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Ab initio study of metallic beryllium

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Hexagonal close-packed beryllium has been studied with an Hartree-Fock (HF) *ab initio* technique, with the use of an extended basis set. The conformational calculated minimum corresponds to a slightly expanded crystal lattice, and total energy is near to the estimated HF limit. The metallic character of the system, as illustrated by the shape of its Fermi surface, is in fair agreement with experiment. The general features of the electron distribution are satisfactorily reproduced both in direct and in reciprocal space, as results by comparison with experimental structure factors and Compton profiles. The present study gives evidence for the fundamental role of *p*-type functions in determining both the metallic character and the partly covalent bonds of beryllium.

I. INTRODUCTION

Among light metals, beryllium presents distinctive features in that it exhibits the largest departure from free-electron behavior. Owing to its peculiar physical properties and its simple crystal structure (it is an hcp crystal, with only four electrons per atom), beryllium has been the object of great attention from both an experimental and a theoretical point of view. However, all electron *ab initio* calculations are still scarce and the only Hartree-Fock (HF) results yet reported[1,2] were obtained in a very crude approximation.

In the present work we report the results obtained using an *ab initio* HF self-consistent-field (SCF) linear-combination-of-atomic-orbitals (LCAO) method.[3] The computer program CRYSTAL is the same that had been used for studying semiconductors and insulators such as graphite and boron nitride,[4] diamond,[5] and silicon[6,7]; preliminary results have also been published for aluminum.[8]

While all previous results were obtained in a minimal basis set, we have employed here an extended set comprising ten atomic orbitals AO's per atom. Much attention was devoted to controlling once again the adequacy of the computational techniques that were submitted to a more severe test than in previous calculations. Owing to the metallic nature of the system, the determination of the Fermi energy, and the subsequent redefinition of the density matrix at each stage of the self-consistent procedure is not a trivial problem. Furthermore, owing to the compactness of the system and to the use of an extended basis set, the number of integrals is increased and the risks of linear dependency are enhanced. Some of those problems are briefly reviewed in Sec. II.

In Sec. III the results for total energy and related quantities are given. The calculated equilibrium lattice parameters are quite near to the experimental ones. On the basis of an approximate evaluation of the correlation contribution to binding energy, it also comes out that the present calculation satisfactorily reproduces the expected value of the HF energy of the crystal. Section IV analyzed the electronic structure of beryllium as resulting from the calculated band structure and from total and projected densities of states. On the whole, the metallic character of beryllium, as illustrated by its Fermi surface, is in fair agreement with experiment. The importance of *p* electrons in determining the metallic behavior and in characterizing the ground state, comes in full evidence from the projected densities of states. The electron charge density is described in Sec. V, both by providing density maps and by comparing the calculated structure factors with the experimental ones. The important general indication is that the valence electron distribution is more structured than that obtained from a superposition of atomic spherical contributions, with charge buildup along bonding directions. Finally in Sec. VI the directional Compton profiles are presented.

II. COMPUTATIONAL ASPECTS

The criteria we adopted to cut the Coulomb and exchange series appearing in the expression of the Fock matrix and of the total energy have been discussed at length in previous papers.[3-5]

An extensive set of calculations was performed to check the computational parameters controlling the truncation criteria, so as to reduce the overall error in total energy to below 0.01 eV per cell. It turned out that these parameters are the same in the present case of beryllium as were found in our previous studies on semiconductors and insulators. The resulting number of two-electron integrals was 16 millions of which only 1 million exchange integrals.

In the HF treatment of a metal system, one must determine the Fermi energy ϵ_F and the bond order P matrix at each cycle in SCF stage. In the present calculation the Fock matrix has been diagonalized in 133 $\vec{k}$ points within the irreducible wedge of the first Brillouin zone (IBZ). The Fermi energy was determined and the P matrix reconstructed using the overlapping sphere technique[3]; to this end, we reconstructed the solution at 793 $\vec{k}\,'$ points in IBZ, by means of a Fourier interpolation[9] of the calculated eigenvalues and eigenvectors. Using 28 and 133 $\vec{k}\,'$ points instead causes a minute change in total energy (0.04 eV per cell) and no appreciable differences in all other calculated quantities. 14 SCF cycles were sufficient to reach convergency in total energy to within 0.005 eV per cell.

Finally, a suitable basis set had to be chosen. For insulators and semiconductors, characterized by prevailingly covalent bonds, the minimal standard sets[10] optimized for molecular systems performed relatively well.[3-7] Such sets are obviously inadequate for a metal system like the present one. We tried, therefore, a number of extended *s-p* sets and several contraction schemes. The quality of the basis does not depend as much on the number of independent Gaussian orbitals, as rather on the range of exponents they span. On the other hand, this kind of variational freedom is limited at the low-exponent end: in fact, using too-wide Gaussian functions brings to catastrophic unphysical solutions via the near singular nature of the overlap matrix. Such problems are particularly acute for dense metallic systems like beryllium or lithium and practically disappear when studying less compact metals like sodium or aluminium. Improved computational techniques and higher numerical precision are required to widen the operational range. In the present case we were restricted to Gaussian α exponents not lower than 0.25 a.u. The basis set we finally adopted for all the calculations here reported is given in Table I and compared with the corresponding set for an atomic reference calculation. The contraction scheme we adopted still allows large variational freedom. We are looking, however, for future work, to more effective contraction schemes so as to reduce the number of basis functions to 6 or 7 AO's per atom, without impairing the solution in any substantial way.

III. ENERGY DATA

Table II reports total energies and related quantities at the experimental and calculated equilibrium conformation. The latter was approximately identified in two steps. The crystal was first isotropically expanded. In order not to alter the num-

TABLE I. Exponents (in a. u.) and coefficients of the *s* and *p* Gaussian functions used in the present calculation for atomic and metallic beryllium. The contraction coefficients multiply normalized individual *s* and *p* Gaussians.

Metal				Atom			
Function number	Type	Exponent	Coefficients	Function number	Type	Exponent	Coefficients
1	*s*	1200	0.001 559	1	*s*	1200	0.001 559
		400	0.003 605			400	0.003 605
		120	0.019 773			120	0.019 773
		32	0.083 441			32	0.083 441
		10	0.287 216			10	0.287 216
2	*s*	3	1	2	*s*	3	1
3–6	*sp*	0.85	1	3	*s*	1	1
7–10	*sp*	0.27	1	4	*s*	0.4	1
				5	*s*	0.16	1
				6	*s*	0.057	1

TABLE II. Energy data for metallic beryllium. a and c are the lattice parameters; $E_{\text{tot}}^{\text{HF}}$ is the total energy and E_b^{HF} is the binding energy per atom; $\eta = 2T/V$ is the virial coefficient.

	Equilibrium conformation	
	Experimental	Calculated
a (Å)	2.29	2.32
c (Å)	3.59	3.64
$E_{\text{tot}}^{\text{HF}}$ (a.u.)	14.6391	14.6393
E_b^{HF} (a.u.)	0.0684	0.0686
η	-1.0018	-1.0006

ber of one- and two-electron integrals with fixed tolerances, the exponent of the outermost Gaussian was changed according to $\alpha a^2 = \text{const}$. The minimum was found to correspond to a linear expansion of 1.6%. With fixed volume, the c/a ratio was then allowed to vary, but no significant departure was observed from the experimental ratio. Only three points were chosen along each direction, which did not allow a reliable estimate of the elastic constants to be obtained. As shown in Table II, the total energy change from the experimental to the calculated minimum is negligible, and all the results reported in the following are referred to the experimental conformation. It can, however, be observed that the virial coefficient η is appreciably improved when moving to the calculated minimum, as a consequence of a variation in the kinetic and potential energies by about 1 eV per cell. The residual deviation from the theoretical $\eta = 1$ value is an indication of the influence of the computational approximations described in the preceding section; in particular, there are indications that lowering the exponent of the outermost Gaussian is an important factor in lowering kinetic energy and leading to better η values.

The HF binding energy reported in Table II was calculated with respect to the HF atomic energy obtained with the atomic basis set of Table I (14.5707 a.u.). Using the accurate[11] HF energy for the free atom (14.5730 a.u.) did not change that result substantially. The experimental value of the binding energy is 0.12 a.u. per atom. Therefore, according to our computation, the correlation contribution to the binding energy is about 0.05 a.u. per atom. It can be questioned how reliable this estimate is. The correlation energy of the valence electrons in the metal can be evaluated theoretically using a free-electron model and local-density

TABLE III. Agreement factors R and standard deviations σ between calculated (this work) and experimental x-ray structure factors. Calculated data have been corrected with different sets of thermal-motion parameters proposed in the literature. R and σ are calculated with respect to the 27 structure factors ($\sin\vartheta/\lambda < 0.9$, Å^{-1}) reported in the next table. R and σ in units of 10^{-3}. B_{11} and B_{33} are in Å^2.

	Thermal-motion parameters			Larsen[a]		Brown[b]	
Data	Refinement	B_{11}	B_{33}	R	σ	R	σ
x rays Brown[b]	Brown	0.54	0.54	47	78	38	95
x rays Brown	Stewart[c]	0.572	0.523	51	83	34	94
x rays Brown	Yang and Coppens[d]	0.599	0.542	58	95	31	91
x rays Manninen and Suortti[e]	Manninen and Suortti	0.460	0.415	15	35	74	128
x rays Larsen *et al.*[f]	Larsen *et al.*	0.482	0.425	19	40	67	121
neutrons Larsen *et al.*[f]	Larsen *et al.*	0.469	0.424	17	38	70	124

[a] Reference 31.
[b] Reference 30.
[c] Reference 28.
[d] Reference 29.
[e] Reference 33.
[f] Reference 34.

correlation functionals; one obtains 0.095 a.u. per atom[12] using the Nozières and Pines formula, and 0.112 a.u. per atom using the Gunnarsson and Lundqvist[13] expression. If one subtracts the correlation energy that can be attributed to valence electrons in the atom according to the data contained in Table III of Ref. 14 (0.042 eV per atom), it can be concluded that the present estimate is quite reasonable.

Total and binding energy data for cubic beryllium were reported by Stoll and Preuss.[2] Using a simplified HF scheme and two or three *s*-type functions per atom, they obtained a total energy of -12.3516 a.u. per atom and binding energies of 0.10–0.13 a.u. per atom. Such a good agreement with the experimental values of the binding energy is clearly fortuitous; we have found, in fact, that the inclusion of *p*-type AO's, which is essential in determining the metallic character of beryllium, also lowers its energy by many eV per atom with respect to an *s*-only calculation. To our knowledge, the only other *ab initio* calculation reporting energy data is the one of Moruzzi *et al.*,[15] using a Korringa-Kohn-Rostoker (KKR) SCF local exchange and correlation method. They give a total energy value of 14.606 a.u. per atom corresponding to a binding energy of 0.146 a.u. per atom with respect to free atoms treated in the same approximation.

IV. BAND STRUCTURE AND DENSITY OF STATES

It is well known that HF eigenvalues give transition energies which are larger by a factor 1.5–2 with respect to the ones obtained by optical excitation experiments. Several methods have been proposed for correcting the HF band structure by taking correlation effects into account. For instance, Mickish *et al.*[16] achieved a substantial reduction of the HF bandwidths of calcium by applying the simple Overhauser's[17] model. It is worthwhile mentioning that such corrections left the shape of the Fermi surface and the topology of the band structure practically unaltered, which is indicative of the fact that the analysis of the uncorrected HF eigenvalues and eigenvectors can give useful information about the electronic properties of metal systems.

It is beyond the scope of the present work to investigate the optical properties of beryllium, and no correlation corrections were attempted. The calculated HF band structure is reproduced in Fig. 1. A number of calculated band structures of beryllium have been reported[18–22] and discussed[23–25] in the literature. They are based as a rule on the augmented plane wave (APW) method with different types of crystal potentials, and their agreement with experiment is generally good. As far as the topology of the occupied bands is concerned, all the reported calculations are very similar to each other and to the present results. In all cases, a maximum of three valence bands lie below ϵ_F and the first Brillouin zone (BZ) is completely occupied, in contrast with the prediction of the free-electron gas model. The experimentally reconstructed Fermi surface (FS) provided by Watts[26] from de Haas–van Alphen data consists of two separate pieces, a six-cornered coronet in the second BZ and a cigar in the third BZ, with major axis along the *HK* symmetry line. These features are reproduced by all the calculations; in addition, according to Taut's[19] results and to the present ones, a nearly spherical piece should occur around the Γ point in the third BZ. It is, however, to be

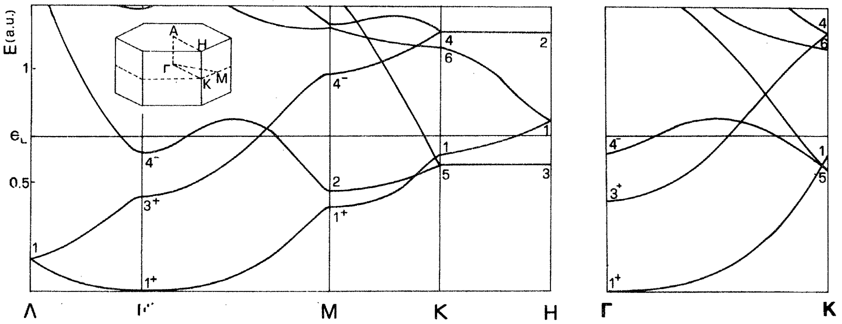

FIG. 1. Energy bands of beryllium along some symmetry lines (see scheme). Energies are measured from the bottom of valence bands.

observed that this result is critically dependent on the computational conditions. In fact, a minor change of the basis set ($\alpha = 0.29$ a.u. for the external Gaussian, instead of $\alpha = 0.27$) shifts the Γ_4^- eigenvalue above ϵ_F. The same result is obtained by increasing the lattice parameters: in correspondence of the calculated equilibrium conformation the Γ_4^- eigenvalue lies above ϵ_F.

Figure 2 shows the density of states whose most evident feature is the dip near ϵ_F. This dip has no relation at all with the extremely narrow singularity which is known to occur in the HF density of states of the electron gas, leading to zero density at ϵ_F. In fact, we found no indication of critical behavior in the immediate neighborhood of the Fermi level. The failure to identify this feature, which is believed to be characteristic of the HF treatment even in nonuniform systems,[16] is probably due to our using a relatively coarse net of $\vec{k}$ points when reconstructing the density of states. The need for a fine mesh of $\vec{k}$ points in order to give evidence for this kind of singularity has been clearly documented by Fry *et al.*[27] who numerically reconstructed the density of states of the electron gas using a basis set of Gaussian functions.

The general features of the data reported in Fig. 2 are similar to those resulting from previous non-HF calculations. The deep departure of beryllium valence electrons from free-electron behavior which was apparent in the band structure, is here even more evident. On the other hand, the simple "chemical" model proposed by Slater[23] (s and p bands essentially separated and overlapping only near ϵ_F) is clearly untenable. In fact, the great importance of the p states in the occupied portion of the DOS is evident from Fig. 2, and even the lowest valence band has a large p participation. On the whole, of the four valence electrons in the unit cell, only 1.18 correspond to s-type functions 0.95 to p_x, 0.95 to p_y, and 0.92 to p_z AO's. An indirect support to the large participation of p orbitals in the electronic structure of the ground state of beryllium is provided by Inoue and Yamashita[20] who proved that beryllium keeps to be a metal up to a constant by 1.6 times as large as the normal lattice.

It can therefore be concluded that the role of p electrons in characterizing the ground state of beryllium is more important than hitherto hypothesized; furthermore, it clearly appears that the way p_x and p_y electrons enter into the electronic structure of the fundamental state is very similar to that of p_z electrons.

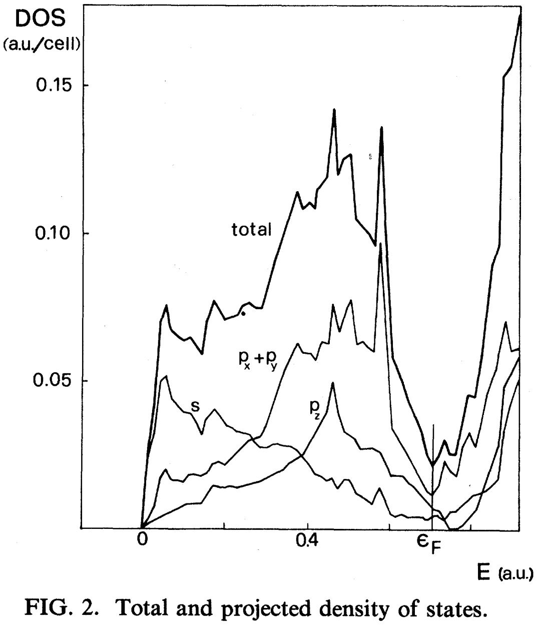

FIG. 2. Total and projected density of states.

V. CHARGE DENSITY AND STRUCTURE FACTORS

To gain deeper insight into the nature of the metallic bond in beryllium, it is interesting to compare its electronic density with the one obtained as a superposition of atomic distributions. Two differential maps (solid minus atomic superposition) are shown in Figs. 3 and 4 referring to sections through the atoms in a plane perpendicular to the $[11\bar{2}0]$ and $[0001]$ directions, respectively. The most characteristic feature of these maps is that the charge density in metallic beryllium looks quite different from what one would expect on the basis of a free-electronlike distribution. In fact, when passing from the atomic superposition (s only orbitals) to the metal, a large amount of charge is transferred from the nonbonding zones to the bonding ones. The differential density is negative near the nuclei because charge is transferred from s-type functions to protruding p orbitals; it is also negative along the large corridor including the octahedral sites, while it is positive along the first, second, and third neighbors's directions. In fact, the total charge density raises from 0.039 electrons per a.u.^{3} to 0.040 at the $B1$ point (see Fig. 3), from 0.038 to 0.040 at $B2$ and from 0.037 to 0.044 at $B3$: note that, unlike covalent systems, the buildup of charge is not strongly decreasing on going from

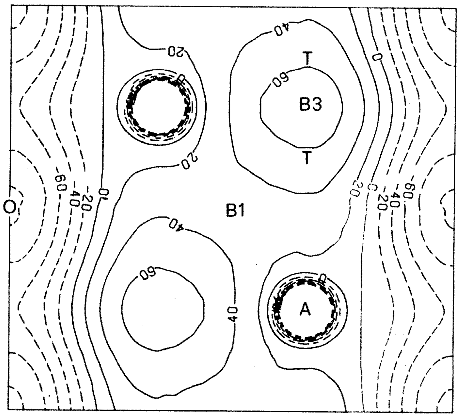

FIG. 3. Map of the difference between the electron charge density in the metal and the density resulting from a superposition of atomic distributions. The map is drawn in a plane through the nuclei perpendicular to the [11$\bar{2}$0] direction. The contour lines are drawn in intervals of 20×10^{-4} e/a.u.^{3}; lines of dashes correspond to a negative difference. A =atom; T =tetrahedral site; O =octahedral site; B1, B2, and B3 are the points midway, respectively, the first, second, and third neighbor's distance.

the first to the third neighbor directions, but it is about the same in the three cases with a maximum in the third-neighbor z direction. Figures 3 and 4 clearly point to the importance of directional p functions in characterizing the electron distribution in the metal: at the octahedral site, along the antibonding direction, the density is only two thirds of that resulting from superimposing atomic s-type distributions (0.021 electrons per a.u.^{3} and 0.031, respectively). The present results are quite at variance with those reported by Stewart[28] and by Yang and Coppens,[29] as reconstructed from the experimental structure factors of Brown.[30] In those cases the differential maps are negative only near the nuclei, and in the positive zones the differences are not as high as in the present calculation. Recently however, many doubts have been raised concerning the correctness of Brown's data, and new sets of experimental structure factors[31,32] are, in fact, quite different from the ones of Brown. In order to compare the different experimental sets with the theoretical structure factors, one must preliminarily correct the latter to include thermal motion. As shown in Table III, quite different values of the thermal parameters B_{11} and B_{33} of beryllium have been proposed in the literature. The various sets can be subdivided into two groups. The first three sets were obtained by best fitting with Brown's data; the other three[33,34] are independent estimates, though very near to each other. The overall agreement between the present data and the experimental structure factors can be described by the standard deviation σ or by the agreement factor defined as

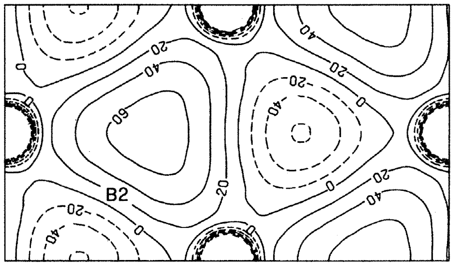

FIG. 4. Differential map as in Fig. 3, in a plane through the nuclei perpendicular to the [0001] direction.

$$R=\sum_i |F_i^{\mathrm{expt}}-F_i^{\mathrm{calc}}| \Big/ \sum_i |F_i^{\mathrm{expt}}| \ .$$

As shown in Table III, the choice of the thermal parameters can heavily affect both R and σ. The general picture is, however, very clear: the last three sets of thermal parameters bring to a very good agreement between the present data and the ones of Larsen; using the less reliable B parameters of the first three sets improves the overall agreement with Brown's data but the discrepancies are still very large. There is another indication that points to some kind of systematic error affecting Brown's data: in fact, they would indicate an appreciable expansion of the beryllium cores in the metal with respect to the isolated atom. This effect, however, is not observed in recent Compton scattering experiments[33,35] and is negligible according to our computations, as discussed at length in a separate paper.[36] In Table IV we have therefore considered only Larsen's data for a comparison with our calculated structure factors, corrected with the B parameters proposed by Manninen and Suortti.[33] It can be observed that, apart from a generally good agreement, the experimental factors are as a rule larger than the theoretical ones, especially at low indices. In comparing the contributions from the valence electrons in the metal with the corresponding ones from a superposition of atomic distributions (columns 6 and 7), it is seen that the latter are much lower. Again, we can conclude that the strong participation of p-type AO's in the definition of the ground state of the solid, makes the corresponding charge distribution more structured than the one obtained as atomic superposition.

TABLE IV. Experimental and calculated structure factors of beryllium. The numbers in parentheses in the second column are estimated errors on the last figures of the experimental data. The calculated data of column three have been corrected with the thermal-motion parameters proposed in Ref. 33 ($B_{11}=0.460$; $B_{33}=0.415$ Å^2).

hkil	Expt. Ref. 31	Solid corrected	Solid total	Atom total	Solid valence	Atom valence
$10\bar{1}0$	1.877(15)	−1.8923	−1.9486	−1.8174	−0.1533	−0.0192
$11\bar{2}0$	2.706(21)	2.6318	2.8740	2.9252	−0.0774	−0.0339
$20\bar{2}0$	1.210(10)	−1.1824	−1.3296	−1.3545	0.0188	−0.0022
$21\bar{3}0$	0.869(8)	−0.8683	−1.0663	−1.0812	−0.0112	−0.0232
$22\bar{4}0$	1.060(10)	1.0682	1.5191	1.5433	0.0283	0.0484
$30\bar{3}0$	1.415(12)	1.4208	1.8502	1.8773	0.0283	0.0505
$10\bar{1}1$	2.882(22)	−2.7983	−2.9049	−2.9734	0.1080	0.0457
$20\bar{2}1$	2.041(16)	1.9978	2.2647	2.2922	−0.0100	0.0111
$21\bar{3}1$	1.458(12)	−1.4590	−1.8061	−1.8318	−0.0204	−0.0412
0002	3.462(27)	−3.3984	−3.5097	−3.4817	−0.0020	0.0354
$10\bar{1}2$	1.493(12)	1.4345	1.5256	1.5570	−0.0626	−0.0358
$11\bar{2}2$	2.382(19)	−2.3304	−2.6281	−2.6644	0.0180	0.0105
$20\bar{2}2$	1.062(9)	1.0496	1.2190	1.2345	0.0034	0.0153
$21\bar{3}2$	0.768(7)	0.7703	0.9769	0.9910	0.0135	0.0249
$30\bar{3}2$	1.256(10)	−1.2671	−1.7041	−1.7300	−0.0290	−0.0504
$10\bar{1}3$	2.194(17)	2.1319	2.3604	2.3935	−0.0285	−0.0035
$20\bar{2}3$	1.567(13)	−1.5568	−1.8823	−1.9087	−0.0180	−0.0390
$21\bar{3}3$	1.150(9)	1.1540	1.5237	1.5466	0.0251	0.0439
0004	2.260(19)	2.2015	2.5043	2.5353	0.0030	0.0250
$10\bar{1}4$	1.007(8)	−0.9896	−1.1592	−1.1754	−0.0068	−0.0193
$11\bar{2}4$	1.619(13)	1.6120	2.0024	2.0314	0.0260	0.0491
$20\bar{2}4$	0.733(7)	−0.7297	−0.9334	−0.9472	−0.0141	−0.0253
$21\bar{3}4$	0.544(5)	−0.5482	−0.7658	−0.7780	−0.0142	−0.0248
$10\bar{1}5$	1.314(11)	−1.3070	−1.6461	−1.6705	−0.0241	−0.0436
$20\bar{2}5$	0.983(8)	0.9803	1.3483	1.3699	0.0247	0.0425
0006	1.221(11)	−1.2147	−1.6233	−1.6489	−0.0289	−0.0497
$10\bar{1}6$	0.554(5)	0.5534	0.7615	0.7739	0.0142	0.0243

TABLE V. Calculated directional Compton profiles for beryllium. The profiles are given from $q=0$ to 2.9 a.u. in intervals of 0.1.

			0001 profile		
1.929	1.446	0.500	0.305	0.217	0.147
1.886	1.323	0.413	0.284	0.201	0.136
1.808	1.196	0.377	0.264	0.186	0.126
1.693	1.058	0.351	0.246	0.171	0.117
1.569	0.807	0.327	0.233	0.159	0.108
			$10\bar{1}0$ profiles		
1.891	1.495	0.564	0.304	0.211	0.147
1.831	1.356	0.453	0.285	0.197	0.136
1.752	1.201	0.389	0.269	0.183	0.125
1.687	1.004	0.354	0.244	0.171	0.116
1.608	0.762	0.327	0.229	0.159	0.108
			$11\bar{2}0$ profile		
1.807	1.496	0.622	0.305	0.213	0.147
1.800	1.312	0.450	0.281	0.196	0.136
1.772	1.137	0.390	0.261	0.182	0.126
1.726	0.964	0.355	0.242	0.170	0.116
1.649	0.791	0.328	0.227	0.159	0.109

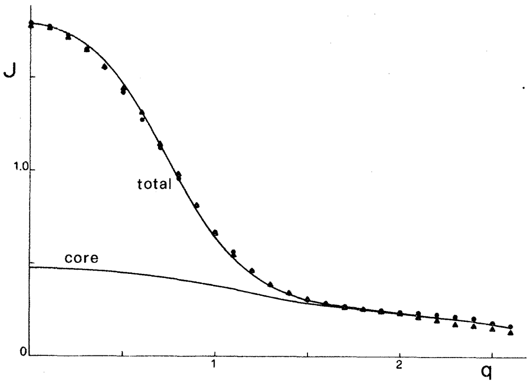

FIG. 5. Average, calculated, and experimental Compton profiles. Hansen's (Ref. 35) data (△) were obtained as an average over three crystallographic directions. Manninen's (Ref. 33) data (●) from a polycrystalline sample as well as the present ones were convoluted to account for limited experimental resolution, using Hansen's parameters. The "core" curve corresponds to the calculated contribution from the two core bands. Both J and q are measured in a.u.

VI. COMPTON PROFILES

Beryllium has been the object of several Compton scattering experiments[33,35,37–41]; owing to the very rapid progress that has been made in recent years, the most recent experimental results[33,35,41] are by far more reliable than the earlier ones. A number of recent theoretical calculations of Compton profiles (CP's) are also available.[38,42–44]

In this section we report preliminary results for the Compton profiles of beryllium; work is in progress to improve the numerical techniques we use to compute, from the HF eigenvectors, reciprocal space quantities related to the electron momentum distribution. Table V lists the calculated CP's in three directions up to 3 a.u. Further information about the high-momentum tail is reported in a separate study devoted to the description of the core electrons in beryllium.[36] When compared with the very accurate experimental results of Manninen *et al.*[33] and Hansen *et al.*,[35] our data show an excellent agreement, better in general than the one obtained with all previous calculations.[38,42–44] The quality of the agreement is apparent from Fig. 5 where we compare our average CP with the experimental data obtained from polycrystalline sample by Manninen[33] and with the arithmetical calculated average of Hansen's directional profiles.[35]

VII. CONCLUSIONS

It is generally believed that the HF approach is inadequate for the study of metallic systems. The results here presented show, on the contrary, that a number of ground state properties of a simple metal like beryllium can be satisfactorily accounted for within the HF approximation. It is important to stress that this comprehensive and substantially correct description of the electronic properties of beryllium (including binding energy, Fermi surface shape, electron charge, and momentum densities) has been obtained using the same technique that had given good results with nonconducting periodic systems. The only significant novelty with respect to previous work has been the need for an extended basis set; in fact, the standard minimal AO sets proposed for use in molecular calculations did not provide a proper description of the metallic character of the system.

Many-body corrections are needed, of course, if one is interested in quantities which are directly related with correlation effects, primarily the one-electron excitation energies and the dielectric matrix. In this respect, along with traditional ways to include correlation corrections according to more or less specific models,[16,17,45] powerful and general approaches are being explored,[46–48] based on Green's-functions techniques. We believe that the very considerable computational effort which is required when following the latter approach is worth being paid only if an accurate *ab initio* HF solution is chosen as the starting point for the iteration process.

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