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Efficient approach to the *ab initio* Hartree-Fock problem of solids, with application to diamond and silicon

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The nonlocal exchange (Hartree-Fock approximation), as a crucial quantity in the correct description of the many-body problem, is gaining increasing attention in the field of electronic structures of solids. Because of the nonlocality, the numerical solution of the Hartree-Fock equation is very cumbersome and *ab initio* Hartree-Fock methods for solids are just now being developed. We suggest an efficient approximation scheme which yields the Fock matrix and the total energy as well as the band structure. Numerical results for diamond and silicon are presented.

I. INTRODUCTION

Until now nearly all calculations in the field of electronic structures of solids were performed within the framework of the local-density approximation (LDA). The latter is a "local" approximation to the density-functional theory (DFT) which provides, at least in principle, an exact description of ground-state properties of electronic systems.[1,2] For a large number of systems, in particular metals, it leads to good results. This is one reason for the increasing success of the LDA, another one is its computational simplicity.

The computation of band structures (excitation energies) goes beyond DFT.[3,4] Despite this, in actual LDA calculations the eigenvalues of the one-particle Schrödinger-type equations are often interpreted as excitation energies. For large-gap semiconductors and insulators this leads to considerable errors (energy gaps are found to be too small typically by 50%). Therefore, other computational schemes are highly desirable.

Ab initio methods as they are used, e.g., in quantum chemistry, have the advantage of allowing for controlled approximations as far as a treatment of electron correlations is concerned. They have the disadvantage, though, that they require a Hartree-Fock calculation as a starting point. In fact, it has recently been shown that it is the Hartree-Fock part, and here in particular the nonlocal exchange, which is the bottleneck even in a calculation which includes electron correlations.[5] On the other hand, the importance of nonlocal features of the exchange in the field of semiconductors and insulators is becoming more and more apparent because they influence strongly, in particular, the energy gap in these systems (see, e.g., Ref. 6). Therefore it is very important to improve on those computational schemes which are based on the Hartree-Fock approximation (HFA).

So far the HFA has not been used widely for solids. Due to the nonlocality of the exchange potential, the solution of the Hartree-Fock equation is very cumbersome, and the development of *ab initio* Hartree-Fock methods for solids is at the very beginning. It is the aim of this paper to report on some progress we have made.

We propose here an efficient approximation scheme that is based on the similarity of the one-particle orbitals in the LDA and the HFA. This point will be discussed in Sec. II. Section III is devoted to the description of a new procedure yielding the required Hartree-Fock quantities and the underlying formalism. Numerical results for diamond and silicon are contained in Sec. IV, while a summary is given in Sec. V.

II. SIGNIFICANCE OF LDA WAVE FUNCTIONS

It is well known that the ground-state density is well described in both the LDA and in the HFA, leading to a conformity of the electronic densities within both approximations. It is reasonable to assume that there should also be an agreement in the wave functions of both one-particle equations. This was investigated for the first time by Slater,[7] who performed numerical calculations for atoms from helium to argon. He calculated the HFA-partial energies (kinetic, Hartree energy, . . .) with $X\alpha$ wave functions.

The agreement, even in all partial energies, is due to the virial theorem which is fulfilled in the LDA as well as in the HFA. The agreement with *ab initio* HF results was best for $\alpha \approx \frac{3}{4}$, which is close to the Kohn-Sham value of $\alpha = \frac{2}{3}$ used in the LDA. The relative errors in the partial energies for the investigated systems were less than 10^{-4}. This shows that at least for those atoms the wave functions of the LDA and the HFA, respectively, do agree very well.

Now let us turn to an extremely different case, i.e., that of the homogeneous electron gas. Here the wave functions do agree exactly (plane waves) in the two approximations under consideration, but the eigenvalues show very different behavior.

While in the LDA the exchange potential is only a constant [due to the constant electronic density $\rho(x)=n$], leading to

$$\begin{aligned} &\varepsilon^{\mathrm{LDA}}(k)=k^2/2m-V_x^{\mathrm{LDA}}\ , \\ &V_x^{\mathrm{LDA}}=(3n/\pi)^{1/3}\ , \end{aligned} \tag{1}$$

the HFA yields a strongly k-dependent exchange part of the self-energy. The HFA energies read

$$\begin{aligned} &\varepsilon^{\mathrm{HFA}}(k)=k^2/2m-V_x^{\mathrm{LDA}}F(k/k_F)\ , \\ &F(x)=1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\ , \\ &F(0)=2\ ,\ \ F(1)=1\ ,\ \ F(\infty)=0\ . \end{aligned} \tag{2}$$

We see a strong discrepancy between both dispersion relations, although the wave functions are identically the same. This means that the local approximation of the nonlocal exchange potential has strong influence on the one-particle energies but none on the wave functions.

We have seen that in two limiting cases, i.e., the atomic limit and the homogeneous electron gas, the wave functions of the LDA agree very well with those of the HFA. In order to see whether this holds true also in the intermediate regime, we performed test calculations for diamond and silicon. For this purpose we took different sets of test functions $\{\phi_i\}$ and determined the Hartree-Fock energies

$$\begin{aligned} &E=\frac{\int\psi^*(\mathbf{x})H\psi(\mathbf{x})d^{3N}\mathbf{x}}{\int\psi^*(\mathbf{x})\psi(\mathbf{x})d^{3N}\mathbf{x}}\ , \\ &\psi=\det\{\phi_i(\mathbf{x})\}\ . \end{aligned} \tag{3}$$

The exact Hartree-Fock wave functions should yield the lowest energy among all Slater determinantal test functions.

The trial functions we used were, on the one hand, the results of an approximate Hartree-Fock calculation[8,9] using the localization potential of Gilbert and Adams (Ref. 10). On the other hand, we applied wave functions of a LDA calculation performed within a linear combination of atomic orbitals (LCAO) scheme which was developed by Appelbaum and Hamann. A detailed description of the method can be found in Ref. 11.

In both cases the same basis sets have been used which will be discussed in Sec. IV. The resulting total energies are given in Table I. For diamond an all-electron calculation has been performed, whereas for silicon the neon core has been replaced by a pseudopotential. Because of the variational principle the LDA wave functions are obviously better HF wave functions than those of the approximate HFA calculations.

TABLE I. Total Hartree-Fock ground-state energy (atomic units) contained with two different sets of trial functions (HF̃A and LDA) as explained in the text.

	HF̃A	LDA
Diamond	−75.595	−75.656
Silicon	−7.542	−7.994

Recently the LDA has been extended by Langreth and Mehl.[12] Their theory is computationally of comparable simplicity as the LDA but is superior to it. Electronic densities seem to be better than HF densities as calculations on atoms demonstrate for which not only HF but also configuration-interaction calculations are available. Therefore, it would be very interesting to use wave functions obtained from their theory as input for a HF energy calculation and to compare the energy with that of a LDA wave function. We leave this problem to a future investigation.

In summary we can say that there is a good agreement between the wave functions of the LDA and those of the HFA for atoms, homogeneous systems and for nonpolar solids. Whether this also holds true for solids with more complex unit cells remains to be seen.

III. FORMALISM

In the preceding section we have seen that the one-particle wave functions of the LDA and the HFA are in very good agreement. Therefore, one can use the efficient algorithms of the LDA to determine approximate HF wave functions. Once the wave functions are known to a good approximation, the nonlocal exchange potential has to be calculated only once. The nonlocal exchange potential together with the kinetic and the Hartree part of the Hamiltonian, which is already known from LDA calculation, form the one-particle Hamiltonian for which the eigenvalue problem has to be solved. Thus one can avoid the repeated calculation of the nonlocal exchange potential that dominates the computational effort. The expense of solving the Hartree-Fock problem is therefore reduced by the factor of ~ 100, which is the number of iterations normally needed for self-consistent Hartree-Fock calculations.

The whole problem has been formulated in second quantization. For a set of basis functions $\{f_m(\mathbf{x})\}$, the Hartree-Fock Hamiltonian for closed-shell systems is given by

$$H^{\mathrm{HF}}=\sum_{m_1,m_2,\sigma}F_{m_1m_2}a^\dagger_{m_1\sigma}a_{m_2\sigma}+E_{nn}-E_{\mathrm{int}}/2\ , \tag{4}$$

with the Fock matrix

$$F_{m_1m_2}=t_{m_1m_2}+\sum_{m_3,m_4}(V_{m_1m_2m_3m_4}-\tfrac{1}{2}V_{m_1m_4m_3m_2})P_{m_3m_4} \tag{5}$$

and the density matrix

$$P_{m_1m_2}=\sum_{\sigma}\langle\mathrm{HF}\,|\,a^\dagger_{m_1\sigma}a_{m_2\sigma}\,|\,\mathrm{HF}\rangle\ . \tag{6}$$

The hopping matrix t is given by

$$t_{m_1m_2}=\int f^*_{m_1}(\mathbf{x})H_0f_{m_2}(\mathbf{x})d^3x\ , \tag{7}$$

with H_0 being composed of the kinetic part

$$H_{\mathrm{kin}}=-\Delta/2m\ , \tag{8}$$

the lattice part

$$H_{\mathrm{en}} = -Z\sum_{\mathbf{x}_\alpha} |\mathbf{x}-\mathbf{x}_\alpha|^{-1} , \tag{9}$$

(Z is the mass number and $\mathbf{x}_a$ is the vector of the atomic positions), and, in the case of silicon, the term of the pseudopotential H_{ps}, which will be discussed later. The interaction matrix is defined as

$$V_{m_1m_2m_3m_4} = \int\int f^*_{m_1}(\mathbf{x}) f_{m_2}(\mathbf{x}) |\mathbf{x}-\mathbf{x}'|^{-1} \times f^*_{m_3}(\mathbf{x}') f_{m_4}(\mathbf{x}') d^3x\, d^3x' . \tag{10}$$

E_{nn} is the nucleus-nucleus interaction energy:

$$E_{nn} = \frac{Z}{2} \sum_{\mathbf{x}_\alpha,\mathbf{x}_{\alpha'}} |\mathbf{x}_\alpha - \mathbf{x}_\alpha|^{-1} . \tag{11}$$

Finally the energy E_{int} is given by

$$E_{\mathrm{int}} = \sum_{\substack{m_1,m_2\\ m_3,m_4}} (V_{m_1m_2m_3m_3} - \tfrac{1}{2} V_{m_1m_4m_3m_2}) P_{m_1m_2} P_{m_3m_4} . \tag{12}$$

The last term in Eq. (4) has to be subtracted in order to avoid double counting of the electron-electron interaction.

The basis sets we used are minimal Gauss-type orbitals of double-zeta quality. Polarization functions are not included (Refs. 13–16). In a lobe-Gauss representation all basis functions can be written as linear combinations of elementary Gauss functions

$$f_m(\mathbf{x}) = f_{\mu,i}(\mathbf{x}) = \sum_n C_{\mu,n} \left[\frac{2\alpha_{\mu n}}{\pi} \right]^{3/4} \times \exp[-\alpha_{\mu,n}(\mathbf{x}-\mathbf{x}_i-\mathbf{r}_{\mu,n})^2] . \tag{13}$$

μ labels the different orbitals in one unit cell while $\mathbf{x}_i$ denotes the lattice vectors. The great advantage of these basis functions is that all integrals [see Eqs. (7) and (10)] can be expressed in terms of elementary functions, error function, and Bessel functions (Ref. 17) for which very fast algorithms are available. The basis functions are not orthogonal to each other. The corresponding operators $a^{(\dagger)}_{m\sigma}$ therefore fulfill the following relations:

$$\langle 0 | a_{m_1\sigma} a^\dagger_{m_2\sigma} | 0 \rangle \neq S_{m_1m_2} = \int f^*_{m_1}(\mathbf{x}) f_{m_2}(\mathbf{x}) d^3x , \tag{14}$$

but

$$\langle 0 | a_{m_1\sigma} a^\dagger_{m_2\sigma} | 0 \rangle = (S^{-1})_{m_1m_2} \tag{15}$$

and

$$[a_{m\sigma}, a^\dagger_{m\sigma'}] = (S^{-1})_{m_1m_2} \delta_{\sigma\sigma'} , \tag{16}$$

but this does not matter, since the basis functions can easily be orthogonalized by

$$f_{m_1}(\mathbf{x}) = \sum_{m_2} (S^{-1/2})_{m_2m_1} f_{m_2}(\mathbf{x}) . \tag{17}$$

Analogously the transformation for the operators $a^{(\dagger)}_{m\sigma}$ is given by

$$\hat{a}_{m_1\sigma} = \sum_{m_2} (S^{1/2})_{m_1m_2} a_{m_2\sigma} . \tag{18}$$

Therefore,

$$[\hat{a}_{m\sigma}, \hat{a}^\dagger_{m'\sigma'}] = \delta_{mm'} \delta_{\sigma\sigma'} . \tag{19}$$

The Hartree-Fock Hamiltonian expressed in the new orthogonal operators has the form

$$H^{\mathrm{HF}} = \sum_{m_1,m_2} F_{mm} \hat{a}^\dagger_{m_1\sigma} \hat{a}_{m_2\sigma} + E_{\mathrm{nn}} - \tfrac{1}{2} E_{\mathrm{int}} , \tag{20}$$

with

$$F_{m_1m_2} = (S^{-1/2} F S^{-1/2})_{m_1m_2} . \tag{21}$$

The expense for calculating the nonlocal exchange part of the Fock matrix has been reduced by a factor of about 16 by making use of the symmetry of the diamond lattice. Further reduction of computer time has been achieved by dynamical truncations of the infinite sums in Eqs. (5) and (12). Each partial sum has been truncated in such a way that the related error in the total energy is less than 10^{-5}. One therefore can be sure that the results are reliable. For diamond we performed an all-electron calculation, whereas in the case of silicon the neon core has been replaced by a suitable pseudopotential (Ref. 8), with respect to which the basis functions have been optimized.

IV. NUMERICAL RESULTS

A. Cohesive energy

The total energy has been calculated in both cases for the experimental lattice parameters ($a = 5.131\,489$ Å for silicon and $a = 3.370\,045$ Å for diamond). By making use of the atomic HF energies, calculated within the same basis sets, we obtain the values for the cohesive energies listed in Table II. For comparison we also present the results of three other calculations.[18–22]

The results of Mauger and Lannoo[19] have been obtained by a different scheme. They derived the cohesive energy from the energy difference of the vacuum level and the top of the conduction band and interpreted it as cohesive energy, which is not reliable.

The work of Euwema *et al.*[17] gives good insight into the influence of different truncation criteria. According to which criterion was chosen they obtained the different values listed in Table II. There is an uncertainty in their cohesive energy which is related to a correction term the

TABLE II. Cohesive energies (atomic units) of diamond and silicon within the HFA using a minimal basis set. The value in parentheses is explained in the text.

	Diamond	Silicon
Present work	0.346	0.182
Reference 19	0.3	
Reference 18	0.30–0.37	
References 20–22	0.41 (0.31)	0.184
Reference 24	0.39	

TABLE III. Cohesive energies (atomic units) of diamond and silicon. The first column contains the Hartree-Fock limit, the second column the difference to the experimental result, which must be compared with the correlation contribution (third column).

	$\varepsilon_{\mathrm{HFA}}$	$\varepsilon_{\mathrm{expt}}-\varepsilon_{\mathrm{HFA}}$	$\varepsilon_{\mathrm{corr}}$
Diamond	0.405	0.154	0.158[a] 0.13[b]
Silicon	0.27	0.08	0.09[a]

[a] Reference 27.

[b] Reference 4.

authors have to add in order to compensate for a loss of translational symmetry due to the truncation criteria.

In our opinion, the only shortcoming in the calculation of Dovesi *et al.* is the small basis set they have used. In the case of diamond they took a minimal (Slater-type orbital) STO-3-*G* basis. The error due to this basis set has been estimated[5] and leads to a cohesive energy as indicated in parentheses (Table II). In the calculation for silicon Dovesi *et al.* used a basis set comparable to ours. Therefore, the good agreement is not astonishing.

By relating HF limits of the total energies for CH_4, C_2H_6, SiH_4, and Si_2H_6 (Refs. 14, 23, and 24) to the values obtained within minimal basis sets for the same molecules it is possible under the assumption that the same relationship holds for solids to determine the HF limits for the cohesive energies of diamond and silicon (first column of Table III). In the second column the differences between the experimental results[25,26] and the HF values are listed. Since the numerical errors of our HF results are estimated to be negligible, these differences give directly the correlation contribution to the cohesive energy. The correlation effects contribute significantly ($\approx 25\%$) to the cohesive energy. The correlation corrections,[27] which are listed in the fourth column of Table III are in good agreement with our results.

B. Charge densities and x-ray factors

The charge densities of the valence electrons computed in this work are shown in Figs. 1 and 2. In Fig. 1 a comparison is made between the densities of diamond and silicon. The difference is remarkable in the peak structure along the bond direction. Whereas in diamond a double peak appears, silicon shows only one peak. This is a consequence of the more diffuse wave functions. The difference in magnitude is mainly due to the different lattice parameters. The computed densities are in good agreement with available experimental results.[28] Densities computed from a superposition of atomic charge densities would give a too small value for the density in the center of the bond. Figure 1 also contains experimental results and atomic-superposition results[28,31] for the densities in the bond center. Figure 2 shows the decrease of the charge densities in a direction orthogonal to the bond direction starting from the center of the bond. There is a similar decay in diamond and in silicon, which can be easily understood because this decrease is dominated by the angular part of the wave functions which are equal in diamond and silicon.

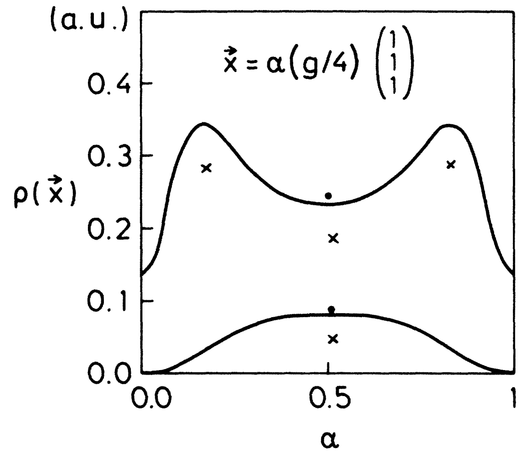

FIG. 1. Density of the valence electrons (atomic units) along the bond direction for diamond (upper curve) and silicon (lower curve). ● indicates experimental results (Ref. 28). × indicates atomic-superposition density (Ref. 28).

The x-ray factor is defined by

$$F(\mathbf{G})=\tilde{\rho}(\mathbf{G})/\tilde{f}(\mathbf{G}) , \tag{22}$$

where $\tilde{\rho}(\mathbf{G})$ is the Fourier transform of the charge density $\rho(\mathbf{x})$, $\tilde{f}(\mathbf{G})$ is the Fourier transform of hypothetical point charges at every lattice site with the normalization $\tilde{f}(\mathbf{0})=1$, and

$$\tilde{f}(\mathbf{G})=\frac{1}{z}\sum_{\mathbf{y}_\alpha} e^{i\mathbf{y}_\alpha\cdot\mathbf{G}} , \tag{23}$$

with z being the number of atoms within a unit cell and $\mathbf{y}_\alpha$ being the corresponding vectors to these atoms.

Table IV gives the structure factors of diamond calculated in this work compared with results of several other publications. The last row contains the so-called agreement factor, defined as

$$R=\sum_n |F(\mathbf{G}_n^{\mathrm{expt}})-F(\mathbf{G}_n^{\mathrm{theor}})| \Big/ \sum_n |F(\mathbf{G}_n^{\mathrm{expt}})| . \tag{24}$$

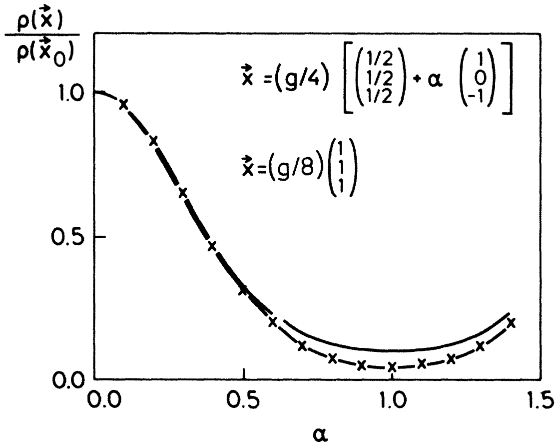

FIG. 2. Density of the valence electrons (atomic units) along a direction orthogonal to the bond direction for diamond (——) and silicon (—×—×—).

TABLE IV. X-ray factors of diamond (atomic units) compared with different other results: R is the agreement factor (see the text).

$G/(2\pi/a)$	Expt[a]	LDA[b]	HFA[a]	HFA[c]	LDA[d]	atomic-superposition density[e]
111	3.321	3.249	3.274	3.298	3.281	3.056
220	1.972	1.960	1.925	1.931	1.995	1.951
311	1.663	1.693	1.659	1.571	1.692	1.755
222	0.144	0.070	0.088	0.086	0.139	0.000
400	1.480	1.543	1.535	1.545	1.493	1.555
331	1.539	1.526	1.533	1.527	1.605	1.509
422	1.443	1.427	1.443	1.417	1.408	1.430
511	1.418	1.381	1.386		1.392	1.391
333	1.418	1.376	1.382		1.392	1.391
R		0.020	0.023	0.024	0.015	0.051

[a] Reference 22.
[b] Present work.
[c] Reference 18.
[d] References 22 and 24.
[c] Reference 30.

When one compares calculated densities with experimental structure factors one must realize that the largest contributions are due to the core electrons. Therefore, such a comparison does not allow any conclusions about the quality of the valence electron description[32] except for reflections which would vanish in the absence of solid-state effects.

The quality of the data of Zunger and Freeman is primarily due to the much larger basis set. This is most important for the 222 peak which is forbidden for atomic-superposition densities. The influence of the basis set on this 222 peak hâs been investigated by Mauger and Lannoo.[19] Apart from this peak, which is very sensitive to the basis set, our results are in good agreement with the experiment.

The x-ray factors for silicon are listed in Table V. Due to the pseudopotential we have used, it has not been possible to calculate the contribution of the core electrons to the x-ray factors. Therefore, comparison with the experiment can only be made for the 222 peak, which is solely determined by the valence electrons. As in the case of diamond there is an enormous discrepancy between the HF value in the minimal basis set and the experimental data, displaying again the sensitivity to the choice of the basis set. According to what has been found for the cohesive energy, the influence of the polarization functions on the result is of more importance in the case of diamond than it is for silicon.

TABLE V. X-ray factors of silicon (atomic units). Due to the pseudopotential calculation only the value of the 222 peak of the present work (b) can be compared with the experimental result (Ref. 28).

$G/(2\pi/a)$	Expt[a]	LDA[b]
111		1.189
220		−0.057
311		−0.224
222	0.18–0.22	0.080
400		−0.183
331		−0.103
422		−0.076
511		−0.060
333		−0.058

[a] Reference 22.
[b] Present work.

C. Band structure

The band structure of diamond is displayed in Figs. 3–5. Figure 3 gives a comparison between the LDA band

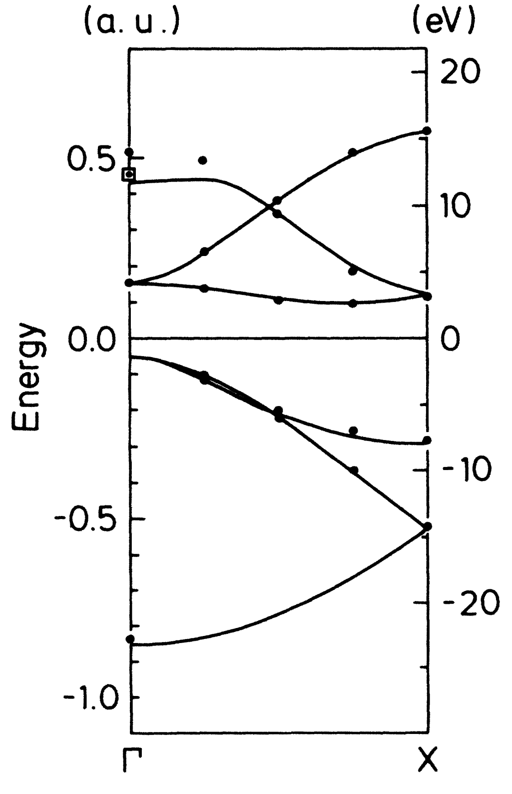

FIG. 3. LDA band structure of diamond. —— indicates this work. ● indicates Ref. 29.

structure calculated in this work (minimal basis set) and that of Ref. 29 (basis set containing polarization functions). We see that the basis set we used is accurate enough for the description of the valence and lower conduction bands. Figures 4 and 5 show the Hartree and the Hartree-Fock energy bands, respectively. The strong influence of the nonlocal exchange potential on the gap and the bandwidths is obvious. It spreads the bands by a factor of about 1.2 and increases the energy gap at the Γ point by a factor of about 3.2. In accordance with the results of Refs. 1—3 the minimum of the lowest conduction band lies at the E_1 point. The deviation from this result found by Dovesi *et al.*[22] is due to their small basis set. There is agreement among all authors about the sequence of excited states at the Γ point.

As in the case of diamond we have tested the basis set for silicon by comparing the band structures obtained within the LDA (Fig. 6). Here the polarization functions are found to be more important than for diamond. In particular, the size of the gap is affected by the basis set. Nevertheless, the results for the valence and lower conduction bands are in reasonable agreement. The Hartree and Hartree-Fock band structures, respectively, are plotted in Fig. 7 and 8. Again the exchange potential causes a big increase in the bandwidth (factor ≈1.5) and in the energy gap at the Γ point (by a factor of ≈6). In the Hartree approximation silicon turns out to be a semimetal. Also in silicon the conduction-band minimum lies near the E_1 point in accordance with the experiment.

Again Dovesi *et al.* find the minimum at the X point together with an inversion of the Γ_{15}^c and the $\Gamma_{2'}^c$ levels. These artifacts result from the small basis set. Contrary

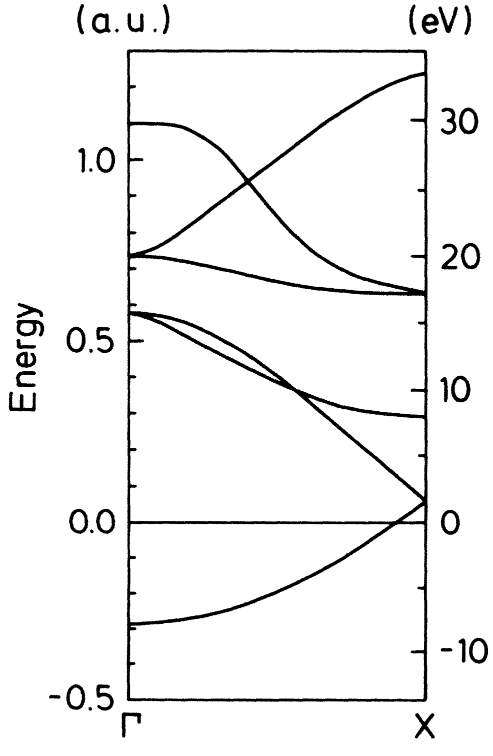

FIG. 4. Hartree band structure of diamond.

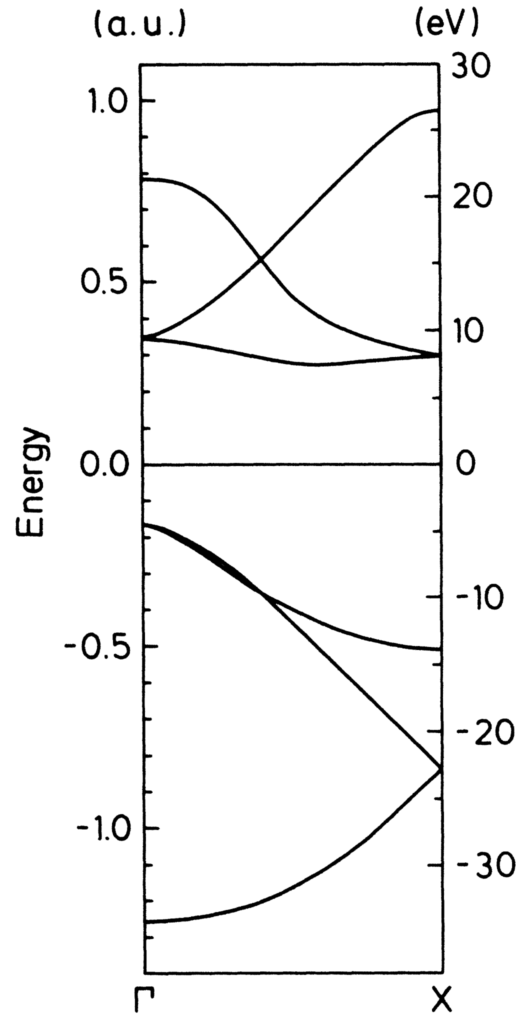

FIG. 5. HFA band structure of diamond.

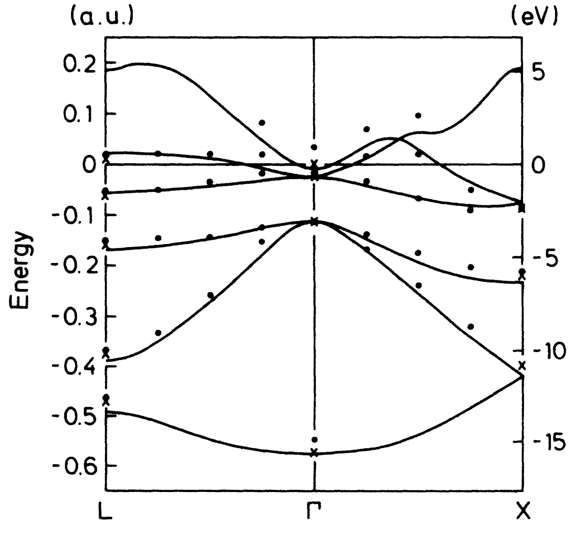

FIG. 6. LDA band structure of silicon. —— indicates this work. ● indicates Ref. 29. × indicates Ref. 33.

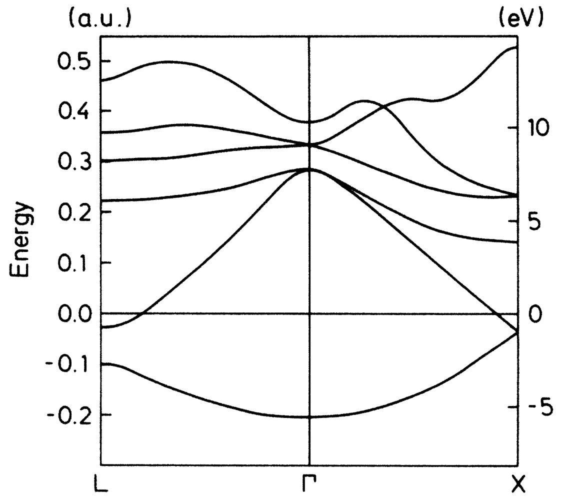

FIG. 7. Hartree band structure of silicon.

to the cohesive energy the band structure has been calculated with a STO-3-3-3 basis set only. The authors mention that the inversion will vanish within a STO-6-6-4 basis. This leads also to an uncertainty in the value of the energy gap at the Γ point. A very recent work by Ohkoshi[34] leads to a direct gap that is in good agreement with ours ($E_g = 8.15$ eV). The same holds true for the cohesive energy.

Table VI shows the band energies for some high-symmetry points in **k** space as they have been calculated by us and other authors. The discrepancy between the HF results and the experimental values is due to the lack of correlation. Horsch *et al.*[35,36] have shown for diamond that, starting from the HF band structure, a correlation contribution within a variational calculation leads to accurate energy bands that do agree very well with the experimental results.

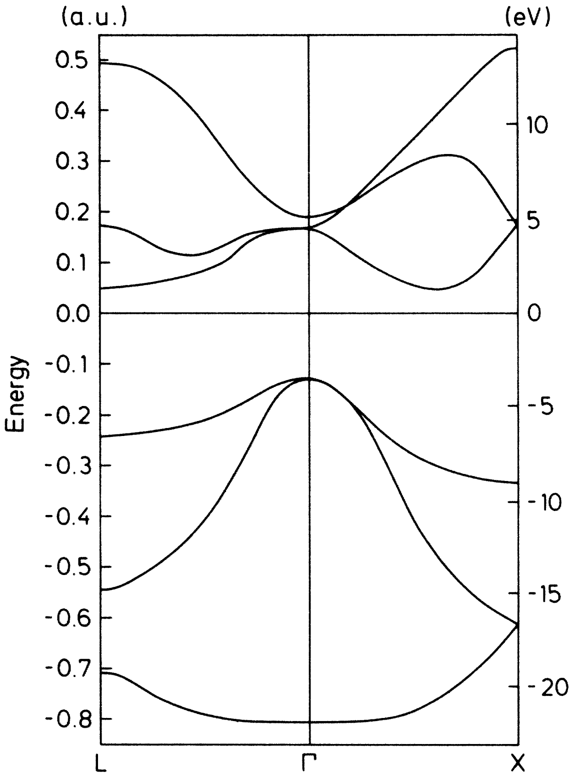

FIG. 8. HFA band structure of silicon.

V. CONCLUSION

In this work it has been explicitly shown for the first time that for real crystals like diamond and silicon the one-particle wave functions of the LDA agree very well with those of the HFA. This enables one to calculate the total energy, electronic density, x-ray factor, and the band

TABLE VI. High-symmetry points of the energy bands of diamond and silicon (atomic units).

		$\Gamma_{25'}$	Λ_v^{Γ} [a]	$E_{\rm gap}^{\Gamma}$ [b]	Δ_c^{Γ} [c]	$X_{4,v}$ [d]	$X_{1,v}$ [d]
Diamond	Mauger und Lannoo (Ref. 19)	−4.1	29.1	15.0	9.1	−9.0	−17.1
	Dovesi *et al.* (Ref. 22)		30.5	13.9	13.3	−8.7	−18.2
	Euwema *et al.* (Ref. 18)	−4.1−5.7	29.5	14.7	11.8	−8.4	−18.8
	HFA[e]	−4.6	29.7	13.9	11.6	−9.3	−18.2
	Hartree[e]	+15.8	23.6	4.3	9.9	−7.8	−14.1
	LDA[e]	−1.3	21.8	5.5	6.3	−6.6	−13.1
	Experiment (Ref. 21)		21−24	7.3			
Silicon	Dovesi *et al.* (Ref. 28)		19.8	9.4	0.7	−5.0	−12.8
	HFA[e]	−3.5	18.5	8.0	0.5	−5.6	−13.2
	Hartree[e]	+7.7	13.3	1.3	1.3	−3.8	−8.7
	LDA[e]	−3.1	12.6	2.3	0.5	−3.3	−8.4
	Experiment (Ref. 28)			3.5			

[a] Width of the valence bands.
[b] Direct gap.
[c] Width of the conduction bands.
[d] Values with respect to the Γ_{25} level.
[e] Present work.

structure by an efficient HF scheme. Actual calculations have been performed based on this idea for diamond and silicon. Due to the gain in computer time it has been possible to do the calculation without further uncontrollable approximations and within a sufficiently large basis set. With these accurate HF results it is now possible to perform real many-body calculations. As an example we have given the results for the cohesive energy, which was in very good agreement with the experimental data.

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