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Pseudopotential Hartree-Fock study of seventeen III-V and IV-IV semiconductors

M. Causà, R. Dovesi, and C. Roetti
Department of Inorganic, Physical and Materials Chemistry, University of Torino, via Giuria 5, I-10125 Torino, Italy

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The binding energy (BE), the equilibrium lattice parameter (a_0), the bulk modulus (B), and the central-zone transverse-optical phonon frequency (ν) of seventeen diamond- and zinc-blende-type-structure semiconductors involving atoms belonging to the second to fifth periods have been evaluated. The periodic *ab initio* Hartree-Fock linear-combination-of-atomic-orbitals program CRYSTAL has been used. Core pseudopotentials have been adopted in order to limit the calculation to valence electrons. Thirteen atomic orbitals ($2s,6p,5d$) per atom have been used. The quality of the pseudopotential results is checked by comparison with all-electron calculations performed on six light-atom systems (diamond, silicon, BN, BP, AlP, SiC). The mean errors of the pseudopotential calculations with respect to experimental data are -38%, $+1.2\%$, $+6.5\%$, and $+7.8\%$ for BE, a_0, B, and ν, respectively. A correlation-only density-functional *a posteriori* correction to the Hartree-Fock total energy is performed, which reduces the absolute BE mean error to 2.6%.

I. INTRODUCTION

The Hartree-Fock (HF) linear-combination-of-atomic-orbitals (LCAO) method is by far the most popular computational technique among quantum chemists for the study of the electronic structure of molecules. Standard programs have been available for at least fifteen years.[1] On the other hand, the HF technique is usually believed to perform very poorly on solid-state problems. This opinion is mainly based on electron-gas results, in particular on the incorrect behavior of the HF density of states at the Fermi energy.[2,3] Besides, the implementation of a periodic HF-LCAO computational scheme is not trivial, due to the nonlocal nature of the exchange term, the large number of four-center integrals to be computed, and the nonorthogonal nature of the basis set. For these reasons few periodic HF-LCAO computational schemes have been proposed,[4] and, as far as we know, only one [CRYSTAL (Ref. 5)] general-purpose computer program has been implemented in the past twenty years.

CRYSTAL,[5-9] implemented by the present authors and collaborators, is able to treat systems of any symmetry periodic in three (crystals), two (slabs), one (polymers), and zero (molecules) dimensions; it has been applied to quite different classes of compounds: ionic crystals,[10] semiconductors,[11,12] molecular crystals,[13] silicates,[14] and chemisorption problems.[15]

In the present paper the HF-LCAO scheme is applied, in conjunction with effective-core pseudopotentials (ECP's), to the study of a large set (seventeen) of *AB* semiconductors with the diamond and zinc-blende structure. Attention is directed to four ground-state properties, namely the binding energy (BE), the equilibrium lattice parameter (a_0), the bulk modulus (B), and the central-zone phonon frequency (ν). The aims of the present study are the following.

(i) First is the comparison of ECP versus all-electron[12] (AE) calculations, performed on a small subset of systems (diamond, silicon, BN, BP, AlP, SiC), in order to estimate the error introduced by the ECP's (Ref. 16) and, more generally, to assess the validity of the "frozen-core" concept.

(ii) Second is the comparison of ECP calculations with previous *ab initio* results, in order to check the performance of the HF-LCAO technique as implemented in CRYSTAL. As a matter of fact, nearly all *ab initio* calculations for crystalline compounds are performed with reference to density-functional (DF) Hamiltonians;[17] very often plane waves (PW's) are used as basis functions, in conjunction with ECP's.[18]

(iii) Third is the comparison of ECP results with experimental data, in order to check the mean error and its dependence on the adopted basis set and computational accuracy. From the molecular experience gained in the past twenty years the mean error on the different computed quantities due to the use of the HF Hamiltonian is well documented. It is of some interest to verify whether the HF performances for periodic compounds are similar to the ones for molecules, and to ascertain if the errors due to the finite basis set and the numerical approximations are negligible with respect to those related to the use of the HF Hamiltonian. If this is the case, and if the computational cost of each energy point is reasonably low, the time is probably ripe for tackling the "correlation correction" problem in a systematic way.

The simplest way of taking into account correlation effects on total energy is to apply correlation-only density-functional formulas to the HF charge density, as proposed by Colle and Salvetti[19] or, more recently, by Perdew.[20] This scheme is quite simple to implement, and the results for the systems investigated here will be presented in the following sections.

Alternatively, many-body-perturbation-theory methods or the closely related coupled-electron-pair models[21] should presently be transferred from the molecular to the nonmetallic crystalline context. Indeed, recent calculations based on coupled-electron-pair approximation (CEPA-0) formalism have been carried out for diamond[22] and silicon.[23] In another interesting development, the quantum Monte Carlo method[24] has been applied to diamond with some success.[25] In both cases the reference Slater determinant has been obtained by local-density approximation (LDA) calculations. One may expect that the HF method will prove useful in supplying a quite reasonable and well-defined starting point for both techniques.

As far as we know, the present paper represents the most systematic study at the *ab initio* level of the abovementioned properties of III-V semiconductors. Other recent investigations, similar to the present one, refer to a smaller set of systems.[26–34]

The plan of the paper is as follows. In Sec. II some computational details are provided. Sections III and IV are devoted to the illustration of the adopted ECP's and basis sets. In Sec. V ECP and AE results are compared. Sections VI and VII are devoted to the comparison with experimental data, and to the Perdew's correlation correction to the HF total energy. In Sec. VIII previous *ab initio* calculations are analyzed, and conclusions are drawn in Sec. IX.

II. COMPUTATIONAL DETAILS

The HF LCAO scheme, as implemented in CRYSTAL, has been described extensively in previous work.[6–9] We simply comment here that in the solution of the HF equations, approximations are introduced both in the treatment of the Coulomb and exchange series (which involve three summations on four-center integrals extended in principle to the infinite set of lattice vectors) and in the reciprocal space integration required at each step of the self-consistent procedure in order to define the iterated density matrix. The related error on the total energy and the wave function can be reduced by adopting stricter computational conditions, with a corresponding increase in the cost of the calculation.[9] With the computational conditions adopted for the present work, the estimated "intrinsic" error (that is excluding correlation and basis-set effects) in the total energy is of the order of 0.001 a.u./cell. The corresponding cost per energy point in CPU time is about 20 min on an IBM 3090 computer in scalar mode.

The BE, a_0, and B parameters have been evaluated numerically by interpolating the energy points with a Murnaghan state function.[35] Eight energy points in the lattice-parameter interval $a_0(\text{expt})\pm5\%$ have been used. The transverse-optical phonon frequency at the Γ point was calculated in the frozen-phonon approximation by a fourth-order polynomial fit of the energy versus displacement values (six points in the range $d_0\pm3\%$, where d_0 is the atom-atom distance).

The "numerical noise" related to the truncation of the Coulomb and exchange infinite series and to the reciprocal space integration is not constant as a function of the geometry and has some influence on the fitted parameters, in particular on those related to the second derivative of the energy. From a systematic analysis of this problem performed in a previous paper,[12] it appears that with the computational conditions adopted here the error due to numerical noise is 1%, 0.1%, and 1.5% for the BE, a_0, and B, respectively.

III. PSEUDOPOTENTIAL

In a preliminary stage of this work we considered three families of tabulated ECP's, namely those implemented by Barthelat and Durand,[36] Stoll and Preuss,[37] and Hay and Wadt.[38] On the basis of the better agreement with all-electron results for two test systems (silicon and AlP), the Barthelat and Durand ECP's have then been chosen for the subsequent calculations, although the comparison of the performance of different pseudopotentials deserves further analysis. The semilocal model potential W_{ps} used in Ref. 36 is defined as follows:

$$W_{\text{ps}}=-\frac{z}{r}+\sum_{l} W_l(r)P_l \ , \tag{1}$$

where z is the net charge of the core and P_l is the angular momentum projection operator

$$P_l=\sum_{m=-l}^{l} |Y_l^m\rangle\langle Y_l^m| \ . \tag{2}$$

The radial function $W_l(r)$ is defined as follows:

$$W_l(r)=\exp(-\alpha_l r^2)\sum_{k=1}^{M} C_k r^{n(k)} \ . \tag{3}$$

The parameters C, α, and n are specific for each atom and are determined by requiring that the valence eigenvalues and eigenvectors of the pseudo-Hamiltonian are as close as possible to the all-electron results. The parameters for B, C, N, Al, Si, P, Ga, Ge, and As can be found in Ref. 39, those for In, Sn, and Sb, provided to us privately by the authors,[36] are reported in the Appendix.

Recently, a systematic comparison between all-electron and pseudopotential calculations has been performed by Bouteiller *et al.*,[39] on a set of seventeen biatomic molecules with elements belonging to the first three periods: the mean difference in the binding energies, equilibrium parameters, and force constants was 5.2%, 0.6%, and 2.8%, respectively.

Regarding periodic compounds, preliminary tests with the ECP version of CRYSTAL have been performed on lithium, diamond, silicon, and magnesium oxide.[40] An application to PbF_2 (Ref. 41) gave quite reasonable results.

IV. BASIS SET

For each atom thirteen "atomic orbitals" (AO) have been used, namely two *s*-, six *p*-, and five *d*-type functions. Each AO is a linear combination of n Gaussian-type functions (GTF's); a GTF is the product of a Gaussian $\exp(-\alpha r^2)$ times a real solid harmonic X_l^m.[9] For computational efficiency, s and p GTF's share the same exponent, and are said to belong to the same shell. In the present case the AO's of the less diffuse *sp* shell are a contraction of two GTF's, whereas the other *sp* shell and the *d* shell contain a single GTF. This basis is indicated as $21G^*$ according to Pople's nomenclature.[42] The exponents and the contraction coefficients have been optimized in the isolated atom; the corresponding atomic energy has been used for the evaluation of the binding ener-

TABLE I. Valence $21G^*$ basis sets. The exponents α (in a.u.) and the coefficients c of the two Gaussian contractions have been optimized in the isolated atoms. The exponents of the single Gaussian *sp* and *d* shells have been optimized in each compound. The coefficients multiply individually normalized Gaussians.

	Two Gaussian contraction			Outer shells					
	α_{sp}	c_s	c_p		α_{sp}	α_d		α_{sp}	α_d
C	2.927 124	−0.146 932	0.165 474	Diamond	0.20	0.80	SiC	0.18	0.80
	0.659 924	0.416 847	0.487 652						
Si	0.882 959	−0.384 853	−0.037 572	Si	0.12	0.50	SiC	0.19	0.50
	0.316 466	0.675 644	0.486 130						
Ge	1.223 024	−0.271 876	−0.050 750	Ge	0.09	0.45			
	0.253 814	0.646 354	0.524 692						
Sn	0.664 045	−0.531 536	−0.094 875	Sn	0.08	0.20			
	0.236 154	0.858 798	0.474 750						
B	1.877 541	−0.158 573	0.152 725	BN	0.19	0.80	BP	0.12	0.80
	0.404 463	0.449 301	0.482 679	BAs	0.12	0.70			
Al	0.815 343	−0.307 155	−0.074 279	AlP	0.12	0.35	AlAs	0.12	0.33
	0.221 894	0.583 305	0.444 160	AlSb	0.12	0.35			
Ga	1.012 705	0.301 302	0.066 299	GaP	0.12	0.30	GaAs	0.12	0.33
	0.225 987	0.638 168	0.443 827	GaSb	0.12	0.30			
In	0.611 613	−0.470 636	−0.069 553	InP	0.10	0.30	InAs	0.10	0.25
	0.203 043	0.781 470	0.381 890	InSb	0.09	0.30			
N	4.361 996	−0.143 954	0.170 537	BN	0.28	0.80			
	0.959 344	0.405 945	0.503 902						
P	1.085 341	−0.440 209	−0.050 750	BP	0.13	0.50	AlP	0.13	0.55
	0.438 259	0.695 685	0.524 692	GaP	0.13	0.50	InP	0.13	0.50
As	1.142 537	−0.741 188	−0.164 649	BAs	0.13	0.40	AlAs	0.12	0.55
	0.438 335	0.622 801	0.503 264	GaAs	0.13	0.55	InAs	0.13	0.50
Sb	0.652 716	−0.818 377	−0.199 304	AlSb	0.10	0.25	GaSb	0.10	0.20
	0.334 043	1.044 557	0.544 199	InSb	0.10	0.30			

gy. The α exponent of the "outer" *sp* shell and of the *d* shell have then been reoptimized for each crystalline compound. The resulting basis sets are reported in Table I. From molecular experience and a few tests on periodic compounds we estimate the basis-set error (that is, the difference between the results obtained with a "complete" and with the present basis set) to be around 0.3% and 3% for the lattice parameters and the force constants, respectively. Systematic calculations with an additional (more diffuse) *sp* shell or with a second set of polarization functions are at the moment out of reach, for cost and computational reasons.

V. PSEUDOPOTENTIAL VERSUS ALL-ELECTRON RESULTS

In Table II the ECP and the corresponding AE results are reported for six systems, containing atoms of the second and third period. The AE data have been obtained with a basis set whose valence part is as similar as possible to that reported in Table I. In particular we used the same exponents for the most diffuse *sp* shell as for the ECP calculation. The core functions are a contraction of six GTF's. The ECP data well reproduce the AE data: the mean percentage errors, reported at the

TABLE II. Comparison of effective-core potential (ECP) and all-electron (AE) results: binding energy (BE) per atom couple, equilibrium lattice parameter (a_0), bulk modulus (B), and frequency of the transverse-optical phonon mode at the Γ point (ν). $\Delta\%$ is the ECP percentage error evaluated with respect to AE data. $\langle|\Delta\%|\rangle$ and σ are the average and the standard deviation of the percentage absolute errors.

	BE (eV)			a_0 (Å)			B (GPa)			ν (THz)		
	ECP	AE	$\Delta\%$	ECP	AE	$\Delta\%$	ECP	AE	$\Delta\%$	ECP	AE	$\Delta\%$
C	10.41	10.78	−3.4	3.58	3.57	+0.1	471	476	−1.1	44.5	44.5	0.0
Si	6.26	6.05	+3.5	5.46	5.50	−0.8	109	107	+1.9	17.9	16.9	+5.9
SiC	9.03	8.91	+1.3	4.39	4.39	0.0	245	238	+3.4	25.8	25.5	+1.2
BN	9.10	9.62	−5.4	3.62	3.62	+0.1	416	416	0.0	34.4	33.8	+1.2
BP	6.56	6.45	+1.7	4.61	4.60	+0.3	171	170	+0.6	27.4	27.5	−0.4
AlP	5.69	5.46	+4.2	5.52	5.55	−0.6	96	92	+4.3	14.0	13.6	+2.9
$\langle\|\Delta\%\|\rangle$			3.2			0.3			1.8			1.9
σ			1.5			0.3			1.7			2.2

bottom of the table, are similar to those obtained in an analogous comparison performed on a set of diatomic molecules (see Sec. III and Ref. 39). Part of the error can probably be traced to basis-set effects (the same valence set can have a different efficiency in ECP or AE calculations) and to a different influence of numerical noise, in particular in the evaluation of B and ν. In some cases (Si and AlP, in particular), however, the largest component of the error is to be attributed to "genuine" pseudopotential effects, which can then be as large as 1% for the lattice parameter and 6% for the force constants.

TABLE IV. Statistical analysis of the ECP vs experimental data. Maximum (maxΔ%), minimum (minΔ%), mean ($\langle \Delta\% \rangle$), and standard deviation (σ) of the percentage errors are reported. N denotes the number of the data.

	a_0	B	ν
maxΔ%	+2.3	+11.8	+16.6
minΔ%	0.0	0.0	+1.0
$\langle \lvert\Delta\%\rvert \rangle$	1.2	6.5	7.8
σ	0.7	3.6	4.7
N	17	15	16

VI. PSEUDOPOTENTIAL VERSUS EXPERIMENTAL RESULTS

In Table III the calculated equilibrium parameter, bulk modulus, and phonon frequency for the seventeen systems considered here are compared with the available experimental data; nearly all the experimental results are from Ref. 43. In the case of BAs only the lattice parameter appears to be known. The experimental bulk modulus of BN is not available.

The data of Table III (and of Table IV, where some statistical data are reported) give rise to the following comments.

Lattice parameter. The error ranges from 0% to +2.3%, the mean being +1.2%. This overestimation of the bond lengths is due to the HF Hamiltonian; the mean error is in line with molecular experience.[42] At the two extremes, the large error for germanium could be related to the large relative importance of correlation effects in this compound, whereas the exact value for BN can be explained by the fact that correlation effects are smaller for second-period compounds. The exact value for Sn is, on the contrary, anomalous when compared to the errors for systems with atoms of the same or of the "previous" period (InSb, InAs, GaSb, GaAs, Ge). The considerable overestimation in the family GaP, GaAs, and GaSb may be related to some inadequacy of the Ga pseudopotential.

Bulk modulus. The error ranges from 0% to +12%, the mean error being +6.5%, with $\sigma = +3.5\%$. The error is again a maximum for Ge, followed by Si and AlP, and decreases for heavier systems; the overestimation of the force constants is in line with the expected behavior for HF solutions.[42]

Transverse-optical phonon frequencies. The pattern or error is similar to that for the bulk modulus; the error reduces going down the Periodic Table, the mean error being slightly larger (+7.8%). The maximum error refers to tin, and is equal to +16.6%; also the silicon error (+15.4%) is abnormally large. It is difficult to explain the Sn and Si anomalous behavior; in our opinion, in Si there is certainly some problem with the ECP (see the comparison with AE results in Sec. V), whereas in Sn the problem could be related to the nometallic HF solution for this system (see Sec. VII).

On the whole, the results appear quite satisfactory

TABLE III. Comparison of ECP and experimental results. Symbols and units as in Table II. ECP percentage errors Δ% are evaluated with respect to the experimental data.

		a_0 (Å)			B (GPa)			ν (THz)	
	calc.	expt.	Δ%	calc.	expt.	Δ%	calc.	expt.	Δ%
C	3.58	3.57^a	+0.3	471	442^a	+6.6	44.5	39.9^a	+11.4
Si	5.46	5.43^a	+0.6	109	99^a	+10.1	17.9	15.5^a	+15.4
Ge	5.79	5.66^a	+2.3	85	76^a	+11.8	10.1	9.1^a	+10.8
Sn	6.49	6.49^a	0.0	56	53^a	+5.7	7.0	6.0^a	+16.6
SiC	4.39	4.36^a	+0.7	245	228^a	+7.5	25.8	23.5^d	+9.8
BN	3.62	3.62^a	0.0	416			34.4	31.8^a	+8.1
BP	4.60	4.54^a	+1.3	171	173^c	−1.2	27.4	24.6^a	+11.3
BAs	4.83	4.78^a	+1.0	149			30.3		
AlP	5.52	5.45^a	+1.3	96	86^a	+11.6	14.0	13.3^a	+5.5
AlAs	5.76	5.66^a	+1.8	79	77^a	+2.6	11.4	10.9^a	+4.3
AlSb	6.22	6.13^a	+1.5	61	58^a	+5.2	10.5	9.6^a	+8.9
GaP	5.56	5.45^a	+2.0	95	91^a	+4.4	11.3	11.0^a	+2.8
GaAs	5.76	5.65^a	+1.9	77	77^a	0.0	8.2	8.1^a	+1.0
GaSb	6.23	6.12^b	+1.8	59	56^a	+5.4	7.2	6.9^a	+4.9
InP	5.93	5.87^a	+1.0	76	72^a	+5.6	9.6	9.2^a	+4.4
InAs	6.15	6.06^a	+1.5	64	58^a	+10.3	6.8	6.6^a	+3.2
InSb	6.56	6.47^a	+1.4	50	46^a	+8.7	5.8	5.5^a	+6.3

[a] Reference 43.
[b] Reference 44.
[c] Reference 26.
[d] Reference 32.

from the point of view of consistency and homogeneity. The errors related to numerical, basis-set, and ECP effects appear to be a small fraction of the total error, which is then mainly determined by the "correlation error."

VII. BINDING ENERGY AND CORRELATION CORRECTION

The Hartree-Fock binding energies per unit cell are reported in Table V. The error, due to the lack of electronic correlation, ranges from -30% to -50% and is qualitatively in line with molecular experience; basis-set and accuracy effects are expected to be of the order of 2–3 %.

Correlation-only density functionals have been known for a long time to be quite effective in correcting HF total energies. A review of the most popular functionals and many applications to atoms and molecules can be found in Ref. 46. In the present work the functional recently proposed by Perdew[20] has been adopted:

$$E_c=\int d^3r\,\rho(r)\varepsilon_c(\rho_\downarrow,\rho_\uparrow)+\int d^3r[d^{-1}e^{-\Phi}C(\rho)|\nabla\rho|^2/\rho^{4/3}]\,, \tag{4}$$

where d is function of the (HF) spin density, ε and C are functions of the charge density, and Φ depends on the gradient of the charge density too.[20] The above formula contains a parameter in the Φ function, which has been chosen to fit the exact correlation energy of the neon atom. The application of Eq. (4) in the case of crystalline compounds is straightforward; the integration is performed numerically, and the cost is slight. Other correlation-only formulas, such as that proposed by Colle and Salvetti,[19] have also been tested;[47] they perform systematically worse, at least for this class of compounds.

The results are reported in Table V. The correlation correction is very effective: the mean error drops from 39.2% to 2.6%. All but one of the corrected BE's are in the range of ±4.2%. This is an excellent result if one takes into account the large number of systems considered and that part of the error could be due to basis-set and accuracy problems. The Sn BE is quite anomalous, with an error 2.5 times larger than the largest of the remaining set. This behavior may be related to the fact that metallic Sn is described at the HF level as an insulator (the indirect gap is 4.8 eV large). This implies a covalent rather than metalliclike charge distribution, with a consequent excessive correlation correction. Further analysis is, however, required, with reference to other metallic compounds, in order to clarify the problem. Note that when Sn is excluded from the statistics the BE mean error reduces to 2.0%.

VIII. COMPARISON WITH OTHER *AB INITIO* RESULTS

In the past decade diamond, silicon, germanium, and the III-V semiconductors have been the object of a large number of calculations with many kind of Hamiltonians, basis sets, and computational techniques. We will limit the comparison to a few first-principles calculations refer-

TABLE V. Hartree-Fock binding energy per unit cell (in eV) and correlation correction using Perdew's (P) density functional. $\Delta\%$ denotes the percentage error evaluated with respect to the experimental data. max$\Delta\%$, min$\Delta\%$, $\langle|\Delta\%|\rangle$, σ, and N as in Table IV. Data in parentheses exclude Sn from statistics. Experimental BE's have been calculated from thermochemical data from Ref. 45 and corrected for the zero-point lattice vibration energy, estimated from Debye temperatures reported in Ref. 43.

	HF	$\Delta\%$	P	HF+P	$\Delta\%$	Expt.
C	10.4	−30.8	4.3	14.7	−2.4	15.1
Si	6.3	−34.0	3.2	9.5	−0.7	9.5
Ge	4.4	−43.5	3.1	7.5	−4.2	7.8
Sn	4.2	−34.2	2.8	7.1	+10.7	6.4
SiC	9.0	−30.3	3.8	12.8	−1.4	13.0
BN	9.1	−33.1	4.0	13.1	−3.8	13.6
BP	6.6	−36.7	3.6	10.2	−1.9	10.4
BAs	5.6		3.6	9.2		
AlP	5.7	−32.4	3.0	8.7	+3.3	8.4
AlAs	4.9	−38.3	3.0	7.9	−1.3	8.0
AlSb	4.0	−39.5	2.8	6.8	+3.0	6.6
GaP	4.2	−41.4	3.0	7.2	+0.0	7.3
GaAs	3.5	−47.3	3.0	6.5	−2.8	6.6
GaSb	3.0	−50.2	2.8	5.8	−3.2	6.0
InP	3.9	−41.5	2.8	6.7	+1.0	6.6
InAs	3.5	−44.5	2.8	6.3	−0.2	6.3
InSb	2.8	−49.6	2.7	5.5	−0.9	5.6
max$\Delta\%$		−50.2			+10.7	(+3.3)
min$\Delta\%$		−30.3			−4.2	(−4.2)
$\langle\|\Delta\%\|\rangle$		39.2			2.6	(2.0)
σ		6.7			2.5	(1.3)
N		16			16	(15)

ring to the properties considered. The set of papers analyzed, although far from complete, should be representative of the state of the art in this field.

In three recent papers[26–28] by Cohen and co-workers, the most popular first-principles technique, the density-functional plane-waves pseudopotential (PP) scheme, is applied to most of the system investigated in the present paper: BN and BP,[26] SiC, Si, and C,[27] and the systems at the bottom of Table V, from AlP to InSb.[28] The mean absolute error for this last set of data (nine systems) is 1.3% for a_0 and 3.6% for B. For the complete set of systems reported in Refs. 25–27 the numbers are 0.9% (a_0, 14 data) and 3.9% (B, 13 data). The binding-energy error ranges from 4.5% for Si to 12.3% for BP. Those numbers are to be compared with the HF-LCAO mean errors reported above, namely 1.2% (a_0), 6.5% (B), and 2.6% (BE plus correlation correction). The difference in the values obtained for the same property by different authors (for example, the bulk modulus of silicon, which is 88, 92, 88, 93, and 96 GPa in Refs. 48, 27, 33, 34, and 49, respectively) are probably related to the most critical parameter of the DF PW ECP scheme, namely the number of plane waves, as suggested from more recent revisitations of the same problem.[50]

DF PP computational schemes based on localized functions (pseudoatomic orbitals) have been presented, among others, by Chelikowsky and Louie[29,30] and by Jansen and Sankey.[31] As stated by Chelikowsky,[30] with this variant of the method "typically, one has confidence in the calculated cohesive energies to within 10%, the lattice parameters to within 2–3 %, and the bulk modulus to within 5%." With regard to Jansen and Sankey,[31] in their study of ten systems (IV-IV, III-V, and II-VI) they obtained errors around −2% for a_0, around 8% for B, negligible for ν (the data are not tabulated, but presented in figures). The mean errors in the "LCAO" version of the DF PP scheme are slightly larger than in the PW variant discussed above (this could be related to some inadequancy of the computational scheme, which is somewhat cumbersom when local functions are involved). A rather different DF-based scheme is the linear muffin-tin orbital approach,[51] which has been applied to many classes of compounds. Recently, in its "full-potential" version it has been used to compute ν for 13 III-V and II-VI semiconductors, the mean error with respect to experiment being 5.6%.[32]

On the whole, the HF LCAO data appear no worse than other *ab initio* results obtained with DF-based Hamiltonians; the HF binding energies, when corrected with the Perdew's functional, are much more accurate than the DF-based results, which, in general are ". . . too large. This is a well-known failure of the local-density approximation (LDA), rather than of our method, and the size of the discrepancy depends somewhat on the parametrization used."[50] It is possible that gradient corrected formulas, such as that proposed by Perdew, are able to improve in a systematic way the semiconductor LDA binding energies.

IX. CONCLUSIONS

The HF ECP LCAO scheme provides quite reasonable and homogeneous results for the seventeen compounds here considered. The largest part of the error with respect to the experimental data is probably to be attributed to the "correlation effects," although the data of Table II show that there is a non-negligible contribution from the ECP. This last point deserves further investigation, and other sets of ECP's are to be tested in order to minimize the discrepancy with respect to AE results. The results for a_0, B and ν are, in the mean, of a similar quality to those provided by other techniques, as discussed in Sec. VII. With regards to the binding energy, the HF plus correlation data reported in Table V are consistently better than the ones obtained with other techniques.

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APPENDIX

The pseudopotential parameters (in a.u.) for In, Sn, and Sb are shown in Table VI. The explicit form of the pseudopotentials is given in Eq. (3).

TABLE VI. Pseudopotential parameters (in a.u.) for In, Sr, and Sb.

				In				
l	M	α	C	n	C	n		
0	2	1.284 762	25.839 362	0	−10.748 624	2		
1	2	0.533 692	4.411 853	0	−0.868 271	2		
2	2	0.644 864	−1.985 157	−2	6.775 058	0		
				Sn				
l	M	α	C	n	C	n		
0	2	1.448 025	30.189 20	0	−12.333 380	2		
1	2	0.620 580	6.264 13	0	−1.343 072	2		
2	2	0.441 197	5.483 58	0	−0.711 756	2		
				Sb				
l	M	α	C	n	C	n	C	n
0	2	1.664 152	35.945 630	0	−14.390 404	2		
1	3	2.836 008	28.525 732	0	−76.911 577	2	103.591 680	4
2	2	0.458 698	2.018 698	−2	0.563 297	0		

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