}-L_{3'v}$	2.78	3.56	Σ_{3c}	2.88	3.88
			Σ_{2v}	−1.27	−1.00
			Σ_{1v}	−3.45	−3.23
			Σ_{3v}	−5.40	−5.41
			Σ_{1v}	−9.74	−9.67
			$\Sigma_{3c}-\Sigma_{2v}$	4.15	4.88

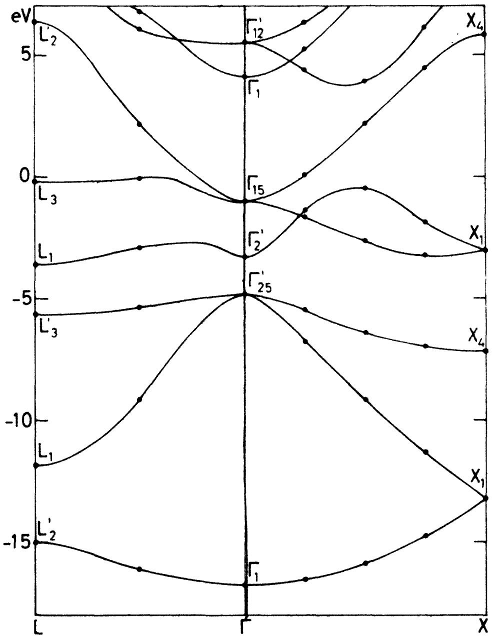

FIG. 3. Self-consistent band structure of Ge along the Λ and Δ symmetry lines. Energies are in eV. Slater exchange approximation was used.

TABLE II. Self-consistent energy eigenvalues for Ge at the high-symmetry points Γ, X, L, W, $\Delta(\frac{1}{2},0,0)$, and $\Sigma(\frac{1}{2},\frac{1}{2},0)$ according to the OPW method (Ref. 18) and to the intersecting-spheres model. The same zone sampling and exchange approximation were used in the two calculations. Energies are in eV.

Level	OPW	ISM	Level	OPW	ISM
Γ_{15c}	3.34	3.80	W_{1c}	5.60	6.30
$\Gamma_{2'c}$	1.20	1.52	W_{2c}	5.22	6.04
$\Gamma_{25'v}$	0	0	W_{2v}	–3.18	–3.31
Γ_{1v}	–11.88	–11.97	W_{1v}	–8.10	–8.29
X_{4c}	10.04	10.67	$W_{2c}-W_{2v}$	8.40	9.35
X_{1c}	1.97	1.80	$\Delta_{2'c}$	3.75	4.35
X_{4v}	–2.56	–2.32	Δ_{1c}	2.12	2.19
X_{1v}	–8.18	–8.39	Δ_{5v}	–1.64	–1.58
$X_{1c}-X_{4v}$	4.53	4.12	$\Delta_{2'v}$	–4.16	–4.35
L_{3c}	4.60	4.67	Δ_{1v}	–10.92	–11.07
L_{1c}	1.30	1.23	$\Delta_{1c}-\Delta_{5v}$	3.76	3.77
$L_{3'v}$	–1.16	–0.86	Σ_{4c}	5.52	5.89
L_{1v}	–6.78	–7.04	Σ_{3c}	3.04	3.01
$L_{2'v}$	–9.93	–10.21	Σ_{2v}	–1.23	–1.04
$L_{3c}-L_{3'v}$	5.76	5.53	Σ_{1v}	–3.12	–3.23
$L_{1c}-L_{3'v}$	2.46	2.09	Σ_{3v}	–5.84	–6.14
			Σ_{1v}	–10.06	–10.30
			$\Sigma_{3c}-\Sigma_{2v}$	4.27	4.05

constant $a = 5.6575$ Å were used. The variationally determined values for the radius of the spheres and for the thickness of the spline regions were 5.5 and 1.2 a.u. respectively. Again a straightforward comparison with a self-consistent OPW calculation[18] can be made through the energy values reported in Table II. Also for germanium the agreement is rather impressive, particularly for the valence levels, for which the average disagreement is 0.20 eV. We note that for germanium the agreement between the conduction levels is more stringent than for silicon.

The only point of sharp disagreement between the two calculations concerns the absolute position of the levels, both for Si and Ge. In Figs. 2 and 3 we report the band structure referred to an energy scale which assumes zero energy for charges at infinite separation. In Figs. 3 and 5 of Ref. 18 the OPW results are reported; if these results are to be referred to the energy scale adopted by us, we find an overall upward shift of the OPW band structure with respect to our results of as much as 9 eV for both Si and Ge. The change in the constant potential needed to bring our eigenvalues in agreement with those reported in Ref. 18 does not affect the kinetic energy, but it would change the total energy per atom by as much as about 9 and 21 Ry for Si and Ge, respectively. We have performed preliminary calculations of the total energy and of the kinetic energy of Si and Ge, since our all-electron treatment allows such a computation to be done in a straightforward manner, and we find virial ratios which are wrong by a few parts times 10^{-5}, while with the above-mentioned shift they are wrong by a few parts times 10^{-3}. The question may be trivial, but perhaps it deserves some more attention.

IV. CONCLUSIONS AND PERSPECTIVES

We hope to have provided with the calculations of the band structure of silicon and germanium a rather interesting evidence for the capability of the intersecting-spheres model to deal with crystalline structures. The convergence properties of the basis set are satisfactory and can be summarized as follows: the use of spline regions allows to obtain good convergence without requiring the large expansions of the trial function in spherical harmonics needed by the cellular method; when compared with a LCAO approach with Slater orbitals[19] the intersecting-spheres model gives slower convergence with respect to the principal quantum number, since more flexibility is needed if the trial functions are not allowed to overlap to a large extent; this slower convergence is however more than compensated by the enormous saving obtained by the minimization of the number of two center integrals and by the complete elimination of the three center integrals.

Since the intersecting-spheres model allows an all-electron treatment, it is well suited for the study of the cohesive energy, lattice constant, and compressibility of solids; this study is under way and preliminary results are encouraging although the numerical accuracy of the present computer code is to be improved to deal with the total energy of medium size atoms like Si and Ge. Being a LCAO approach, the intersecting-spheres model can be applied with no change to one- and two dimensional structures; we hope to provide soon evidence for its usefulness in calculating the electronic structure of polymers.

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