

# Relativistic effects in molecules: Pseudopotential calculations for $\text{PbH}^+$ , $\text{PbH}$ , $\text{PbH}_2$ , and $\text{PbH}_4$

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Nonrelativistic, relativistic, and semiempirical pseudopotentials for the Pb atom have been generated to replace the chemically inert core electrons for investigating the effects of relativity and correlation on molecular properties of  $\text{PbH}^+$ ,  $\text{PbH}$ ,  $\text{PbH}_2$ , and  $\text{PbH}_4$ . Spin-orbit effects are taken into account by using a quasirelativistic two-spinor pseudopotential. The relativistic bond contraction is found to be dependent on the  $\text{Pb}(6s)$  orbital participation in the Pb-H bond ( $\Delta_{\text{rel}} r_e$ : 0.04 Å for  $\text{PbH}^+$ ,  $\text{PbH}$ , and  $\text{PbH}_2$  and 0.07 Å for  $\text{PbH}_4$ ). The calculated and measured values agree excellently [e.g.,  $r_e(\text{PbH}) = 1.839$  Å; expt. 1.839 Å]. The inert pair effect for the lead hydrides will be discussed.

## I. INTRODUCTION

In a previous paper one of us (P. S.) presented pseudopotential calculations on thallium hydrides<sup>1</sup> using nonrelativistic (NRPP), spin-orbit averaged relativistic (ARPP), quasirelativistic two-component (QRPP), and semiempirical (SEPP) pseudopotentials to investigate the effects of relativity and correlation. The relativistic pseudopotentials have been directly introduced into a relativistically corrected Schrödinger-Hamiltonian by adjusting the pseudopotential parameters to calculated atomic Dirac-Fock (DF) values.<sup>2,3</sup> As pointed out, this has the advantage, that such an approximation does not have variational problems as occur in Dirac or Breit-Pauli operators; in common pseudopotential approximations the model valence Hamiltonians have no divergent matrix elements caused by singularities of the operator, are bounded from below and can simply be treated like nonrelativistic semibounded operators. Furthermore, using an appropriate core definition, the pseudopotential approximation can give nearly as highly accurate results as those obtained from all-electron calculations.

The purpose of the present work is to show that the pseudopotential approximation can be successfully used to predict properties of molecules containing heavy atoms. Thus, we have studied relativistic and correlation effects for several molecular ground state properties (bond lengths, dissociation energies, harmonic force constants, and dipole moments) of  $\text{PbH}^+$  ( $^1\Sigma^+$ ),  $\text{PbH}$  ( $^2\Pi$ ),  $\text{PbH}_2$  ( $^1A_1$ ;  $C_{2v}$ ), and  $\text{PbH}_4$  ( $^1A_1$ ;  $T_d$ ) applying nonrelativistic (NR), relativistic ( $R$ ) and correlated pseudopotentials using a [Pt]-core definition for the Pb atom. Accurate experimental results are available only for  $\text{PbH}$  reported by Huber and Herzberg,<sup>4</sup> which is therefore our test case for the quality of the pseudopotential approximation. The synthesis of  $\text{PbH}_4$  has been a very controversial topic because of its proposed instability at room temperature,<sup>5-10</sup> but it was found by mass spectroscopic methods.<sup>11</sup>  $\text{PbH}$ ,  $\text{PbH}_2$ , and  $\text{PbH}_4$  have been studied before by other authors to investigate the effects of

relativity.<sup>12-21</sup> In this paper we have also taken correlation effects into account using a configuration interaction with single and double excitations (CISD) and a core dipole polarization potential (CPP) for describing core-valence correlations<sup>22-25</sup> for the molecules  $\text{PbH}^+$ ,  $\text{PbH}$ , and  $\text{PbH}_2$ . Intercore overlaps are also accounted for by using a core-core correction potential (CC).<sup>26</sup>

In the next section we describe briefly the method used for our calculations. A more detailed description is given in Ref. 1. We then present our results and discuss the effects of relativity and correlation for the Pb atom and the hydrides. A summary is given in Sec. IV.

## II. METHOD

We start with the valence model Hamiltonian (in atomic units)<sup>1</sup>

$$H_{\text{mod}} = -\frac{1}{2} \sum_i \Delta_i + V_p + \sum_{i,j} \frac{1}{r_{ij}} + \sum_{\lambda < \mu} \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}}, \quad (1)$$

$i, j$  are indices for valence electrons,  $\lambda, \mu$  are core indices, and  $Q_\lambda$  is the core charge of atom  $\lambda$  ( $Q_\lambda = Z_\lambda$  if  $V_p = 0$  and  $Q_{\text{Pb}} = 4$  using a [Pt]-core definition). The pseudopotential  $V_p$  has the following functional form:

$$V_p = \sum_\lambda V_{pp}^\lambda + \sum_\lambda V_{\text{pol}}^\lambda + \sum_{\lambda < \mu} V_{cc}(r_{\lambda\mu}) \quad (2)$$

with

$$V_{pp}^\lambda = \sum_i \left\{ -\frac{Q_\lambda}{r_{\lambda i}} + \sum_{l=0}^{l_{\text{max}}} (A_{\lambda l} e^{-a_{\lambda l} r_{\lambda i}^2} + B_{\lambda l} e^{-b_{\lambda l} r_{\lambda i}^2}) P_{\lambda l} \right\}. \quad (3)$$

Here,  $P_{\lambda l}$  projects onto the Hilbert subspace of angular symmetry  $l$  with respect to core  $\lambda$ . Note, that the index  $\lambda$  in Eq. (1) runs over all atoms whereas in Eq. (2) runs only over atoms containing pseudopotentials with  $V_p \neq 0$ . The pseudopotential parameters  $A_{\lambda l}$ ,  $a_{\lambda l}$ ,  $B_{\lambda l}$ ,  $b_{\lambda l}$  are fitted to atomic data<sup>1</sup> and are listed in Table I for the different levels of approximation. Note that for the spin-orbit coupled pseudopotential (QRPP) a  $(l, j)$ -dependent form in Eq. (2) is used.<sup>2,3</sup> The intercore overlap correction is approximated by a linear combination of exponentials<sup>1</sup>

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TABLE I. Pseudopotential parameters for Pb (in a.u.), defined in Eqs. (3) and (6). NRPP denotes the nonrelativistic, ARPP, the  $j$ -averaged relativistic, QRPP, the spin-orbit coupled relativistic, and SEPP, the semiempirical pseudopotential.  $\alpha_D$  is taken from Ref. 27.

$A_i \dots$	NRPP	ARPP	QRPP	SEPP
$A_0$	-1.070 93	-1.423 16	-1.423 16	-5.051 37
$a_0$	0.5	0.5	0.5	0.723 6
$B_0$	34.303 4	45.351 0	45.351 0	29.579 6
$b_0$	1.564	2.0	2.0	1.447 2
$A_{1(1/2)}$	-2.087 15	-3.115 77	-2.623 89	-3.631 52
$A_{1(3/2)}$			-3.284 90	
$a_{1(1/2)}$	0.6	0.6	0.6	0.65
$a_{1(3/2)}$			0.6	
$B_{1(1/2)}$	21.644 8	20.637 7	22.389 39	31.862 5
$B_{1(3/2)}$			19.84 26	
$b_{1(1/2)}$	1.128 2	1.099 7	1.28	1.3
$b_{1(3/2)}$			1.028 3	
$A_{2(3/2)}$	-0.196 555	0.135 487	0.121 150	-0.593 661
$A_{2(5/2)}$			0.143 972	
$a_{2(3/2)}$	0.3	0.3	0.3	0.126
$a_{2(5/2)}$			0.3	
$B_{2(3/2)}$	6.455 82	8.655 21	8.954 64	2.802 85
$B_{2(5/2)}$			8.435 82	
$b_{2(3/2)}$	0.580 95	0.702	0.729 9	0.263
$b_{2(5/2)}$			0.683	
$A_3$	-0.035 569	-0.035 569	-0.035 569	-1.441 82
$a_3$	0.2	0.2	0.2	0.004 51
$B_3$	-6.982 02	-6.982 02	-6.982 02	-0.235 266
$b_3$	0.970 2	0.970 2	0.970 2	0.07
$\alpha_D$				3.94
$\delta$				1.748

$$V_{cc}(r_{\lambda\mu}) = \sum_j C_j^{\lambda\mu} e^{-\gamma_j^{\lambda\mu} r_{\lambda\mu}}, \quad (4)$$

where in our case  $r_{\lambda\mu}$  is the Pb-H bond distance.  $C_j^{\text{PbH}}$  and  $\gamma_j^{\text{PbH}}$  are listed in Table II for both the nonrelativistic and relativistic case. To account for core-valence correlation contributions we used a dipole polarization potential of the form<sup>23,24</sup>

$$V_{\text{pol}}^\lambda = -\frac{1}{2} \alpha_D^\lambda f_\lambda^2 \quad (5)$$

with

$$f_\lambda = \sum_i \frac{r_{\lambda i}}{r_{\lambda i}^3} (1 - e^{-r_{\lambda i}^2 \delta_\lambda^{-1}}) - \sum_{\lambda \neq \mu} Q_\mu \frac{r_{\lambda\mu}}{r_{\lambda\mu}^3}, \quad (6)$$

$\alpha_D^\lambda$  is the dipole polarizability and  $\delta_\lambda$  the cutoff factor of core  $\lambda$  (Table I). Formulas (5) and (6) show that multicenter one- and two-electron matrix elements have to be solved. A general analytical solution of such integrals has been published by us earlier.<sup>28</sup> The valence correlation is included by a CISD procedure. To achieve higher accuracy in the ionization potentials of Pb and  $\text{Pb}^+$  we allowed also for triple excitations (CISDT).

For the molecular NRPP and ARPP calculations we used a modified version of GAUSSIAN 82,<sup>29</sup> whereas for the atomic calculations a modified version of the numerical program MCHF<sup>30</sup> was used, primarily to avoid basis set effects. The molecular QRPP calculations have been done using

TABLE II. Core-overlap correction potential  $V_{cc}$  for the lead hydrides (deviation from the point charge approximation). Parameters  $C_j$  and  $\gamma_j$  from Eq. (5) ( $j = 1, \dots, 4$ ).

NRPP		ARPP	
$C_j$	$\gamma_j$	$C_j$	$\gamma_j$
$-4.268\,87 \times 10^{-4}$	0.8	$5.031\,42 \times 10^{-4}$	0.9
$1.791\,84 \times 10^{-1}$	1.8	$2.039\,30 \times 10^{-2}$	1.7
$-1.484\,26 \times 10^1$	2.7	$-4.660\,50$	2.7
$5.259\,90 \times 10^1$	3.1	$5.122\,13 \times 10^1$	3.3

Hafners program UHREL<sup>31</sup> while the atomic and molecular SEPP/CI calculations for the molecules  $\text{PbH}^+$ ,  $\text{PbH}$ , and  $\text{PbH}_2$  were performed with a modified version of Davidsons MELD.<sup>32</sup> The program UHREL is limited to closed shell molecules only, thus molecular spin-orbit effects have been studied only on  $\text{PbH}^+$ ,  $\text{PbH}_2$ , and  $\text{PbH}_4$ . The Gaussian basis sets (GTO) for the Pb atom have been energy optimized by using the program PSATOM<sup>33</sup> and are listed in Table III. The  $d$ -polarization functions are taken from Huzinaga.<sup>34</sup> The GTO basis set for H is taken from Botschwina and Mayer.<sup>35</sup>

### III. RESULTS AND DISCUSSION

#### A. The Pb atom

The nonrelativistic and relativistic valence spectra of the Pb atom are calculated by using the programs MCHF<sup>30</sup> and MCDF/BENA<sup>36-38</sup> and presented together with the experimental data<sup>39-41</sup> in Table IV. The all-electron results are compared with calculated atomic NRPP, ARPP, and SEPP/CISDT values. Also given in Table IV are the various contributions of relativity and correlation to the valence ionization energies and the electron affinity. In most cases relativistic effects predominate over the correlation contributions! The NRPP and ARPP results are in most cases in excellent agreement with the all-electron numerical HF and DF values.<sup>30,36-38</sup> The experimental electron affinity given in the review article of Hotop and Lineberger<sup>40</sup> has been remeasured recently by Feigerle *et al.*<sup>41</sup> and detected to be a  $\text{Pb}(^3P_0) \rightarrow \text{Pb}^-(^4S_{3/2})$  transition with a value of  $0.365 \pm 0.008$  eV. From this we get the spin-orbit averaged value given in Table IV. The very low value of the electron affinity reflects both, the spin-orbit stabilization in Pb and the relativistic  $6p_{3/2}$  destabilization in  $\text{Pb}^-$ . Our calculated  $^4S_{3/2}$  state of  $\text{Pb}^-$  was found not to be stable within the DF approximation.

The CISD ionization energy for the  $\text{Pb}^+$  ion has been calculated to be 13.683 eV so that triple excitations contribute 0.05 eV, which is only 3% of the total correlation. Core-valence correlation is quite important as indicated by our SEPP (without valence CISD) results, but clearly they become less important in the ionization potentials from  $\text{Pb(IV)}$  to  $\text{Pb(I)}$ . We get a maximal deviation in the SEPP  $\text{Pb}(^3P) \rightarrow \text{Pb}^+(^2P)$  ionization of about 0.55 eV, which is not only a correlation effect (compare to the ARPP value). The question arises if this is due to our fit procedure (one valence electron fit, functional form of  $V_p$ , etc.) or to our core defini-

TABLE III. GTO basis sets for Pb and H for the different used pseudopotentials. In parentheses: the total energies  $E$  are compared with the HF, DF, and experimental values, obtained from the programs MCHF (Ref. 30), MCDP (Refs. 36–38), and Ref. 39.

Type	Exponent
Pb NRPP	7s/7p/2d ( $E = -2.999\ 86$ a.u.; HF: $-3.001\ 76$ a.u.)
s	5.109/1.575 92/0.836 89/0.185 22/0.070 746/0.0301/0.012
p	2.1/1.263 90/0.877 90/0.341 72/0.154 58/0.054 111/0.037
d	0.062/0.213
Pb ARPP/QRPP	7s/7p/2d ( $E = -3.304\ 45$ a.u.; DF: $-3.326\ 28$ a.u.)
s	5.0/1.562 40/1.267 08/0.234 81/0.086 473/0.0423/0.0195
p	2.453 09/1.687 66/0.866 42/0.480 42/0.180 20/0.060 274/0.033
d	0.062/0.213
Pb SEPP	9s/8p/4d [ $E(\text{CISD}) = -3.473\ 92$ a.u.; expt: $-3.494\ 17$ a.u.]
s	3.045 13/2.215 20/1.496 40/0.520 82/0.206 32/0.063 454/0.019 89/0.008/0.003
p	2.881 35/1.649 98/0.828 32/0.231 17/0.087 940/0.021 242/0.007 947/0.003
d	0.9/0.4/0.2/0.06
H	5s/2p ( $E = -0.499\ 81$ a.u.; expt: $-0.500\ 00$ a.u.)
s	33.64/5.058/1.147/0.3211/0.1013
p	1.0/0.25

tion. To clarify this situation, we performed DF calculations with different frozen core definitions. The results are presented in Table V. The maximal error using the best core definition ([Pt 6s<sup>2</sup>]) is 0.16 eV so that part of our errors are due to the fit procedure. Thus a multielectron fit as discussed in Wedig's thesis,<sup>42</sup> would probably give better values. However, another core definition, such as a [Xe 4f<sup>14</sup>] core, is necessary to produce significantly better atomic results, but this would extend our computational time. Nevertheless, our calculated ARPP values are much better than those of Wadt and Hay,<sup>43</sup> who used a [Xe 4f<sup>14</sup>] core definition for the Pb atom (which is a result of their fit procedure). Furthermore, we will see below that we can get excellent results for

TABLE IV. Ionization potentials (I–IV) and electron affinity (EA) of the Pb atom in eV. I: Pb(<sup>3</sup>P); II: Pb(<sup>2</sup>P); III: Pb(<sup>2</sup>S); IV: Pb(<sup>3</sup>S). HF, NRPP, and ARPP results from the program MCHF (Ref. 30),  $j$ -averaged DF results from program MCDP (Refs. 36–38),  $j$ -averaged experimental values from Refs. 39 and 41, and SEPP/CISDT results from the program MELD (Ref. 32). Relativistic and correlation contributions to the ionization energies and the electron affinity. R:  $j$ -averaged relativistic. SO: including spin–orbit coupling. CV: core–valence correlation only.

	IV	III	II	I	EA
HF	35.879	26.102	13.036	6.6655	1.1497
NRPP	35.879	26.013	13.045	6.6916	1.1862
Ref. 33 <sup>a</sup>	36.303	26.269	13.056	6.6630	1.1573
DF	40.553	29.829	13.213	6.9183	0.9502
ARPP	40.553	29.606	13.172	6.5860	0.9377
Ref. 43 <sup>b</sup>	41.315	30.077	13.095	6.4728	0.8422
Expt.	42.333	31.938	13.868	7.5240	1.7
SEPP	42.333	31.571	13.733	6.9711	1.2202
R	4.674	3.727	0.177	0.253	–0.200
R + SO	4.674	3.727	1.314	0.206	1.014
Cor.	1.780	2.109	0.655	0.606	0.8
Cor. + SO	1.780	2.109	0.682	0.545	1.8
CV Corr.	1.780	1.268	0.237	0.155	0.024

<sup>a</sup> [Pt]–core NRPP from Barthelat *et al.* (Ref. 33).

<sup>b</sup> [Xe 4f<sup>14</sup>]–core ARPP from Wadt and Hay (Ref. 43).

PbH compared to experiment using our simple one-valence electron adjusted pseudopotentials.

Let us now discuss the relativistic effects on the Pb atom which are, in our opinion, important for understanding the chemical behavior of Pb compounds. The relativistic increase of the Pb(6s) ionization potentials are quite significant [Table IV; 4.7 eV for Pb(IV) and 3.7 eV for Pb(III)]. This is explained by the relativistic 6s orbital contraction which is about 12% for the neutral Pb atom, using the  $\langle r \rangle$  expectation values as a measure of the orbital radii. As a result, the chemistry of Pb is effected in two different ways. First, the Pb(6s) promotion energy is much larger than in the nonrelativistic case. In other words, the 6s electrons are more inert, more core-like. This is nothing more than the inert pair effect and may in some cases explain why Pb prefers the oxidation state II over IV.<sup>44</sup> Second, the 6s orbital contraction shortens the bond length between the Pb atom and other bond partners whenever the 6s orbital participates in the bond. Using the simple hybridization model, we expect a larger contraction for PbH<sub>4</sub> (“sp<sup>3</sup>”) compared to PbH (“p”). The relativistic effects on the Pb(6p) orbital are rather more complicated, because the 6p orbitals are split by spin–orbit coupling by more than 1.7 eV (which is, in fact, the <sup>2</sup>P<sub>1/2</sub>/<sup>2</sup>P<sub>3/2</sub> splitting of Pb<sup>+</sup>). The spatial part of the energetically lower p<sub>1/2</sub> orbital is a mixture of 1/3σ and 2/3π symmetry. Therefore we may get destabilizations in the Pb–H bond by π admixtures, but as pointed out by Pitzer<sup>45</sup> for the TiH molecule, the metal–hydrogen bond tends to achieve large σ character by p<sub>3/2</sub> admixture near the equilibrium distance. Thus, it is most sufficient to correct for atomic spin–orbit coupling only. Furthermore, the Pb(6p<sub>1/2</sub>) orbital contracts by about 10%, whereas the 6p<sub>3/2</sub> orbital expands by about 3%. If we take the average of 1/3p<sub>1/2</sub> and 2/3p<sub>3/2</sub>, which is necessary to form p<sub>σ</sub> for a σ bond, we get a resulting relativistic 6p contraction of 2%. Therefore, relativistic effects on p(σ) bonds in Pb compounds are assumed to be small.

TABLE V. Frozen core effects. Deviations from the DF-ionization potentials using different frozen core definitions calculated with program MCDP (Ref. 36) (in eV).

	[Pt]	[Pt 6s <sup>1</sup> ]	[Pt 6s <sup>2</sup> ]	[Pt 6s <sup>2</sup> 6p <sup>1</sup> ]	[Pt 6s <sup>2</sup> 6p <sup>2</sup> ]
Pb <sup>2+</sup> ( <sup>1</sup> S) → Pb <sup>2+</sup> ( <sup>2</sup> S)	0.581	0.206	0.161	0.093	0.450
Pb <sup>+</sup> ( <sup>2</sup> P) → Pb <sup>2+</sup> ( <sup>1</sup> S)	0.403	0.235	0.063	0.517	0.107
Pb <sup>+</sup> ( <sup>3</sup> P) → Pb <sup>+</sup> ( <sup>2</sup> P)	0.286	0.147	0.094	0.007	0.012

## B. The hydrides

The results of our calculations for the ground state lead hydrides [PbH<sup>+</sup> (<sup>1</sup>Σ<sup>+</sup>), PbH (<sup>2</sup>Π), PbH<sub>2</sub> (<sup>1</sup>A<sub>1</sub>; C<sub>2v</sub>), and PbH<sub>4</sub> (<sup>1</sup>A<sub>1</sub>; T<sub>d</sub>)] using NRPP, ARPP, QRPP, and SEPP with the basis sets presented in Table III are shown in Table VI and compared with results from other authors<sup>15–21</sup> and experiments.<sup>4,11</sup> The relativistic bond contraction is 2.3% for PbH<sup>+</sup>, 2.1% for PbH, 2.3% for PbH<sub>2</sub>, and 4.1% for PbH<sub>4</sub>. This indicates a larger Pb(6s) contribution in PbH<sub>4</sub> compared to the other hydrides, which is also supported by the order of bond length: PbH > PbH<sub>2</sub> > PbH<sup>+</sup> > PbH<sub>4</sub>. A more detailed discussion is found in Refs. 1 and 47. The relativistic effects on the PbH<sub>2</sub> bond angle is small, and this agrees with calculations of Pelissier who obtained a relativistic decrease (NRPP/ARPP) of about 0.5°. Effects of spin-orbit coupling are also small. At the highest level of approximation, our SEPP/CISD value for the bond distance in PbH reproduces the experimental value. Also our bond distance for PbH<sub>4</sub> agrees well with the empirically estimated val-

ue.<sup>4,46</sup> The bond distance of PbH<sub>4</sub> by Aguilar-Ancono *et al.*,<sup>18</sup> calculated with a relativistic X<sub>α</sub> method, seems to be overestimated.

We now discuss the effects of relativity and correlation on the dissociation energies. The atomic spin-orbit corrections Δ<sub>so</sub><sup>A</sup> for D<sub>e</sub> are calculated from all-electron DF results<sup>36–38</sup> (expt. values in parentheses<sup>39</sup>): Pb 1.09 eV (1.06 eV), Pb<sup>+</sup> 1.14 eV (1.16 eV). The molecular spin-orbit contributions Δ<sub>so</sub><sup>M</sup> are calculated from QRPP/ARPP results<sup>31</sup>: PbH<sup>+</sup> 0.21 eV, PbH<sub>2</sub> 0.14 eV, PbH<sub>4</sub> – 0.18 eV. The Δ<sub>so</sub><sup>M</sup> values are much larger than the previously reported molecular spin-orbit effects on the thallium hydrides.<sup>1</sup> Hence, molecular spin-orbit contributions are not negligible, but they are only 10%–20% of the atomic corrections. Using a single group one-spinor (Λ–S coupling for linear molecules) or the more difficult to handle double group two-spinor (ω–ω coupling for linear molecules) coupling scheme for the lead hydrides is therefore a question of the desired amount of accuracy. Clearly, this is not true for the whole region of the potential curve, because the spin-orbit splitting for the Pb

TABLE VI. Equilibrium distances r<sub>e</sub>, bond angles α<sub>e</sub> [∠(HPbH)], dissociation energies D<sub>e</sub> (PbH<sub>n</sub> → Pb + nH), harmonic force constants k<sub>e</sub>, dipole moments μ<sub>e</sub>, and adiabatic ionization energies I<sub>e</sub> for the lead hydrides. Experimental values from Huber and Herzberg (Ref. 4).

		NRPP	ARPP	QRPP	SEPP <sup>a</sup>	R <sup>a</sup>	Expt.
r <sub>e</sub> [Å]	PbH <sup>+</sup>	1.834	1.792	1.787	1.806		
	PbH	1.857	1.818		1.839	1.95 <sup>f</sup>	1.839
	PbH <sub>2</sub>	1.853	1.811	1.816	1.833	1.837 <sup>c</sup>	
	PbH <sub>4</sub>	1.806	1.732	1.739		1.795 <sup>c</sup>	1.752 <sup>b</sup>
α <sub>e</sub> [deg]	PbH <sub>2</sub>	93.0	92.1	90.8	90.3	92.7 <sup>c</sup>	
D <sub>e</sub> [eV]	PbH <sup>+</sup>	1.96	1.81	0.88	1.82		
	PbH	1.77	1.62	0.53	1.56	1.64 <sup>f</sup>	1.69(?) <sup>i</sup>
	PbH <sub>2</sub>	3.78	3.54	2.59	3.99	3.33 <sup>c</sup>	
	PbH <sub>4</sub>	8.65	7.51	6.24		6.97 <sup>c</sup>	8.5(?) <sup>h</sup>
k <sub>e</sub> [10 <sup>–3</sup> a.u.]	PbH <sup>+</sup>	121	131	136	116		
	PbH	114	109		103	76 <sup>f</sup>	93
	PbH <sub>2</sub>	246	230	241	189		
	PbH <sub>4</sub>	579	630	630		770 <sup>c</sup>	
∠(HPbH)	PbH <sub>2</sub>	158	156	151	122	152 <sup>d</sup>	
μ <sub>e</sub> [D]	PbH	0.32	0.98		1.21		
	PbH <sub>2</sub>	0.39	1.28		1.64		
I <sub>e</sub> [eV]	PbH	6.60	6.39		6.84		

<sup>a</sup> Relativistic results from other authors.

<sup>b</sup> Calculated from r<sub>e</sub> (PbH<sub>4</sub>) = r<sub>e</sub> (PbH) × r<sub>e</sub> (SnH<sub>4</sub>) / r<sub>e</sub> (SnH). Sn–H bond distances from Refs. 4 and 46.

<sup>c</sup> Pelissier (ARPP) (Ref. 15).

<sup>d</sup> Hafner *et al.* (QRPP) (Ref. 17).

<sup>e</sup> Aguilar-Ancono *et al.* (relativistic X<sub>α</sub>) (Ref. 18).

<sup>f</sup> Balasubramanian *et al.* (QRPP) (Ref. 19).

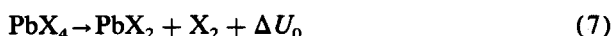
<sup>g</sup> SEPP values for D<sub>e</sub> are SO corrected, Δ<sub>so</sub> = Δ<sub>so</sub><sup>A</sup> – Δ<sub>so</sub><sup>M</sup> using the experimental values for Δ<sub>so</sub><sup>A</sup> (Ref. 39). For PbH the atomic correction Δ<sub>so</sub><sup>A</sup> was taken only.

<sup>h</sup> From mass spectroscopic measurements (Ref. 11).

<sup>i</sup> The expt. D<sub>e</sub> given in Ref. 4 is uncertain.

atom is more than 1.3 eV.<sup>39</sup> It is also remarkable that the value of  $\Delta_{\text{so}}^M$  in  $\text{PbH}_4$  is negative which probably results from a larger  $p_{3/2}$  contribution in the Pb–H bond. Now we give the total spin–orbit destabilizations  $\Delta_{\text{so}} = \Delta_{\text{so}}^A - \Delta_{\text{so}}^M$  of the lead hydrides for the overall dissociation  $\text{PbH}_n \rightarrow \text{Pb} + n\text{H}$ :  $\text{PbH}^+$  0.93 eV,  $\text{PbH}$  1.09 eV (using  $\Delta_{\text{so}}^A$  only),  $\text{PbH}_2$  0.95 eV, and  $\text{PbH}_4$  1.27 eV. So the relativistic effects are of the same order of magnitude as the correlation effects, as found for the Pb atom. Finally, our SEPP/CISD value for  $\text{PbH}$  is in good agreement with the (relatively uncertain) experimental value.<sup>4</sup>

From Table VI we get the order of Pb–H bond stabilities:  $\text{PbH}_4 > \text{PbH}_2 > \text{PbH}^+ > \text{PbH}$ . Hence, from the energetic point of view, the oxidation state IV is rather more preferred than II. Also,  $\text{PbH}_4$  is destabilized by relativistic effects by the same amount as  $\text{PbH}_2$ , 0.6 eV per Pb–H bond. We may then conclude that the inert pair effect is small for the lead hydrides. But, if we consider the reaction



which is important for discussing the stability of  $\text{Pb(IV)}$  compounds, we get for  $\text{X} = \text{H}$   $\Delta U_0 \cong 0$  eV. Here we used  $D_e(\text{PbH}_4) = 8.5$  eV,<sup>11</sup>  $D_e(\text{PbH}_2) = 4.0$  eV (Table VI), and  $D_e(\text{H}_2) = 4.5$  eV.<sup>4</sup> The experimental value for  $\text{PbH}_4$  is relatively uncertain<sup>11</sup> and the CISD value for  $\text{PbH}_2$  is lower than the experimental value so we do not know exactly if reaction (7) is exothermic or not. Nevertheless, the relativistic contributions to  $\Delta U_0$  are quite large,  $\Delta U_0^R = -0.93$  eV using ARPP and  $\Delta U_0^{R,\text{so}} = -1.22$  eV including spin–orbit coupling. Neglecting in the first step entropy effects and shift of the equilibrium in Eq. (7) through  $\text{H}_2$  loss (which surely is important), relativistic effects shift the equilibrium from the left to the right. This explains the instability of  $\text{PbH}_4$  in contrast to  $\text{SnH}_4$ .<sup>10</sup> But why is organolead chemistry mainly that of  $\text{Pb(IV)}$  rather than of  $\text{Pb(II)}$ , just as organothallium is mainly that of  $\text{Tl(III)}$  rather than of  $\text{Tl(I)}$ ?<sup>48,49</sup> For example  $\text{Pb}(\text{CH}_3)_4$  is well known,<sup>50</sup> but  $\text{Pb}(\text{CH}_3)_2$  is postulated only as an intermediate in several reactions.<sup>51,52</sup> One reason could be that  $\text{PbR}_4$  compounds ( $\text{R} = \text{any organic group}$ ) are thermodynamically unstable (as is probably the case for  $\text{PbH}_4$ ), but kinetically stable because of steric hindrance and molecular rearrangements of the organic groups to form  $\text{R}_2$ . Therefore, the activation energy in reaction (7) should be high. Another reason may be that the inert pair effect is smaller in covalent bonds than in ionic bonds (smaller  $6s$  participations), therefore,  $\text{PbR}_4$  ( $\text{R} = \text{H}$  or an organic group) compounds are more stable than  $\text{PbX}_4$  compounds ( $\text{X} = \text{F}, \text{Cl}, \dots$ ). This interesting question needs more detailed theoretical investigation.

The relativistic effects on the force constants are small, whereas the dipole moment is more sensitive to relativistic effects. For example, the relativistic contribution in  $\mu_e(\text{PbH})$  is 0.89 D, much larger than the correlation effect of 0.23 D (neglecting spin–orbit contributions, which are assumed to be small at the equilibrium distance; e.g., compare Refs. 53 and 54).

#### IV. SUMMARY

We have used different kinds of pseudopotential to study the effects of relativity and correlation for various lead

hydrides. Relativistic effects are found to be as important as correlation effects for most molecular properties. A [Pt]–core ARPP including correlation and corrections for spin–orbit coupling is sufficient to yield accurate results for all the lead hydrides. Molecular spin–orbit coupling effects are found to be not important for calculating bond distances, but should not be neglected for dissociation energies. The inert pair effect for the Pb hydrides has been discussed. A dominance of the oxidation state II in Pb was not clearly found. Accurate experimental data for  $\text{PbX}_4$  and  $\text{PbX}_2$  ( $\text{X} = \text{any inorganic or organic group}$ ) dissociation energies are necessary to discuss and understand the inert pair effect in more detail.

*Note added in proof:* Recently, Chapman *et al.* published a study of the effect of spin–orbit coupling on the  $\text{PbH}$  dipole moment showing that the  $^2\Pi_{3/2}$  state has a smaller  $\mu_e$  of about 0.26 D compared to the  $^2\Pi_{1/2}$  state.<sup>21</sup>

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