

# Quasirelativistic *ab initio* model potential calculations on the group IV hydrides (XH<sub>2</sub>, XH<sub>4</sub>; X=Si,Ge,Sn,Pb) and oxides (XO; X=Ge,Sn,Pb)

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In this paper we present the results of a systematic comparison between the values of the bond lengths, bond angles, and vibrational frequencies of group IV dihydrides and tetrahydrides (XH<sub>2</sub>, XH<sub>4</sub>, X=Si,Ge,Sn,Pb), and monoxides (XO, X=Ge,Sn,Pb), as well as the XH<sub>4</sub>→XH<sub>2</sub>+H<sub>2</sub> reaction energies, calculated with the spin-free (Cowan–Griffin based) quasirelativistic *ab initio* core model potential method (AIMP) and the all-electron Dirac–Hartree–Fock method (DHF), using basis sets of similar quality in their valence part. The deviations between the AIMP and DHF results on the absolute values of the properties and on the sizes of the relativistic effects are of the order expected for an effective core potential method and follow the expected tendency of importance of the spin–orbit effects. The quality of the AIMP results is shown to be consistent going down the group IV of the Periodic Table.

## I. INTRODUCTION

Effective core potential (ECP) methods are widely used as a practical means for including, in an approximate manner, relativistic effects in molecular and solid state electronic structure calculations.<sup>1</sup> Some of these methods rely on the pseudorbital transformation and are known as pseudopotential methods.<sup>2–6</sup> Others do not rely on this transformation and rather handle node-showing valence orbitals which are approximations to the all-electron ones; these are known as model potential methods<sup>7–10</sup> and effective core potential methods.<sup>11</sup> What they all have in common is that they incorporate the contributions of the major relativistic effects into the effective core potential, so enabling the calculations to be performed within traditional nonrelativistic schemes, if the spin-free core potentials are used; moreover, inclusion of spin–orbit effects does not usually mean dramatic changes in the computational methods.<sup>12–16</sup> Probably it is this simplicity that made them so popular for the study of relativistic effects,<sup>1</sup> together with the reliability of the results, which has been made apparent mainly from comparison with experiments, since results of Dirac–Hartree–Fock (DHF) calculations, of which the relativistic ECP methods are an approximation, were scarcely available.<sup>17,18</sup>

Recently, efficient DHF codes have been developed and the results of systematic DHF calculations on molecules are being available,<sup>19–24</sup> so providing a standard for comparison of the relativistic ECP methods. For methods which do not include spin–orbit effects, the all-electron no-pair approximation<sup>25</sup> could perhaps provide a better standard, but DHF should be a good one as long as the spin–orbit effects are not large. DHF results on the group IV dihydrides, tetrahydrides, and monoxides, have been recently published<sup>19,20–22,24</sup> and systematic comparisons with a series of relativistic pseudopotential methods have been performed,<sup>20–22</sup> reaching the conclusion that none of the sets of the relativistic pseudopotentials examined showed a consistent quality going down the group IV of the Periodic

Table. To our knowledge, no systematic comparisons with quasirelativistic model potentials or ECP's using node-showing valence orbitals has been published for this group.

In Ref. 9, the quasirelativistic version of the *ab initio* model potential method (AIMP) was proposed, following Katsuki and Huzinaga;<sup>15</sup> it shows the peculiar characteristics: (i) The effective core potentials are not parameterized in order to reproduce valence properties of any kind, rather, they are obtained directly from the core orbitals which are arbitrarily kept frozen in the molecular calculation; in a quasirelativistic calculation, these core orbitals come from a Cowan–Griffin–Hartree–Fock atomic calculation.<sup>26</sup> (ii) Spectral representations of the mass-velocity and Darwin potentials corresponding to the atomic valence orbitals are added to the effective core potentials, so making these relativistic effects explicit. The AIMP quasirelativistic results compared successfully with the available DHF calculations of Lee and McLeen<sup>17</sup> on AgH.<sup>9</sup>

In this paper we present a systematic comparison of the DHF and the quasirelativistic AIMP results on the group IV hydrides and oxides, in order to monitor the quality of the spin-free quasirelativistic model potentials and basis sets<sup>10</sup> and their ability to represent genuine relativistic effects in a consistent manner going down a group of the Periodic Table.

## II. METHOD

The one-electron contribution to the quasirelativistic AIMP valence Hamiltonian of a molecule is<sup>9,10</sup>

$$h(i) = -\frac{1}{2}\Delta_i - \sum_I (Z^I - Z_{\text{core}}^I)/r_{iI} + \sum_I V^{I,\text{AIMP}}(i), \quad (1)$$

$$V^{I,\text{AIMP}}(i) = V_{\text{Coul}}^{I,\text{MP}}(i) + V_{\text{exch}}^{I,\text{MP}}(i) + V_{\text{MV}}^{I,\text{MP}}(i) + V_{\text{DW}}^{I,\text{MP}}(i) + P^I(i), \quad (2)$$

where  $I$  runs over the nuclei. In order to obtain all the components of the AIMP, an atomic all-electron numerical Cowan–Griffin–Hartree–Fock calculation<sup>26</sup> is firstly performed, of which the core orbitals and the valence mass-

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velocity and Darwin potentials obtained at self-consistency are stored. With these, the atomic core model potential components are built; they are as follows.

(i) The Coulomb core model potential,

$$V_{\text{Coul}}^{I,\text{MP}}(r_{II}) = \sum_k \frac{A_k^I \exp(-\alpha_k^I r_{II}^2)}{r_{II}}, \quad (3)$$

where the parameters  $\{A_k^I, \alpha_k^I\}$  are determined through least-squares fitting to the genuine core Coulomb operator (including  $-Z_{\text{core}}^I/r_{II}$ ) corresponding to the Cowan–Griffin core orbitals.

(ii) The core exchange model potential plus the relativistic mass-velocity and Darwin model potentials, which are the spectral representation of the genuine operators on the subset of the molecular primitive basis set that is centered on each nucleus (note that the mass-velocity and Darwin potentials have already been fixed in the atomic calculation<sup>26</sup> and they will never change during molecular self-consistency, so that boundary conditions at the nuclei are fulfilled):

$$V_{\text{exch}}^{I,\text{MP}}(i) + V_{\text{MV}}^{I,\text{MP}}(i) + V_{\text{DW}}^{I,\text{MP}}(i) = \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |alm;I\rangle A_{i;ab}^{I,\text{MP}} \langle blm;I|, \quad (4)$$

where the  $\{|alm;I\rangle\}$  are the spherical primitive Gaussian-type functions in the molecular basis set centered on  $I$ , and the spectral representation coefficients  $A_{i;ab}^{I,\text{MP}}$  are the elements of the matrix

$$A^{I,\text{MP}} = (\mathcal{S}^I)^{-1} V_{\text{EMD}}^I (\mathcal{S}^I)^{-1}, \quad (5)$$

where  $\mathcal{S}^I$  and  $V_{\text{EMD}}^I$  are the overlap matrix and the matrix of the genuine core exchange plus mass-velocity and Darwin operators of atom  $I$  on the basis set  $\{|alm;I\rangle\}$ .

(iii) The core projection operator,

$$P^I = - \sum_c^{\text{core}-I} 2\epsilon_c^I |\phi_c^I\rangle \langle \phi_c^I|, \quad (6)$$

where  $\epsilon_c^I$  and  $\phi_c^I$  are the core orbital energies and functions of atom  $I$  obtained in the Cowan–Griffin–Hartree–Fock calculation.

This quasirelativistic (Cowan–Griffin) AIMP method does not take into account spin–orbit interactions. A procedure for including them in molecular calculations, specially suited for the configuration interaction (CI) level, has been proposed<sup>15,16</sup> following Wood and Boring.<sup>27</sup> All the calculations reported in this paper exclude the spin–orbit interaction.

### III. DETAILS OF THE CALCULATIONS

Since the aim of this work is to compare the quasirelativistic AIMP results with those of the all-electron DHF method, we have performed all our calculations at the self-consistent field (SCF) level using valence basis sets of similar quality as the valence parts of the DHF bases. They are presented in Table I and correspond, in general, to a double-splitting of the valence plus the same number of polarization functions as used in the DHF calculations. The  $3s$  and  $4p$

TABLE I. Core definitions and valence basis sets. See text for comments.

Atom	Core	Valence	Basis set pattern
H	...	1s	(3,1,1/1)
O	[He]	2s,2p	(4,1,1/4,1,1/1*,1*)
Si	[Ne]	3s,3p	(5,1,1/4,1,1/1*,1*)
Ge	[Ar],3d	4s,4p	(7,1,1/6,1,1/6*,1*,1*)
Ge	[Ar]	3d,4s,4p	(7,1,1/6,1,1/4,1,1*)
Sn	[Kr],4d	5s,5p	(9,1,1/8,1,1/7*,1*,1*)
Sn	[Kr]	4d,5s,5p	(9,1,1/8,1,1/5,1,1*)
Pb	[Xe],4f,5d	6s,6p	(11,1,1/10,1,1/10*,1*,1*/4*,1*)
Pb	[Xe],4f	5d,6s,6p	(11,1,1/10,1,1/6,1,1*/4*,1*)

contaminants are excluded. The quasirelativistic core model potentials and the valence basis sets of Si, Ge, and Sn corresponding to the  $[ns,np]$ -valence have been taken from Ref. 10; those of Pb, as well as the ones of the  $[(n-1)d,ns,np]$ -valence of Ge and Sn, have been obtained in this work. We have also obtained the respective AIMP's and basis sets for the complete In–Xe and Tl–Rn rows. The resulting atomic valence basis sets are presented in the PAPS document,<sup>28</sup> libraries with the new core model potential and valence basis set data, as well as those of previous publications, are available from the authors upon request. As in standard AIMP calculations, the polarization functions are taken from Ref. 29; we have repeated all the calculations on the dihydrides and tetrahydrides using the same polarization functions as in the DHF calculations,<sup>20,21</sup> but this did not show any significant change of the results. The functions showing an “o” superscript are the outermost core orbitals of the given symmetry block, which have been used in order to provide a high degree of two-center orthogonality between the valence molecular orbitals and the corresponding core orbitals;<sup>30</sup> the size of these orthogonalization functions can certainly be reduced, but efforts in this direction have been omitted and, rather, the use of a  $[(n-1)d,ns,np]$ -valence and a smaller core is recommended for Sn and Pb rows, since any possible  $(n-1)d$  participation in bonding can be represented without significant increase of the basis set size.

In order to calculate the magnitude of the relativistic effects on the properties under consideration, nonrelativistic AIMP calculations are necessary. We have performed these using the nonrelativistic AIMP's and valence basis sets corresponding to the  $[3s,3p]$ -valence of Si, which have been taken from Ref. 30, and the  $[(n-1)d,ns,np]$ -valences of Ge, Sn, and Pb, which have been obtained in this work and are available from the authors upon request.

### IV. RESULTS AND DISCUSSION

Bond lengths and vibrational frequencies of the  $\text{XH}_4$  molecules are given in Table II; their deviations from the DHF calculations of Dyall *et al.*<sup>20</sup> are presented in Fig. 1 ( $r_e$ ) and PAPS document<sup>28</sup> ( $\omega_e$ ), together with the results of the quasirelativistic pseudopotential methods studied there.<sup>20</sup> The results of a recent energy-adjusted pseudopotential calculation<sup>31</sup> are also included. All these AIMP results remain within error limits that one should accept for ECP methods, even at the nonrelativistic level, since the basic

TABLE II. Bond lengths  $r_e$  (Å) and breathing mode vibrational frequency  $\omega_e(a_1)$  ( $\text{cm}^{-1}$ ) of the  $\text{XH}_4$  molecules. Numbers in parentheses correspond to the relativistic effects.

	DHF <sup>a</sup>	$[ns,np]$ QR-AIMP <sup>b</sup>	$[(n-1)d,ns,np]$ QR-AIMP <sup>b</sup>	PT <sup>c</sup>	Expt. <sup>d</sup>
Bond length $r_e$ (Å)					
SiH <sub>4</sub>	1.477(−0.001)	1.477		1.477	1.475
	1.487(−0.001) <sup>e</sup>				
GeH <sub>4</sub>	1.525(−0.007)	1.528	1.526(−0.009)	1.524(−0.008)	1.520
	1.557(−0.007) <sup>e</sup>				
SnH <sub>4</sub>	1.706(−0.021)	1.709	1.712(−0.022)	1.706(−0.021)	1.700
	1.733(−0.021) <sup>e</sup>				
PbH <sub>4</sub>	1.742(−0.073)	1.736	1.744(−0.081)	1.740(−0.075)	
	1.735(−0.071) <sup>e</sup>				
Vibrational frequency $\omega_e$ (cm <sup>−1</sup> )					
SiH <sub>4</sub>	2348(−0)	2347		2349(+1)	2246
	2290(−30) <sup>f</sup>				
GeH <sub>4</sub>	2279(+3)	2281	2273(+19)	2281(+5)	2168
	2060(+30) <sup>f</sup>				
SnH <sub>4</sub>	2069(+10)	2063	2039(+12)	2073(+14)	1955
	1860(+0) <sup>f</sup>				
PbH <sub>4</sub>	1995(+27)	2001	1978(+77)	2017(+49)	
	2020(+20) <sup>f</sup>				

<sup>a</sup>Reference 20.<sup>b</sup>This work.<sup>c</sup>Relativistic correction included by perturbation theory (Ref. 20).<sup>d</sup>Taken from Ref. 20.<sup>e</sup>References 19.<sup>f</sup>Reference 19, with a reported accuracy of around  $20 \text{ cm}^{-1}$ .

approximations involved of freezing the core and representing operators cannot be removed. The  $r_e$  values stay within a  $0.01 \text{ Å}$  margin and the  $\omega_e$  errors are at most of  $30 \text{ cm}^{-1}$ . Also, the deviations from the DHF reference is stable down the group IV; this is probably the most remarkable difference between the AIMP results and those of the pseudopotential methods studied on Ref. 20. The energy-adjusted pseudopotential calculations of Steinbrenner *et al.*<sup>31</sup> enjoy as well this stability.

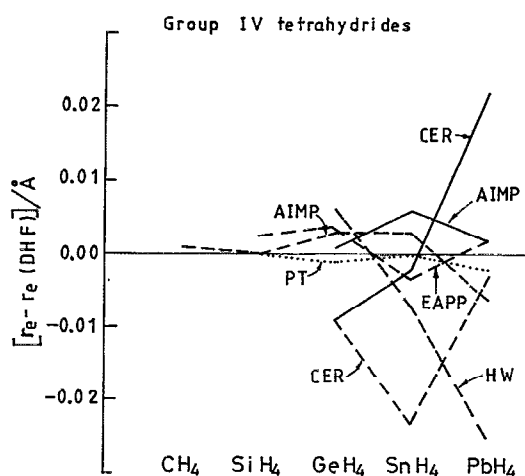


FIG. 1. Bond lengths of the group IV tetrahydrides referred to the all-electron Dirac-Hartree-Fock results of Ref. 20. PT: perturbation theory (Ref. 20). AIMP: this work. CER: pseudopotentials of Ref. 4. HW: pseudopotentials of Ref. 3. EAPP: energy-adjusted pseudopotentials of Ref. 31. The CER and HW results have been calculated in Ref. 20. Dashed lines stand for [ $ns,np$ ]-valence calculations; full lines stand for [ $(n-1)d,ns,np$ ]-valence calculations.

The relativistic effects are also presented in Table II (numbers in parentheses). The AIMP ones have been calculated as the difference between the quasirelativistic AIMP results and the nonrelativistic AIMP ones. (Note that these calculations use different model potentials and basis sets, keeping only in common the size of the basis sets and the polarization functions.) The relativistic effects on  $r_e$  are well reproduced and the same is true for  $\omega_e$  except for that of  $\text{PbH}_4$  which, although qualitatively correct, is overestimated. We should bear in mind, in any case, that the accuracy of the vibrational frequencies obtained by fitting procedures such as those of Ref. 20, also used here, is limited, so that the number of significant figures of the  $\omega_e$  would hardly be larger than 3.

In Table II the bond lengths and vibrational frequencies corresponding to the DHF calculations by Visser *et al.*<sup>19</sup> are also presented. The most remarkable difference between these calculations and the ones by Dyall *et al.*<sup>20</sup> seems to be the basis set. As it can be observed, the differences between both DHF results are much larger than those between DHF and quasirelativistic ECP methods which use basis sets of a similar kind in their valence parts. This could indicate that a not too successful selection of a basis set for an all-electron DHF calculation could lead to more error in the absolute values of these properties than the intrinsic approximations involved in quasirelativistic ECP methods, in spite of the fact that the relativistic corrections to the  $r_e$  and  $\omega_e$  of the group IV tetrahydrides do not appear to be very sensitive to the details of the basis sets in DHF calculations.<sup>20</sup>

The results for the  $\text{XH}_2$  molecules are given in Table III; their deviations from the DHF calculations of Dyall<sup>21</sup> are presented in Fig. 2 ( $r_e$ ) and PAPS document<sup>28</sup> (bond angle, symmetrical stretching vibrational frequency, and bending vibrational frequency,) together with the results of some qua-

TABLE III. Bond lengths  $r_e$  (Å), bond angles  $\theta_e$  (°), and vibrational frequencies ( $\text{cm}^{-1}$ ) of the  $\text{XH}_2$  molecules. Numbers in parentheses correspond to the relativistic effects.

	DHF <sup>a</sup>	[ <i>ns,np</i> ] QR-AIMP <sup>b</sup>	[( <i>n-1</i> ) <i>d,ns,np</i> ] QR-AIMP <sup>b</sup>	PT <sup>c</sup>	Expt. <sup>d</sup>
Bond length $r_e$ (Å)					
SiH <sub>2</sub>	1.510(-0.000)	1.511		1.510(-0.000)	1.516
GeH <sub>2</sub>	1.575(-0.003)	1.581	1.580(-0.004)	1.574(-0.004)	
SnH <sub>2</sub>	1.759(-0.011)	1.763	1.768(-0.013)	1.756(-0.014)	
PbH <sub>2</sub>	1.817(-0.044)	1.831	1.831(-0.044)	1.814(-0.047)	
Bond angle $\theta_e$ (°)					
SiH <sub>2</sub>	93.67(-0.05)	93.51		93.69(-0.02)	92.8
GeH <sub>2</sub>	92.96(-0.21)	93.06	93.03(-0.13)	92.94(-0.22)	
SnH <sub>2</sub>	92.55(-0.36)	92.58	92.32(-0.45)	92.58(-0.33)	
PbH <sub>2</sub>	92.29(-0.35)	92.04	91.88(-0.75)	91.53(-1.11)	
Vibrational frequency $\omega_1$ ( $\text{cm}^{-1}$ ) (symmetric stretching)					
SiH <sub>2</sub>	2187(-3)	2184		2189(-1)	2032
GeH <sub>2</sub>	2059(-12)	2023	2015(-10)	2060(-11)	1887
SnH <sub>2</sub>	1874(-24)	1850	1833(-4)	1886(-9)	
PbH <sub>2</sub>	1753(-55)	1658	1669(-42)	1763(-45)	
Vibrational frequency $\omega_2$ ( $\text{cm}^{-1}$ ) (bending)					
SiH <sub>2</sub>	1116(0)	1109		1116(0)	1008
GeH <sub>2</sub>	1036(+2)	1026	1021(+3)	1038(+4)	920
SnH <sub>2</sub>	884(+3)	878	871(+11)	890(+9)	
PbH <sub>2</sub>	813(-4)	815	802(+17)	842(+25)	
Vibrational frequency $\omega_3$ ( $\text{cm}^{-1}$ ) (asymmetric stretching)					
SiH <sub>2</sub>	2178(-2)	2188		2179(-1)	2022
GeH <sub>2</sub>	2057(-10)	2025	2017(-10)	2058(-9)	1864
SnH <sub>2</sub>	1867(-17)	1850	1834(-4)	1880(-4)	
PbH <sub>2</sub>	1745(-52)	1832	1669(-42)	1757(-40)	

<sup>a</sup>Reference 21.<sup>b</sup>This work.<sup>c</sup>Relativistic correction included by perturbation theory (Ref. 21).<sup>d</sup>Taken from Ref. 21.

sirelativistic pseudopotential methods.<sup>21</sup> The  $\text{XH}_4 \rightarrow \text{XH}_2 + \text{H}_2$  reaction energies  $\Delta E_e$  (kcal/mol) without zero-point corrections appear in Table IV. As in the case of  $\text{XH}_4$  molecules, the AIMP  $r_e$  values remain within acceptable margins of error, the deviations varying smoothly down the group. Bond angles are also acceptable. The agreement of the vibrational frequencies is again poorer. The AIMP reaction energies are of the correct order, both in their absolute values and in their variation down the group. The sizes of the relativistic effects are, in general, well calculated, especially those on  $r_e$ ; they are very close to the ones estimated by perturbation theory, as one could, in principle, expect, since both perturbation theory (PT) and AIMP methods include relativistic effects through the explicit use of mass-velocity and Darwin operators. This is consistent with negligible spin-orbit effects on  $r_e$  and  $\theta_e$  of the ground states of  $\text{GeH}_2$ ,  $\text{SnH}_2$ , and  $\text{PbH}_2$ , as found by Balasubramanian<sup>32</sup> by means of spin-orbit CI calculations using core pseudopotentials of Refs. 4 and 14. The relativistic effects on  $\Delta E_e$  are in accordance with estimates of the spin-orbit contributions of -7 kcal/mol for lead hydrides and of -1 kcal/mol for tin hydrides.<sup>21</sup> This contribution has been, however, calculated to be of marginal influence for lead hydrides (-0.7 kcal/mol) in an energy-adjusted quasirelativistic pseudopotential calculation using a  $[6s,6p]$ -valence for Pb.<sup>33</sup> [Note that the spin-free SCF re-

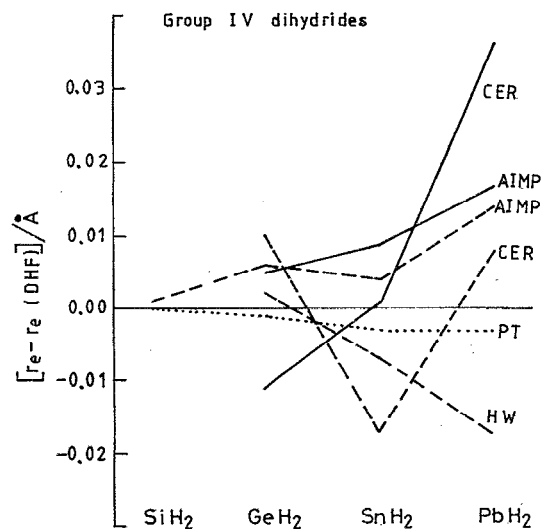


FIG. 2. Bond lengths of the group IV dihydrides referred to the all-electron Dirac-Hartree-Fock results of Ref. 21. The CER and HW results have been calculated in Ref. 21. See footnotes on Fig. 1.

TABLE IV.  $\text{XH}_4 \rightarrow \text{XH}_2 + \text{H}_2$  reaction energies  $\Delta E_c$  (kcal/mol) without zero-point corrections. Numbers in parentheses correspond to the relativistic effects.

	DHF <sup>a</sup>	[(n-1)d,ns,np] QR-AIMP <sup>b</sup>	PT <sup>c</sup>
X=Si	62.3(-0.6)		62.6(-0.3)
X=Ge	42.4(-3.1)	41.7(-2.1)	42.6(-2.9)
X=Sn	23.2(-7.7)	21.6(-6.6)	26.6(-4.3)
X=Pb	-6.2(-27.4)	-2.2(-18.7)	7.1(-13.5)

<sup>a</sup>Reference 21.<sup>b</sup>This work.<sup>c</sup>Relativistic correction included by perturbation theory (Ref. 21).

sults of this Ref. 33 show very good quality:  $r_e(\text{PbH}_4) = 1.742(-0.066)\text{\AA}$ ,  $r_e(\text{PbH}_2) = 1.834(-0.023)\text{\AA}$ ,  $\theta_e(\text{PbH}_2) = 92.3(-0.5)^\circ$ ,  $\Delta E_c(\text{PbH}_4 \rightarrow \text{PbH}_2 + \text{H}_2) = -3.0(-27.2)$  kcal/mol, the relativistic effects being in parentheses.]

Finally, the results for the monoxides are given in Table V and the deviations from the DHF calculations of Dyal<sup>22</sup> are presented in Fig. 3 ( $r_e$ ) and PAPS document<sup>28</sup> ( $\omega_e$ ). The same kind of comments on the absolute values can be made here. The AIMP bond lengths show deviations from the all-electron calculations which are of the size usually accepted for the intrinsic approximations involved in an ECP method, disregarding its nonrelativistic or quasirelativistic nature. In any case, the value of the bond length of PbO calculated with the [6s,6p]-valence of Pb is comparatively poorer than those of the rest of the molecules; this is consistent with a certain participation on the bonding of the 5d orbitals of Pb, enhanced by the presence of oxygen, and it suggests the systematic use of a [5d,6s,6p]-valence AIMP for Pb and its row as a safe procedure.

The deviations from the DHF results vary smoothly from Ge to Pb, in agreement with the growing importance of the spin-orbit effects in these oxides down the group;<sup>22</sup> they follow the tendency of the PT calculations; here, and with respect to the hydrides, the different behavior of the AIMP's and the pseudopotentials studied in Ref. 22 is enhanced. Also, the relativistic effects calculated with the AIMP method (i) are closer to the PT results than to the DHF ones,

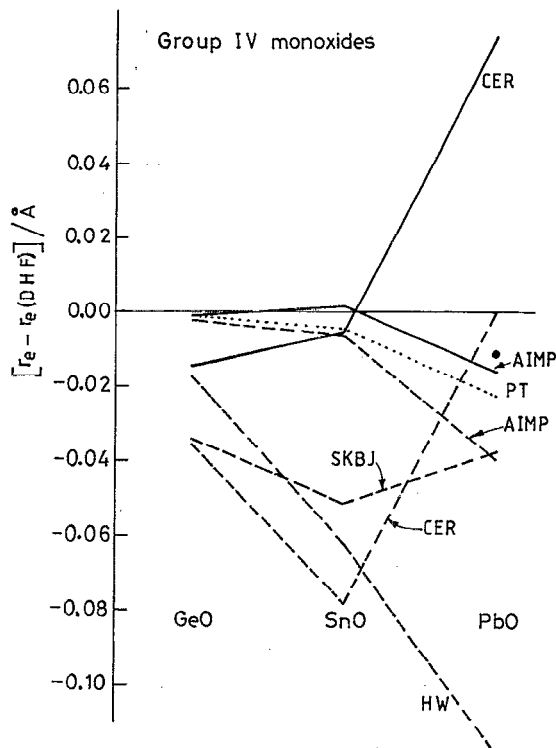


FIG. 3. Bond lengths of the group IV monoxides referred to the all-electron Dirac-Hartree-Fock results of Ref. 22. The CER and HW results have been calculated in Ref. 22. See footnotes on Fig. 1. SKBJ: pseudopotentials of Ref. 34. The full dot is the all-electron DHF result of Ref. 24.

(ii) are larger than the DHF results, in agreement with the fact that spin-orbit effects partially cancel the relativistic contraction resulting from the spin-free terms in these molecules,<sup>22</sup> and (iii) are smaller than in the hydrides, coinciding with the PT results.

The vibrational frequencies are, as in the hydrides, poorer when compared with the DHF reference values; they are much closer to the PT ones.

Another DHF calculation on PbO has been published by Matsuoka *et al.*,<sup>24</sup> which differs from the DHF calculation by

TABLE V. Bond lengths  $r_e$  (Å) and vibrational frequencies  $\omega_e$  ( $\text{cm}^{-1}$ ) of the XO molecules. Numbers in parentheses correspond to the relativistic effects.

	DHF <sup>a</sup>	[ns,np] QR-AIMP <sup>b</sup>	[(n-1)d,ns,np] QR-AIMP <sup>b</sup>	PT <sup>c</sup>	Expt. <sup>d</sup>
Bond length $r_e$ (Å)					
GeO	1.594(-0.003)	1.592	1.593(-0.004)	1.593(-0.004)	1.625
SnO	1.801(-0.007)	1.795	1.803(-0.010)	1.797(-0.011)	1.833
PbO	1.893(-0.014)	1.854	1.878(-0.029)	1.871(-0.036)	1.922
	1.882(-0.015) <sup>e</sup>				
Vibrational frequency $\omega_e$ ( $\text{cm}^{-1}$ )					
GeO	1123(-4)	2281	1144(+1)	1124(-3)	987
SnO	946(-9)	2063	971(+3)	954(-1)	815
PbO	785(-88)	2001	870(-6)	867(-6)	721
	800(-81) <sup>e</sup>				

<sup>a</sup>Reference 22.<sup>b</sup>This work.<sup>c</sup>Relativistic correction included by perturbation theory (Ref. 22).<sup>d</sup>Taken from Ref. 22.<sup>e</sup>Reference 24.

Dyall<sup>22</sup> in the basis set used and in the fact that the neglect of integrals involving small components assumed by Dyall<sup>20</sup> is disregarded. The values of  $r_e$  and  $\omega_e$  are included in Table V and Fig. 3. We can observe that the differences in  $r_e$  are of the same size as in the case of our best AIMP calculation. The relativistic effects on  $r_e$  and  $\omega_e$  are very close for both DHF calculations. The DHF value of the dissociation energy  $D_e$  of PbO reported by Matsuoka *et al.*<sup>24</sup> is 1.3 eV, with a relativistic effect of -0.1 eV; the  $[(n-1)d,ns,np]$ -valence quasirelativistic AIMP results are 0.9 and -0.2 eV, respectively.

## V. CONCLUSIONS

A systematic comparison of the results of spin-free (Cowan–Griffin based) quasirelativistic *ab initio* core model potential calculations and all-electron Dirac–Hartree–Fock calculations using basis sets of similar quality in their valence part, on the bond lengths, bond angles, and vibrational frequencies of group V tetrahydrides, dihydrides, and monoxides, have been conducted, which reveals a consistent behavior of the AIMP's down the group VI of the Periodic Table.

The bond length (and bond angle) deviations from the DHF results are within the margins expected for an effective core potential approach. (Similar or even larger deviations can be found, in fact, between DHF calculations using different basis sets.) The vibrational frequencies show larger deviations, though not much larger than the accuracy expected from the fitting procedures used for their calculation. The  $\text{XH}_4 \rightarrow \text{XH}_2 + \text{H}_2$  reaction energies show an acceptable agreement.

The relativistic effects on the properties under study, when calculated as the difference between quasirelativistic and nonrelativistic AIMP calculations, show a systematic qualitative agreement with the DHF results, which is often also quantitative. This is in part a consequence of the spin-orbit effects not being very large here; in any case, the disagreement with the DHF relativistic effects follows the tendency expected on the basis of the growing importance of the spin-orbit interactions. In fact, the AIMP relativistic effects are in general closer to the perturbation theory values, as one could expect, since both methods handle spin-free relativistic corrections through the use of mass-velocity and Darwin operators.

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