Exact-exchange Hartree-Fock calculations for periodic systems.
V. Ground-state properties of silicon

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An all-electron *ab initio* calculation of the ground-state properties of silicon is present-
ed. The method is the linear-combination-of-atomic-orbitals self-consistent-field Hartree-
Fock scheme previously applied to first-row systems. Computational problems associated
with the presence of large cores are discussed. The calculations have been performed us-
ing a minimal basis set (nine atomic orbitals per atom: $1s$, $2s$, $2p$, $3s$, $3p$ functions; d orbi-
tals are excluded). Results for total, binding, and correlation energy, band structure,
charge distribution, and x-ray factors are given.

INTRODUCTION

In recent years an increasingly great number of
papers have been devoted to the theoretical study
of the ground-state properties of silicon.[1-14] In
general they are valence-only calculations in the lo-
cal exchange approximation. The pseudopotential
simulating the core electrons are empirical, fitted
to the spectra of the solid[12] or of the bare
ion.[1,3,5,7,8,10,11] In one instance they are derived
from first principles.[9] All electron "first-principle"
calculations in the local exchange approximation
have also been published.[13,14] To our knowledge,
no applications to silicon have yet been reported of
all-electron *ab initio* Hartree-Fock (HF) schemes
which have been successfully used in the study of
diamond, cubic boron nitride, and other first-row
crystals.[15-20]

An all-electron treatment has the obvious advan-
tage in that it avoids the frozen-core approxima-
tion and permits more direct comparison with all
the experimental data. Furthermore, it can be used
as a reference for rougher approximations. These
advantages are counterbalanced by the need for
greater computational effort connected with the
presence of larger basis sets and with the require-
ment of higher numerical accuracy due to the dif-
ferent ratio between absolute and relative quantities
(total to binding energy, for example). While in
the study of low-symmetry or heavy-atom systems
such problems become of primary importance and
impose the use of pseudopotential techniques, we
want to show in the present paper, devoted to the
study of silicon, that for second-row crystals rela-
tively accurate HF all-electron calculations are
feasible with reasonable computational effort. Our

linear-combination-of-atomic-orbitals self-
consistent-field exact-exchange *ab initio* method
has been discussed in previous papers[17-19]; results
have been published for graphite,[18] diamond,[19] and
hexagonal[18] and cubic boron nitride.[20]

The results presented here have been obtained
with the same basis set as in previous papers, i.e., a
standard STO-$3G$ minimal basis set,[21] hereafter re-
ferred to as 3-3-3 set. We also report the results of
some test calculations performed using a minimal
6-6-4 set (six Gaussians for core orbitals and 4
Gaussians for $3sp$ orbitals). Satisfactory results
have been generally reached at the 3-3-3 level;
some definite improvements (for instance, in the
calculated lattice parameter) have been observed
using the 6-6-4 set. The use of an extended basis
set, in particular the inclusion of d orbitals, is ex-
pected to improve some features of the band-
structure and electron-momentum distribution.[22]

In the next section we will point out some com-
putational aspects of our silicon calculation. The
weight of the inclusion of core electrons and the
importance of the atomic orbitals size will be
analyzed. In the third section results will be
presented for total and binding energy, correlation
corrections, charge density, band structure, and x-
ray factors.

COMPUTATIONAL ASPECTS

The general formulation of the direct-space ap-
proach to the study of solids and a first analysis of
its critical points have already been presented[17,18]
with reference to a very simple system, i.e., the
graphite monolayer. In this section we want to ex-

amine more closely the importance of some characteristic parameters of the system under study (extent of the basis set and size of the atomic orbital with respect to lattice spacing) in determining the overall weight of the computation.

The central point of our method is the evaluation of sums of bielectronic integrals:

$$d_{\mu\nu\lambda\rho}(\vec{g}, \vec{l}) = \sum_{\vec{m}} (\chi_\mu^{\vec{0}} \chi_\nu^{\vec{g}} | \chi_\lambda^{\vec{m}} \chi_\rho^{\vec{m} + \vec{l}})$$
$$- \frac{1}{2} \sum_{\vec{m}} (\chi_\mu^{\vec{0}} \chi_\lambda^{\vec{m}} | \chi_\nu^{\vec{g}} \chi_\rho^{\vec{m} + \vec{l}}) \quad (1)$$

where $\vec{m}$, $\vec{l}$, and $\vec{g}$ are direct lattice traslational vectors, and $\chi_\nu^{\vec{g}} \equiv \chi_\nu(\vec{r} - \vec{g} - \vec{s}_\nu)$ is the νth atomic orbital (AO) of the cell characterized by the vector $\vec{g}$ and centered on the atom identified by the fractional vector $\vec{s}_\nu$. In Eq. (1) the usual notation has been adopted to indicate two-electron integrals, the two AO's on either side of the bar corresponding to the same electron. The sum over $\vec{m}$ is in principle infinite; in fact, when $|\vec{m}|$ is sufficiently large, groups of bielectronic integrals are approximated by simpler expressions or disregarded, as discussed at length in Ref. 17. Our program uses a "direct-space" approach in the sense that all relevant quantities are constructed in direct-space representation. The Fock matrix is reconstructed at each iterative cycle as follows:

$$F_{\mu\nu}^{\vec{g}} = H_{\mu\nu}^{\vec{g}} + \sum_{\lambda\rho} \sum_{\vec{l}} P_{\lambda\rho}^{\vec{l}} D_{\mu\nu\lambda\rho}^{\vec{g}, \vec{l}} \quad (2)$$

where H is the monoelectronic part of F, the D matrices are related to the d ones by point-group symmetry operations,[17] and P is the density matrix represented in the basis of the AO's. The Fock matrix is Fourier transformed to reciprocal space just before the solution (at each $\vec{k}$ point of the irreducible part of the first Brillouin zone) of the matrix equation

$$F(\vec{k})A(\vec{k}) = S(\vec{k})A(\vec{k})E(\vec{k}) . \quad (3)$$

The eigenvectors' and eigenvalues' matrices A and E (with general elements $a_{\mu i}$ and ϵ_i) are then used to redefine the $P^{\vec{l}}$ matrices, going back to direct space:

$$P_{\lambda\rho}^{\vec{l}} = \sum_i^p \int_{BZ} d\vec{k} \, a_{\lambda i}^*(\vec{k}) a_{\rho i}(\vec{k})$$

$$\times \exp(i\vec{k} \cdot \vec{l}) \Theta(\epsilon_F - \epsilon_i(\vec{k})) . \quad (4)$$

In Eq. (3) $S(\vec{k})$ is the overlap matrix between Bloch functions. In Eq. (4) p is the number of

AO's in the cell, ϵ_F is the Fermi energy, and Θ is the step function.

It can be interesting to analyze the percentage of the total computer time required by the main steps of our scheme synthesized in Eqs. (1)—(4) and see how those times are dependent on p, the number of AO's of the cell. In particular we will compare diamond and silicon to exhibit the role of a relatively large core in such calculations. For step 1 (evaluation of mono- and bi-electronic integrals), the computer time t is roughly proportional to $p^4 n^3$, where n is the average number of direct-space vectors considered in Eq. (1). For step 2 [reading from external devices the D matrices and reconstructing the Fock matrix according to Eq. (2)], $t \propto p^4 n^2$. For step 3 [diagonalization of the Fock matrices, Eq. (3)]. $t \propto p^3 q$, where q is the number of $\vec{k}$ points (29 in our case). For step 4 [reconstruction of the P matrix, Eq. (4)], $t \propto p^3 qn$. It must be noticed that the coefficients of proportionality can be very different for the four steps.

The strong dependence (third or fourth power) of all the four steps on p, and of three of them on n is evident; in step 1, in particular, the computer time is critically dependent of both parameters. Surprisingly enough, silicon calculations are appreciably quicker than the diamond ones performed in the same conditions (truncation criteria, number of points in reciprocal space, number of iterative cycles, 3G basis sets, etc.),[23] in spite of the fact that p rises from 10 to 18. As appears in Table I, this effect is essentially related to a strong contraction in step 1, which is not compensated for by the increase of the time required for the other three steps. To understand the reasons for this apparent paradox, we must make it clear why the number of two-electron integrals is higher in diamond than in silicon. This number, which is determined in a complicated way by the truncation criteria discussed at length in Ref. 17, is in any case related to the overlap S between AO's centered on different atoms. In Fig. 1 we reported the decimal logarithm of S as a function of the distance between carbon (a) or silicon (b) atoms. Comparing the valence $2s$-$2s$ and $3s$-$3s$ curves it is evident that the larger lattice parameter of silicon (5.42 Å against 3.56 Å) overcompensates the larger size of the functions. So fixing, for example, $\log_{10} S = -5$ as value below which mono or bielectronic integrals are disregarded, we must consider 5 stars of neighbors (47 atoms) for silicon and 8 stars (99 atoms) for diamond. Figure 1 shows that, when only core functions are involved, n collapses to 1 so that the

TABLE I. Analysis of the computer time employed for a minimal-basis-set Hartree-Fock calculation of the diamond and silicon wave functions.

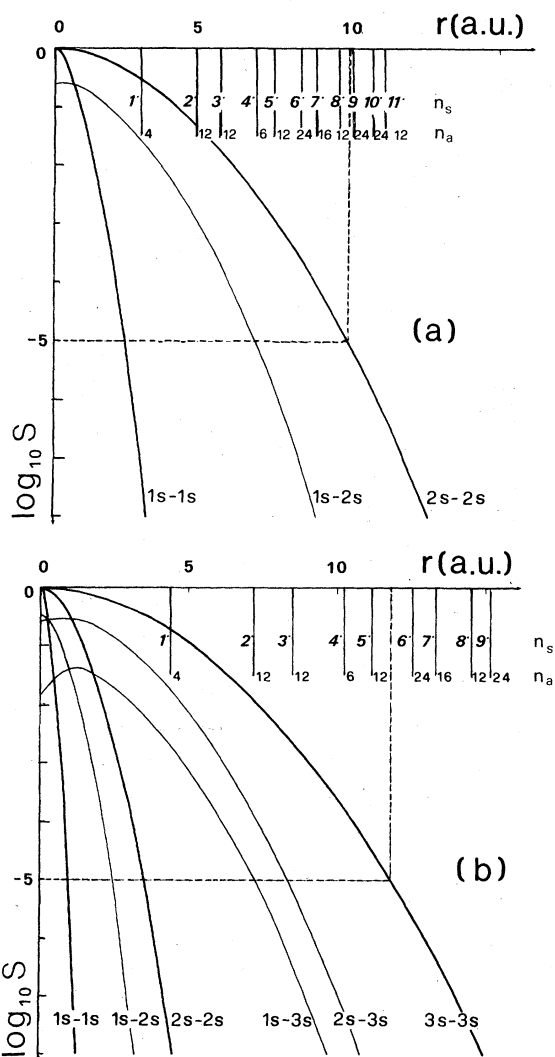|	Diamond	Silicon
Step 1: mono- and bielectronic integrals	74%	47%
Step 2: reconstruction of the Fock matrix	13%	26%
Step 3: diagonalization of the Fock matrix	1%	6%
Step 4: reconstruction of the density matrix	2%	10%
Other	10%	11%

FIG. 1. Decimal logarithm of the overlap between s-type atomic orbitals as a function of the distance r. n_s labels a star of neighbors; n_a is the number of atoms in the star. (a): Diamond, (b): silicon.

presence of the core does not produce dramatic effects on the computing time.

Table II lists the total number of exchange and Coulomb bielectronic integrals and the number of integrals with four valence indices. For silicon, the all-electron calculation requires only twice the number of integrals with respect to a valence-only calculation. The 2.5 million nonvalence integrals have mixed core-valence atomic orbitals; in fact, the all-core index integrals are only a few thousand.

In conclusion, in our direct-space approach an all-electron calculation is not much heavier than a corresponding valence-only one, even when relatively large cores are considered. In fact, in order to better estimate the time required in the critical step 1, a factor proportional to $p_V^4 n_V^3$ should be used, p_V being the number of valence orbitals and n_V the corresponding number of direct-space vectors. In "reciprocal-space" approaches,[24-28] in which the basis set, the local or nonlocal potential, and/or all intermediate quantities are Fourier expanded, the presence of high atomic number atoms can give rise to difficulties, and pseudopotential techniques are used even for first-row systems.[24]

RESULTS AND DISCUSSION

Table III lists the energy data of silicon obtained with the 3-3-3 set[21] For comparison the corresponding calculated data of diamond are also shown.[19] We found a total energy for silicon of 15 545.40 eV/cell. This value is 7 times larger than the corresponding one for diamond, and about 2000 times larger than the experimental binding energy. With reference to the atomic energy obtained with the same basis,[21] the calculated binding energy was 2.56 eV/atom, against an experimental one of 4.6 eV/atom.[29] The difference, 2.04 eV/atom, is about the same as we had for diamond (1.93 eV/atom). A large part of this error (1 − 1.5

TABLE II. Number (in 10^6 units) of Coulomb and exchange bielectronic integrals to be computed for a valence only and an all-electron calculation for diamond and silicon.

| | Diamond | | Silicon | |
	All-electron	Valence only	All-electron	Valence only
Coulomb	13.0	12.5	4.1	2.1
Exchange	1.8	1.5	1.1	0.6

eV/atom) is due to the neglected contribution of the electronic correlation to the binding energy; the remaining part can be traced back to the poorness of the basis set. The error associated with the various approximations connected with the method (truncation criteria, sampling points in k space, numerical errors in large summations, etc.) can be estimated to be less than 0.1 eV/atom. As for diamond,[19] we estimated a posteriori using the self-consistent HF charge distribution, the correlation energy of the system in the local-density-functional approximation. The functional we used is the one of Gunnarsson and Lundqvist (GL) (Ref. 30) and the one that more recently Stoll, Pavlidou, and Preuss (SPP) (Ref. 31) employed to study finite systems. The binding energies including the correlation contribution are reported in the third and fourth row of Table III. The GL functional gives the larger (and nearer to the expected one) contribution: 1.30 eV/atom for diamond, 1.34 eV/atom for silicon. With those contributions the error with respect to the experimental data is reduced to 0.63 eV/atom and 0.70 eV/atom for the two systems. At the moment there are no other all-electron ab initio estimates of the total energy of silicon. Table III also reports the calculated equilibrium lattice

parameter a_0^e and the bulk modulus B, as obtained by a quadratic best fit with 5 energy points evaluated in the interval 5.42−5.72 Å. The fit was quite satisfactory in spite of the fact that the energy variations in the interval are quite limited (about 0.11 eV). In fact, for the five determinations obtained choosing four points out of five, a_0^e is stable whereas B varies from 1.17 to 1.30×10^{12} dyn/cm². With respect to the experimental values, the lattice parameter is less than 3% and bulk modulus 25% too high.

To test the influence of the basis set, we repeated the calculations with a 6-6-4 set. The exponents and coefficients of the Gaussians were the standard ones.[21] We only adjusted variationally the coefficient of the most expanded Gaussian in the valence orbitals so as to minimize the energy corresponding to the experimental value of the lattice parameter. A large gain in the total energy was observed, of course ($E = -15\,673.25$ eV/cell), especially due to the better description of the core functions. The binding energy, as evaluated with respect to a "6-6-4 modified" atomic calculation, was practically unchanged (2.50 eV/atom). However, the determination of the bulk modulus (1.20×10^{12} dyn/cm²) was slightly better and the

TABLE III. Experimental and calculated energy data for diamond and silicon. HF + LDF(SSP) is the Hartree-Fock binding energy plus the correlation contribution evaluated using the HF charge density by the local-density functional (LDF) proposed by Stoll, Pavlidou, and Preuss (Ref. 31). GL refers to the functional proposed by Gunnarsson and Lundqvist (Ref. 30). Energies in eV.

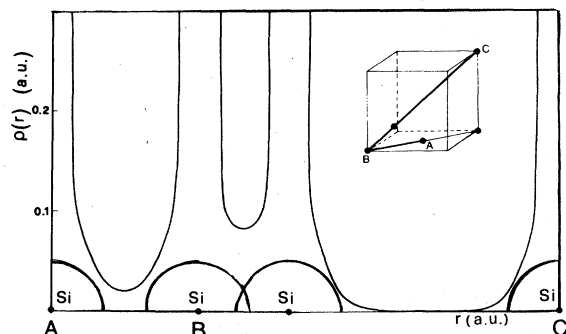| | | Diamond | | Silicon | |
		Calc.	Expt.	Calc.	Expt.
E_{tot} (eV/cell)		2037.32		15 545.40	
E_b (eV/atom)	HF	5.69		2.56	
	HF + LDF(SPP)	6.42	7.62	3.37	4.6
	HF + LDF(GL)	6.99		3.90	
a_0^e (Å)		3.59	3.57	5.58	5.43
B (10^{12} dyn/cm²)		5.90	4.42	1.25	0.99

FIG. 2. Hartree-Fock total charge density of silicon along the [110] (line AB) and [111] (line BC) directions.

calculated equilibrium lattice parameter (5.42 Å) was practically coincident with the experimental one.

The covalent character of the bond in silicon is apparent from Fig. 2, where the total charge distribution along the [111] (first neighbors) and the [110] (second neighbors) directions are reported. Midway between nearest neighbors the charge is $0.08e/(\text{a.u.})^3$, between second neighbors it is about a quarter, and in the antibonding zone it falls practically to zero. The charge densities of diamond and silicon in the [111] bond direction are compared in Fig. 3. The stronger covalent character of the $C-C$ with respect to the $Si-Si$ bond is not so apparent from the higher value of the charge density along the bond in the former case, as rather from the fact that the increase in electronic density with respect to atomic superposition data is twice as large in diamond as in silicon midway between nearest neighbors. This is also revealed by the Mulliken bond populations which are 0.74 and 0.64 in the two cases, respectively. Full and open circles in Fig. 3 show the charge densities obtained by
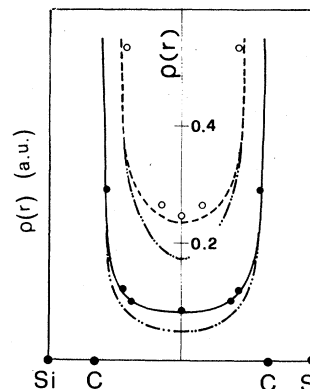

FIG. 3. Hartree-Fock charge density in silicon (—) and diamond (- - -) along the bonding direction. The total charge density in the atomic superposition approximation is also reported $(-\cdot\cdot-\cdot\cdot-)$. Open and full circles refer to the charge density reconstructed from the experimental x-ray structure factors (Ref. 32) ρ in $e/(\text{a.u.})^3$.

Göttlicher and Wölfel,[33] starting from the experimental structure factors. The agreement is very good.

Table IV shows the structure factors calculated with the 3-3-3 basis set at the experimental value of the lattice parameter, and the contribution from core states. For comparison, the two most recent experimental sets[33,34] and the atomic superposition data[33] are also reported. The present results are generally intermediate between the two experimental determinations. If more credit is given to the accurately discussed data by Aldred and Hart,[33] it should be concluded that the largest errors occur for low-index factors, that is, the ones associated with the largest valence contributions. In fact, using the 6-6-4 basis set, F_{111} reduces to 10.89 and

TABLE IV. Experimental and calculated structure factors for silicon.

| h | k | l | Experimental | | Calculated (this work) | | Atomic superposition |
			Ref. 33	Ref. 34	Total	Core	Ref. 33
1	1	1	10.74	11.12	11.00	9.46	10.55
2	2	0	8.65	8.78	8.79	8.68	8.71
3	1	1	8.02	8.05	8.11	8.26	8.17
2	2	2	0.18	0.22	0.11	0.00	0.00
4	0	0	7.44	7.40	7.47	7.62	7.51
3	3	1	7.25	7.32	7.22	7.27	7.19
4	2	2	6.71	6.72	6.72	6.74	6.71
3	3	3	6.43	6.43	6.46	6.46	6.44
5	1	1	6.44	6.40	6.46	6.46	6.44
4	4	0	6.04	6.04	6.07	6.02	6.04
4	4	4	4.98	5.00	4.99	4.88	4.98

TABLE V. Agreement factors R_{ij} between structure factors.

	Reference	i \ j	1	2	3	4	5	6	7	8	9
Experimental	32	1		1.71	1.72	1.50	1.44	1.63	3.22	2.03	1.63
	35	2	1.71		0.28	1.11	0.71	1.27	2.31	1.47	1.53
	34	3	1.72	0.28		1.03	0.83	1.20	2.27	1.41	1.50
	33	4	1.50	1.11	1.03		1.06	0.38	1.46	0.41	0.84
Calculated	This work	5	1.44	0.71	0.83	1.06		0.97	2.41	1.11	1.20
	13	6	1.63	1.27	1.20	0.38	0.97		1.63	0.44	0.77
	9	7	3.22	2.31	2.27	1.46	2.41	1.63		1.42	1.95
	14	8	2.03	1.47	1.41	0.41	1.11	0.44	1.42		0.65
	33	9	1.63	1.53	1.50	0.84	1.20	0.77	1.95	0.65	

F_{220} to 8.74, while the other reflexes are practically unchanged. The largest relative error occurs for the "forbidden" F_{222} factor which is lower by a factor of 1.7 with respect to the experiment. A similar underestimation was observed for diamond. In order to gain an overall picture of the similarities and discrepancies between available experimental and calculated sets of data, agreement factors were calculated according to the formula

$$R_{ij} = 100 \left[\sum_l |F_l^i - F_l^j| \right] \Big/ \left[\sum_l \frac{|F_l^i + F_l^j|}{2} \right] .$$

Apart from the present HF results, the calculated data are taken from the papers by Heaton and Lafon[14] (all-electron, *ab initio*, local exchange), Zunger[9] (pseudopotential, local density functional), Stukel and Euwema[13] (their best results, obtained with a combination of Kohn-Sham-Gaspar wave functions for valence states, and Hartree-Fock wave functions for core states), and Aldred and Hart[33] (atomic superposition from Clementi's data). The $\sum_l$ in R_{ij} was extended to all the 15 reflexes included in Table II of Ref. 33 (plus the 222 factor) or to the subset of those reflexes that are actually reported by the above-cited authors, and that are common to the sets i and j. The minimum number (eight) of calculated reflexes is provided by Heaton and Lafon.[14] When all the agreement factors are calculated with respect to that minimal set, the largest difference with respect to the data of Table V is only 0.3 ($i = 9$, $j = 1$). The most striking feature of the table is the excellent agreement of Aldred's[33] data with the results of Heaton and Lafon[14] and especially with those of Stukel and Euwema.[13] Such a good agreement is somewhat surprising if one considers that differences between experimental sets are appreciably higher than that.

On average, the present results exhibit the best overall agreement with available experimental data.

In Fig. 4 the calculated HF band structure of silicon along some high-symmetry direction is finally shown. The qualitative features of the valence part of our calculated spectrum are very similar to the ones obtained with previous calculations.[2-4,6,7,10-14,36] As usual, Hartree-Fock band structures are larger by a factor of 2 or more with respect to the structures suggested by optical excitation data.[19,24] For example, we obtained for L_3^v, $-L_1^v$ transition 8.76 eV, against an experimental data of 3.40 eV.[37] The calculated valence $\Gamma_{25'}^v$, $-\Gamma_1^v$ bandwidth is equal to 19.8 eV, about one-half of the one we had for diamond (37 eV). The conduction bands are instead quite different from the ones resulting from other calculations. We have an inversion between the Γ_{15}^c and the Γ_2^c, levels (which disappears with the 6-6-4 basis set); furthermore the lowest point is $\Gamma_{2'}^c$, whereas other
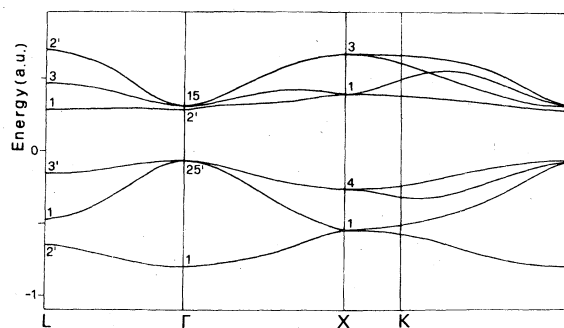

FIG. 4. Hartree-Fock self-consistent band structure of silicon. The symmetry type of the eigenvectors at L, Γ, and X points is reported.

calculations show a minimum in the X_1 point[36] or midway along the $\Gamma - X$ line,[1,7,14] as suggested by the experiment.[38] Our valence-conduction gap $(\Gamma^c_{25'} - \Gamma^c_{2'})$ is 9.40-eV wide, against an experimental value of 3.54 eV.[37] The quality of the basis and in particular the absence of d orbitals is probably the origin of such qualitative differences, while the quantitative differences are, as known, associated with the Hartree-Fock model.

ACKNOWLEDGMENT

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