All-electron molecular Dirac-Hartree-Fock calculations: the group IV tetrahydrides CH_4, SiH_4, GeH_4, SnH_4 and PbH_4.

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Abstract

We describe a basis-set-expansion Dirac-Hartree-Fock program for molecules. Bond lengths and harmonic frequencies are presented for the ground states of the group IV tetrahydrides CH_4, SiH_4, GeH_4, SnH_4 and PbH_4. The results are compared with relativistic effective core potential (RECP) calculations, first-order perturbation theory (PT) calculations and with experimental data. The bond lengths are well predicted by first-order perturbation theory for all molecules, but none of the RECPs considered provides a consistent prediction. Perturbation theory overestimates the relativistic correction to the harmonic frequencies; the RECP calculations underestimate the correction.

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I. INTRODUCTION

The chemistry of heavy elements is strongly influenced by relativistic effects. This has led to the development of a number of methods for incorporating relativistic effects in molecular electronic structure calculations. It is generally agreed that to include relativity in a rigorous manner, the Dirac equation should be used as the basis for such methods. It is also recognized that using finite-basis-set methods in a full 4-component treatment makes so much greater demands on computing resources than the corresponding nonrelativistic treatment that the calculations may be prohibitively expensive [1 – 3].

Since the effects of relativity are small for much of the periodic table, perturbation theory (PT) has been a popular way of adding relativistic effects. These are usually based on the Breit-Pauli Hamiltonian, often including only the mass-velocity and Darwin terms in the one-electron operator, and neglecting spin-orbit coupling entirely [4, 5]. With the development of effective core potential (ECP) methods in the 1970s [6, 7] use was made of relativistic numerical atomic structure calculations to include the effect of relativity on the core in determining the effective potential [1, 8, 9]. These relativistic effective core potentials (RECPs) are commonly presented in a spin-free or spin-averaged form [2, 10, 11] which enables the calculations to be done with the traditional nonrelativistic methods.

Other work has taken advantage of numerical atomic methods in different ways. Desclaux and Pyykkö used a one-center expansion method to calculate relativistic corrections to hydrides of heavy atoms [12]. Rosén and Ellis [13] developed a discrete variational method based on the Slater exchange approximation which has been applied to a number of systems containing heavy elements, and Malli and Pyper [14] have used numerical atomic functions supplemented with Slater functions in a basis set approach for molecules.

Another approach involves reducing or transforming the Dirac equation in some fashion to obtain an effective Hamiltonian which operates only on a one-component or two-component wave function instead of on the full four-component

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wave function [15 – 19]. Some methods based on this approach were derived to overcome problems with variational collapse [20], which plagued the first attempts at molecular Dirac-Hartree-Fock (DHF) calculations in a finite basis set [21]. These problems arise because in a finite basis representation of the Dirac Hamiltonian, the large and small component basis sets may not be chosen independently, but are related [22 – 25]. The relation to lowest order in $1/c^2$ is known as "kinetic balance" [25]. The issues of the solution of the Dirac equation in a finite basis set, and the more fundamental questions of the foundations of relativistic electronic structure theory have been investigated at length and the problems largely resolved (see Ref. 26), so that it is now possible to proceed with confidence in the construction of electronic structure codes based on the Dirac equation.

The first basis set DHF calculations on many-electron molecules using kinetic balance were done by Lee and Mclean [22] using Slater functions for AgH and AuH, and Datta and Ewig [27] using Gaussian functions for Be_2, and the first calculations on polyatomic molecules by Aerts and Nieuwpoort [28] for CH_4, SiH_4 and GeH_4, using Gaussian functions. While much has been done recently on atomic systems [29 – 34], there have been relatively few calculations on molecular systems [35 – 38], since these remain very computationally expensive. In this paper we describe a DHF program for polyatomic molecules and present results for the ground states of the group IV tetrahydrides CH_4, SiH_4, GeH_4, SnH_4 and PbH_4. Relativistic effects on the structure of these molecules have previously been studied using the one-center expansion method [12a] and perturbation theory with only the mass-velocity and Darwin terms [39]. We compare the results with first-order perturbation (PT) calculations and RECP calculations. We believe this is the first time properties predicted by RECP and PT calculations have been calibrated against all-electron DHF calculations on molecules containing heavy elements.

The basic DHF theory is presented in section II, and the implementation discussed in section III. Basis sets used in the calculations are presented in section IV, the computational details are given in section V, and the results in section VI.

II. THEORY

Dirac-Hartree-Fock-Roothaan theory has been presented before for atoms [40] and molecules [41]. We summarize the derivation for completeness and to facilitate discussion of the implementation.

With a single determinant many-electron wave function constructed from 4-spinors $|j\rangle$, we may write the (unrestricted) Dirac-Fock energy as

$$E = \sum_{j=1}^{n} \langle j | \hat{h}_D | j \rangle + \frac{1}{2} \sum_{j,k=1}^{n} [\langle jk | \hat{g} | jk \rangle - \langle jk | \hat{g} | kj \rangle]. \tag{1}$$

The one-electron operator in the field of the nuclei is

$$\hat{h}_D = -ic\,\boldsymbol{\alpha} \cdot \nabla + (\beta - 1)c^2 + V^{nuc}, \tag{2}$$

where $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$; α_x, α_y, α_z and β are 4×4 matrices,

$$\alpha_x = \begin{pmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{pmatrix}, \ \alpha_y = \begin{pmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{pmatrix}, \ \alpha_z = \begin{pmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{pmatrix}, \ \beta = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix}.$$

σ_x, σ_y and σ_z are the Pauli spin matrices, and I_2 and 0_2 are the 2×2 unit and zero matrices, respectively. The fully covariant electron-electron interaction can be expanded in a power series in c^{-2}. The lowest order term, which is $\mathcal{O}(c^0)$, is the Coulomb interaction,

$$\hat{g} \equiv \hat{g}(1,2) = \frac{1}{r_{12}}. \tag{3}$$

The term which contributes at the next order, $\mathcal{O}(c^{-2})$, is the Breit interaction, whose contribution to the energy comes mainly from the region near the nuclei. For present purposes, the Coulomb interaction is an adequate description of the electron-electron interaction. Writing the 4-spinors in terms of large and small component 2-spinors j^L and j^S,

$$|j\rangle = \begin{pmatrix} j^L \\ i j^S \end{pmatrix} \tag{4}$$

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where the superscripts L and S indicate large and small components respectively, we obtain for the matrix elements of the one- and two-electron operators

$$\langle j|\hat{h}_D|j\rangle = c\left[\langle \mathbf{j}^L|(\sigma \cdot \nabla)|\mathbf{j}^S\rangle - \langle \mathbf{j}^S|(\sigma \cdot \nabla)|\mathbf{j}^L\rangle\right]$$

$$+ \langle \mathbf{j}^L|V^{nuc}|\mathbf{j}^L\rangle + \langle \mathbf{j}^S|V^{nuc} - 2c^2|\mathbf{j}^S\rangle,$$

(5)

$$\langle j\,k|\hat{g}|j\,k\rangle = (\mathbf{j}^L\mathbf{j}^L|\mathbf{k}^L\mathbf{k}^L) + (\mathbf{j}^L\mathbf{j}^L|\mathbf{k}^S\mathbf{k}^S)$$

$$+ (\mathbf{j}^S\mathbf{j}^S|\mathbf{k}^L\mathbf{k}^L) + (\mathbf{j}^S\mathbf{j}^S|\mathbf{k}^S\mathbf{k}^S)$$

(6a)

$$\langle j\,k|\hat{g}|k\,j\rangle = (\mathbf{j}^L\mathbf{k}^L|\mathbf{k}^L\mathbf{j}^L) + (\mathbf{j}^L\mathbf{k}^L|\mathbf{k}^S\mathbf{j}^S)$$

$$+ (\mathbf{j}^S\mathbf{k}^S|\mathbf{k}^L\mathbf{j}^L) + (\mathbf{j}^S\mathbf{k}^S|\mathbf{k}^S\mathbf{j}^S).$$

(6b)

Note that, since the 2-spinors are complex, the integrals may also be complex. We expand the large and small components in basis sets of 2-spinors $\{\mu^L\}$ and $\{\mu^S\}$

$$|\mathbf{j}^L\rangle = \sum_{\mu=1}^N c^L_{\mu j}|\mu^L\rangle; \quad |\mathbf{j}^S\rangle = \sum_{\mu=1}^N c^S_{\mu j}|\mu^S\rangle,$$

(7)

and define the nuclear potential energy, overlap, kinetic energy and density matrix elements by

$$V^{XX}_{\mu\nu} = \langle \mu^X|V^{nuc}|\nu^X\rangle,$$

(8)

$$S^{XX}_{\mu\nu} = \langle \mu^X|\nu^X\rangle,$$

(9)

$$\Pi^{XY}_{\mu\nu} = \langle \mu^X|\sigma \cdot \nabla|\nu^Y\rangle,$$

(10)

$$D^{XY}_{\mu\nu} = \sum_{j=1}^n c^{X*}_{\mu j}c^Y_{\nu j},$$

(11)

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respectively, where X and Y can be L or S, except that for the kinetic energy matrix elements, $X \neq Y$. The Dirac-Fock energy can then be written

$$E = \sum_{\mu\nu}^{N} \left[c(D_{\mu\nu}^{LS} \Pi_{\mu\nu}^{LS} - D_{\mu\nu}^{SL} \Pi_{\mu\nu}^{SL}) + D_{\mu\nu}^{LL} V_{\mu\nu}^{LL} + D_{\mu\nu}^{SS} (V_{\mu\nu}^{SS} - 2c^2 S_{\mu\nu}^{SS}) \right]$$

$$+ \frac{1}{2} \sum_{\mu\nu\kappa\lambda}^{N} \left[D_{\mu\nu}^{LL} D_{\kappa\lambda}^{LL} \{ (\mu^L \nu^L | \kappa^L \lambda^L) - (\mu^L \lambda^L | \kappa^L \nu^L) \} \right. \tag{12}$$

$$+ D_{\mu\nu}^{SS} D_{\kappa\lambda}^{SS} \{ (\mu^S \nu^S | \kappa^S \lambda^S) - (\mu^S \lambda^S | \kappa^S \nu^S) \}$$

$$\left. + 2 D_{\mu\nu}^{LL} D_{\kappa\lambda}^{SS} (\mu^L \nu^L | \kappa^S \lambda^S) - 2 D_{\mu\nu}^{LS} D_{\kappa\lambda}^{SL} (\mu^L \lambda^L | \kappa^S \nu^S) \right].$$

From this expression we obtain the matrix representation of the Dirac-Hartree-Fock equations,

$$\begin{pmatrix} \mathbf{F}^{LL} - \epsilon \mathbf{S}^{LL} & \mathbf{F}^{LS} \\ \mathbf{F}^{SL} & \mathbf{F}^{SS} - \epsilon \mathbf{S}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{c}^L \\ \mathbf{c}^S \end{pmatrix} = 0, \tag{13}$$

with the elements of the various blocks of the Fock matrix defined by

$$F_{\mu\nu}^{LL} = V_{\mu\nu}^{LL} + \sum_{\kappa\lambda}^{N} \left[D_{\kappa\lambda}^{LL} \{ (\mu^L \nu^L | \kappa^L \lambda^L) - (\mu^L \lambda^L | \kappa^L \nu^L) \} \right.$$

$$\left. + D_{\kappa\lambda}^{SS} (\mu^L \nu^L | \kappa^S \lambda^S) \right], \tag{14a}$$

$$F_{\mu\nu}^{SS} = V_{\mu\nu}^{SS} - 2c^2 S_{\mu\nu}^{SS} + \sum_{\kappa\lambda}^{N} \left[D_{\kappa\lambda}^{SS} \{ (\mu^S \nu^S | \kappa^S \lambda^S) - (\mu^S \lambda^S | \kappa^S \nu^S) \} \right.$$

$$\left. + D_{\kappa\lambda}^{LL} (\mu^S \nu^S | \kappa^L \lambda^L) \right], \tag{14b}$$

$$F_{\mu\nu}^{LS} = c \Pi_{\mu\nu}^{LS} - \sum_{\kappa\lambda}^{N} D_{\kappa\lambda}^{SL} (\mu^L \lambda^L | \kappa^S \nu^S) = F_{\mu\nu}^{SL*}. \tag{14c}$$

The 2-spinors may be written as a combination of scalar functions $|a\rangle$ and $|b\rangle$ with spin functions:

$$|\mu^X\rangle = \sum_{a} T_{\mu a}^{X\alpha} |a\rangle \chi(\tfrac{1}{2}) + \sum_{b} T_{\mu b}^{X\beta} |b\rangle \chi(-\tfrac{1}{2}). \tag{15}$$

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where $\chi(\frac{1}{2}) = \binom{1}{0}$ and $\chi(-\frac{1}{2}) = \binom{0}{1}$ are unit vectors in spin space corresponding to $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$, conventionally labelled α and β. The summations usually extend over only a few functions. (15) may be used to further reduce the Fock matrix expressions:

$$F_{\mu\nu}^{XY} = \sum_{\sigma\tau}\sum_{ab} T_{\mu a}^{X\sigma*}\, F_{ab}^{\sigma\tau}\, T_{\nu b}^{Y\tau}, \tag{16}$$

where σ and τ run over both m_s values. The Fock matrix elements in the scalar basis are given by the following expressions. If functions a and b belong to the same component (L or S),

$$F_{ab}^{\sigma\sigma} = V_{ab}^{\sigma\sigma} + \sum_{cd}(\,ab\,|\,cd\,)\left[D_{cd}^{\sigma\sigma} + D_{cd}^{\tau\tau}\right] - \sum_{cd}(\,ad\,|\,cb\,)D_{cd}^{\sigma\sigma}, \tag{17a}$$

$$F_{ab}^{\sigma\tau} = -\sum_{cd}(\,ad\,|\,cb\,)D_{cd}^{\tau\sigma}. \tag{17b}$$

The sums over c and d for the direct integrals $(\,ab\,|\,cd\,)$ extend over both components, while those for exchange integrals $(\,ad\,|\,cb\,)$ extend only over the same component as a and b. For the blocks connecting the large and small components,

$$F_{ab}^{\sigma\sigma} = (2\sigma)\,c\Pi_{ab}^{0} - \sum_{cd}(\,ad\,|\,cb\,)D_{cd}^{\sigma\sigma} \tag{17c}$$

$$F_{ab}^{\sigma\tau} = c\Pi_{ab}^{2\tau} - \sum_{cd}(\,ad\,|\,cb\,)D_{cd}^{\tau\sigma} \tag{17d}$$

where a and d are large component functions, and b and c are small component functions. The kinetic energy matrix elements are defined by

$$\Pi_{ab}^{0} = \langle\, a\,|\,\tfrac{\partial}{\partial z}\,|\,b\,\rangle, \quad \Pi_{ab}^{\pm 1} = \langle\, a\,|\,\tfrac{\partial}{\partial x} \pm i\tfrac{\partial}{\partial y}\,|\,b\,\rangle. \tag{18}$$

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III. IMPLEMENTATION.

The principal causes of variational collapse in attempts to solve the Dirac equation were the failure to satisfy the boundary conditions at the nucleus [26], and the failure to ensure the proper relations between the large and small component basis functions [22–25]. If the nuclear model is chosen to be a point charge, the solutions of the Dirac equation have weak singularities at the nuclei; for any nuclear model with a charge distribution of finite radius, the Dirac wave function is finite and approximately Gaussian in shape at the nuclear origins. The first case is well described with the relativistic Sturmians of Drake and Goldman [42] or the Slater- or Laguerre-spinors introduced by Quiney et al. [29c]. However, use of such functions cannot be readily extended to polyatomic molecules, for which Gaussian functions are the only practical choice. We have therefore chosen to use Gaussian functions with a nuclear model of finite radius. For the purposes of electronic structure calculations, the details of the model for the nuclear charge distribution are not critical, provided they approximately represent the real distribution. (This will not necessarily be true, of course, for properties such as nuclear hyperfine structure and parity non-conservation effects, which may be sensitive to the nuclear model.) One approach [31, 33, 34] is to use a uniform charge distribution for the nuclear model,

$$\rho_{nuc}(r) = \rho_0, \ r \leq r_0$$
$$= 0, \ r > r_0. \tag{19}$$

We follow Visser et al. [43] and use a single Gaussian function for the nuclear charge distribution,

$$\rho_{nuc}(r) = \rho_0 \exp(\eta_{nuc} r^2). \tag{20}$$

For this choice, the integrals may be evaluated using existing technology, with minor changes to the expressions for point charge nuclear integrals, whereas the expressions for the uniform nuclear model are a little more complex [44]. The nuclear exponent is chosen to match the rms radii of the Gaussian and the nucleus,

$$\eta_{nuc} = 3/2r_{rms}^2. \tag{21}$$

The nuclear rms radius is represented by a function of the nuclear mass, A,

$$r_{rms} = \langle r^2 \rangle_{nuc}^{1/2} = 0.836 A^{1/3} + 0.57, \tag{22}$$

where A is in amu and r_{rms} is in fm. The constants are derived from a fit to RMS radii determined from nuclear scattering data [45].

There has been some recent discussion of whether it is necessary to have the same number of 2-spinor basis functions for the large and small components [26, 46]. We have concluded [47] that it is important to do this, and therefore we have chosen the basis sets for the large and small components to be matched in pairs. The primitive basis functions from which contracted sets are constructed are chosen to satisfy the kinetic balance criterion [25], in its restricted form [47]:

$$\mu^S = \mathcal{N}\, \sigma . \nabla\, \mu^L, \tag{23}$$

where $\mathcal{N}$ is a normalization factor.

Basis set contraction in DHF calculations has been discussed recently by Ishikawa et al. [31c] and Visscher et al. [38a]. Ishikawa et al. showed that contraction causes only a small increase in atomic energies, in contrast to the findings of Aerts and Nieuwpoort [28]. There is no *a priori* reason why contracted functions should not provide an adequate basis set for DHF calculations, provided that the contraction coefficients are chosen with care, as Visscher et al. [38a] have discussed. We have adopted a general contraction scheme in our calculations, since this has proved to be an efficient means for contracting the core orbitals in nonrelativistic calculations [48] — though there is no limitation in the program, apart from space considerations, on the use or nature of contracted functions. The contraction coefficients for large and small component basis functions are determined from basis set calculations on the appropriate atom. We have made an adaption of the program GRASP [49] for this purpose. The contracted functions, however, no longer satisfy (23) but rather approximate the more accurate relation

$$\mu^S \simeq (V - E - 2c^2)^{-1} \sigma . \nabla\, \mu^L. \tag{24}$$

Basis sets are discussed further in the next section, in relation to the nonrelativistic limit of DHF calculations.

For the scalar basis our program uses spherical harmonic Gaussian functions that are symmetry-adapted for D_{2h} and its subgroups. Since each of these symmetry functions has a unique set of atomic quantum numbers, the 2-spinors constructed from them are symmetry functions for the corresponding double group. For linear molecules advantage is taken of the higher symmetry when constructing 2-spinors. The symmetry 2-spinors may also be regarded as being constructed from jj-coupled atomic 2-spinors, which are defined by

$$\mu_{An\ell jm} = R_{n\ell j}(r) \sum_{m_s = \pm 1/2} \langle \ell\, s\, m - m_s\, m_s \,|\, j\, m \rangle Y_{\ell m}(\theta, \phi)\, \chi(m_s) \qquad (25)$$

where A denotes the atomic center, $R_{n\ell j}(r)$ is the radial part of the atomic orbital and $Y_{\ell m}(\theta, \phi)$ is a complex spherical harmonic. Operating on this 2-spinor with the time-reversal operator, $\hat{T} = -i\sigma_y \hat{\mathcal{K}}$, produces the spinor with opposite m value:

$$\hat{T} \mu_{An\ell jm} = (-1)^{j+m-\ell} \mu_{An\ell j-m}, \qquad (26)$$

where $\hat{\mathcal{K}}$ is the complex conjugation operator. We choose the overall phase of the symmetry 2-spinors to incorporate the phase factor for negative m:

$$|\mu\rangle = \sum_A b_{A\mu} |\mu_{A\ell jm}\rangle, \quad m > 0$$
$$= (-1)^{j+m-\ell} \sum_A b_{A\mu} |\mu_{A\ell jm}\rangle, \quad m < 0. \qquad (27)$$

For small component spinors, the time-reversal operator has the opposite sign, which carries over into the definition of the negative m spinors. Thus in a Kramers-restricted Dirac-Fock calculation, the coefficients $c_{\mu i}$ for a given molecular spinor and its corresponding time-reversed spinor are related by complex conjugation.

The one- and two-electron integrals are generated by an adaption of the program MOLECULE (Almlöf and Taylor, unpublished), and are kept in the scalar basis. Of the possible classes of integrals arising from different combinations of

scalar basis functions of the two component types, only three are required for DHF calculations within the Coulomb approximation to the electron-electron interaction. They are of the type (LL|LL), (LL|SS) and (SS|SS). The (LS|LS) integrals come from the magnetic (Gaunt) interaction and are not used in the current implementation; the remaining classes never appear in the formulation of the Dirac-Fock problem. The three classes used are written to separate files. The advantage of this is that the SCF calculations can be done in three stages, with only the (LL|LL) integrals in the first, adding the (LL|SS) integrals in the second, and adding the (SS|SS) integrals in the third. Due to the numbers of scalar functions for large and small components, there is almost an order of magnitude more (LL|SS) integrals than (LL|LL), and a factor of 2 or 3 more (SS|SS) integrals than (LL|SS). In most systems, the large component provides most of the electron density, so that an SCF calculation with only the (LL|LL) integrals is expected to require the greatest number of iterations to converge. Since the small component density is $\mathcal{O}(c^{-2})$ relative to the large component density, the addition of the (LL|SS) integrals will perturb the density by the same order, and the (SS|SS) integrals by $\mathcal{O}(c^{-4})$. Depending on the system under study, it may be possible to omit the (SS|SS) integrals entirely without adversely affecting the calculated properties.

The Fock matrix is constructed in the scalar basis using (17). Since this is the most time-consuming step in the SCF calculation, we have endeavoured to make it efficient. Each $(\,a\,b\,|\,c\,d\,)$ integral with distinct indices contributes in 36 unique places to the scalar Fock matrix. By constructing the required combinations of density matrices for all possible cases beforehand, it is possible to vectorize the construction of the Fock matrix using sparse vector operations. After construction, the Fock matrix is first transformed to the 2-spinor basis, then each (double group) symmetry block of the Fock matrix is transformed to the molecular spinor basis. Density damping, level shifting and DIIS extrapolation [50], which have been implemented to accelerate convergence, are then applied as selected, and the resultant Fock matrix is diagonalized. The initial guess vectors are either obtained by diagonalizing the one-electron Hamiltonian or read in. In the former case, if damping is used, the density matrix is scaled by the damping factor on the first iteration. Since this initial guess

has functions which are too tight, scaling helps offset the resultant overestimation of the screening, and has been found to save one or two SCF iterations. Several damping models have been introduced, but the one found to work best scales the damping factor according to the logarithm of the maximum density difference. The DIIS extrapolation is used only after the density damping is turned off, and in any case not until the maximum density difference is less than 10^{-2}.

A fuller discussion of the considerations for implementation is given in the article by Dyall et al. [37].

IV. BASIS SETS

In order to make useful comparisons of nonrelativistic and relativistic molecular properties, it is necessary to use basis sets which are reasonably well saturated. However, because the equivalent relativistic calculations require much larger basis sets than the nonrelativistic calculations, due to the small component, it is also necessary to keep the basis to a manageable size. The basis sets we have chosen are as follows.

For hydrogen, we used the same $(5s\,1p) \to [3s\,1p]$ basis in all calculations, with contraction coefficients taken from relativistic and nonrelativistic calculations on the atom. The s exponents are from Huzinaga [51], scaled as suggested by Dunning [52]; the p exponent is from Roos and Siegbahn [53]. For the group IV elements, the primitive basis sets were energy-optimized in nonrelativistic ground state SCF calculations. The primitive basis sets were chosen to give the same quality of basis in the valence region — approximately double-zeta — and similar relative errors in the total energy. For C and Si, two d polarization functions were added to each set, with exponents 1.0 and 0.4 for C, and 0.5 and 0.2 for Si. Only one d polarization function was added to each set for Ge, Sn and Pb, since the outermost d function from the $(n-1)d$ orbital serves also as a polarization function. The added function had an exponent 0.4 times the exponent of the outermost d. Contraction coefficients for these basis sets were determined from atomic SCF calculations using a general contraction scheme. The relativistic contraction coefficients were obtained from an adaption of GRASP [49] in which the converged numerical potentials were used to construct the Fock matrix, so that only one diagonalization was necessary to obtain the AO coefficients. The coefficients were determined for the $(2J+1)$-weighted average of the configuraton state functions (CSFs) from the p^2 configuration. For each heavy atom, the core was left generally contracted. For C the core included the inner parts of the $2s$ and $2p$ valence orbitals. The valence basis then consisted of $3s$, $3p$ and $2d$ functions. The basis set information is summarized in Table 1. To assess the adequacy of the basis sets, additions of d and f polarization functions and diffuse s, p and d functions were made in a series of calculations, some

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nonrelativistic and some both nonrelativistic and relativistic.

The main purpose of molecular all-electron DHF calculations is to determine the corrections to molecular properties due to relativity — whether directly or in calibrating approximate methods, such as RECPs. These relativistic corrections should be determined from a comparison of relativistic and nonrelativistic calculations, made at an equivalent level of theory with an equivalent basis set. The nonrelativistic equivalent of a relativistic calculation is found by taking the value of the speed of light, c, to infinity.* Formally, this leads to the use of the Schrödinger equation in place of the Dirac equation. In practice, it has often been achieved by scaling the value of the speed of light in calculations using the Dirac equation [21, 22, 31, 41b]. In numerical calculations, scaling is a relatively simple procedure, but in finite basis set calculations, the issues are more complex than simply scaling the value of c used in the SCF procedure. The finite-basis equivalent of a numerical calculation is one in which not only the MO coefficients are optimized, but also the contraction coefficients and the exponents of the primitive functions. Simply scaling c in the SCF calculation has no effect on the basis, and will lead to errors in the computed relativistic corrections. Whether it is possible to make some compromise will depend on the properties required from the calculations. In most molecular calculations, the core orbitals are not of much interest, and a deficiency in the core basis set may be tolerable provided it does not significantly affect the properties of the valence orbitals. Since it is the core exponents that are affected most by relativity, it may be possible to use the same set of exponents for both relativistic and nonrelativistic calculations. However, the changes in the core wave functions due to relativity must be incorporated in some form, so that if the same set of exponents is used, the contraction coefficients should depend on the value of c.

There is also a practical problem in the scaling of c in relativistic calculations to obtain the nonrelativistic limit. In numerical calculations, there are no problems with the accuracy of the calculations, provided the exponent range of the computer

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* This is not a one-to-one mapping: there are many relativistic calculations which reduce to the same nonrelativistic calculation in the limit of infinite c.

used is sufficiently large to prevent underflow or overflow. In finite basis calculations, scaling leads to a loss of significant figures in the results, since the number of significant figures depends on the range of diagonal elements in the Fock matrix, which scales with c^2. This scaling behaviour has been investigated by Laaksonen et al [36]. It is therefore not a practical procedure for obtaining nonrelativistic energies, particularly for molecules containing heavy elements. This is because it is necessary to scale c by an amount which makes the relativistic correction to the energy insignificant in comparison to the total energy – at least to the level of accuracy required in the calculations. While for first-row elements a factor of 10 to 100 is usually sufficient, for elements such as Pb it is often necessary to use a factor of 10^5 to 10^6. This would explain the discrepancy between the RSCF($c = 10^5$) and NRSCF results of Lee and McLean [21] for AgH and AuH, for example. Scaling the value of c to obtain the nonrelativistic limit in a finite basis set DHF calculation is therefore not recommended. The correct procedure is to do an HF calculation in an equivalent nonrelativistic basis set.

Matsuoka and Okada [33], in their DHF calculations on the sixth-row elements Tl – Rn, found it necessary to add two tight p functions to the nonrelativistic p basis sets of Fægri [54] in order to get agreement with the numerical total energy to better than about 0.2 E_h. Without the extra tight p functions, the agreement with the numerical results ranged from 1.1 E_h for Tl to 2.0 E_h for Rn. The p spin-orbit splittings also improved when the tight p functions were added: even halving the error in the $6p$ splitting. Their results are clear evidence for the dependence of the basis sets on the value of c: for the purpose of DHF calculations, nonrelativistically optimized basis sets have significant deficiencies in the core region for sixth-row elements, due to the relativistic orbital contraction. This deficiency is clearly displayed in Fig. 1, in which the difference between numerical and finite basis $1s$ functions is plotted for both relativistic and nonrelativistic cases. The deficiency arises from both an inadequate exponent range, shown by the large discrepancy for small r, and a shift in the optimal values of the exponents, shown by the oscillations at larger r. The exponent range may be improved — as Matsuoka and Okada have done — by adding tight functions; the re-optimization of basis sets is a more dif-

ficult task, which we have not yet attempted. Adding a single p function with an energy-optimized exponent to our basis for Pb decreased the difference between the basis set and numerical total energies by 1.2 E_h to 0.5 E_h, (82ppm to 23ppm), and adding a second p function with both exponents reoptimized gave an extra 0.2 E_h. The relative error obtained with these two extra p functions was 13ppm, which is in the same range as the relative errors for C, Si and Ge. For Sn, one extra optimal p function was needed to obtain a relative error of 17ppm. As shown below, these additional tight functions have only a small effect on the valence properties and are only included in calibration calculations.

V. COMPUTATIONAL DETAILS

The DHF calculations were done in three stages, according to the prescription given in section III. It was found that damping was only required in the first stage, and in fact slowed convergence in the second and third stages. DIIS was used to accelerate convergence in all stages. For PbH_4 we checked that the same results were obtained from the three-stage calculation as from a calculation in which all the integrals were included from the beginning, and found that they agreed to within the convergence tolerance. Comparison of the timing for the two calculations clearly showed the benefit of the three-stage calculation, which took only 60% of the CPU time used by the one-stage calculation. Integral generation and SCF calculations for PbH_4 required about $2\frac{1}{2}$ and $1\frac{3}{4}$ hours respectively on the Cray-YMP.

Nonrelativistic and perturbation theory (PT) results including the mass-velocity and Darwin terms were obtained with the MOLECULE/SWEDEN [55] package. The basis sets used were chosen to match the basis sets used in the DHF calculations: the primitive basis set used for the large component was used for the nonrelativistic calculations with a similar contraction pattern, giving a generally contracted core and a $3s\,3p\,2d$ uncontracted valence set. RECP results were obtained with the MOLECULE/SWEDEN package with the same size valence set. Two sets of RECPs were used for Ge, Sn and Pb, those of Wadt and Hay [2], and those of Hurley et al., Lajohn et al. and Ross et al. [11], without the spin-orbit terms. For the latter set, the semi-core RECP was also used, with the supplied basis set uncontracted. The RECP valence basis sets were similar to the valence basis sets in the all-electron calculations.

The bond lengths and harmonic frequencies for the breathing (a_1) mode were determined for each molecule from a quartic fit of the potential to five points in the breathing coordinate spanning the equilibrium geometry. For PbH_4, these results were checked against quartic polynomial fits in r to seven points around r_e. For CH_4 up to ten points were used to determine the best quartic fit. In the basis set tests, a quadratic function in $1/r$ was used, which takes account of most of the effects of anharmonicity and gives similar results to the quartic fit.

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VI. RESULTS AND DISCUSSION

A. Bond lengths

The equilibrium bond lengths and total energies of the molecules at r_e from the quartic fits to the DHF calculations are given in Table 2. Bond lengths from all-electron HF, DHF and PT calculations are presented in Table 3, along with experimentally-derived results. The experimental bond length for CH_4 is that of Gray and Robiette [56]. For SnH_4, values of B_e and B_0 were obtained from the data of Kattenberg and Oskam [57] and used with the value of r_0 from Ohshima et al. [58] to obtain r_e. The r_e values for SiH_4 and GeH_4 were obtained by adding an estimate of the appropriate correction to the experimental values of r_0 [59, 60]. The values of r_e given by Ohno et al. [61] would appear to be somewhat too small, and that given by Halonen et al. [62] too large. The PT results agree remarkably well with the DHF results — the relativistic corrections are neither consistently high nor low, but the relative error appears to decrease as the atomic number increases. The bond lengths and relativistic corrections to r_e obtained by Almlöf and Faegri [39] using PT are in good agreement with the present results except for PbH_4, where the bond length contraction is predicted to be much larger. The discrepancies can probably be ascribed to basis set differences. Their basis set for Pb lacked the d polarization function included in our calculations, which has the effect of lengthening the bond, and they included the contaminant $3s$ and $4p$ functions in their basis, eliminating linearly dependent functions by canonical orthonormalization. The somewhat more compact d and f set may also allow a little more penetration of the core by the valence, leading to a contraction in the bond and an overestimate of the relativistic contribution.

Bond lengths from RECP calculations for GeH_4, SnH_4 and PbH_4 are given in Table 4, along with the HF and DHF results. The Hay and Wadt [2] RECP gives a bond length that is a little too long for GeH_4, slightly too short for SnH_4, and substantially too short for PbH_4. The second set of RECPs [11] gives too short a bond length for GeH_4 and SnH_4, but about the right value for PbH_4 when only the ns and np orbitals are included in the valence space. When the $(n-1)d$ orbital

is included as well, the bond length for GeH$_4$ is unaffected, for SnH$_4$ it lengthens to give the DHF value but for PbH$_4$ it becomes too long by 0.026 Å. The RECP results of Pelissier (taken from Ref. 39) show the opposite trend — the SnH$_4$ bond length is too long but the PbH$_4$ bond length is about right — but this is a similar trend to the Wadt and Hay RECP results. Clearly the RECP predictions of the bond length are only accurate to about 0.03 Å, and depend on the nature of the RECP. What is a little more disturbing is that the trend from GeH$_4$ to PbH$_4$ does not match the DHF trend, particularly for the second set of RECPs, which are based on DHF atomic functions. Given that the PT results match the DHF results so well, it is also a little surprising that the Hay and Wadt RECPs, which are based on Cowan-Griffin atomic functions, do not perform better. We conclude that the discrepancies between the various RECPs are due to inherent deficiencies and not in their treatment of relativistic effects.

It is a little more difficult to make a valid comparison with the results of Schwerdtfeger et al. [63] since they include some correlation effects in their calculation. However, their results are similar to the DHF results. Both their relativistic and nonrelativistic bond lengths are somewhat shorter than ours, so that the relativistic correction to the bond length of 0.074 Å without spin-orbit interaction and 0.081 Å with spin-orbit interaction is in good agreement with our all-electron result. Correlation effects shorten the bond lengths in AgH and AuH [64], so it is possible that the differences are due to electron correlation: the comparison with experiment indicates that this is the case. Since their valence basis is also larger than the one we have used, some of the difference may be due to the basis sets; we discuss basis set effects in more detail below. Schwerdtfeger et al. also see a lengthening of the bond by 0.007 Å when spin-orbit effects are included. Our all-electron PT bond length is only 0.0015 Å shorter than the DHF value. Provided that correlation and relativistic effects of higher order in c^{-2} have no influence, this result indicates that the effect of the spin-orbit interaction may be much smaller than predicted by their pseudopotential model.

B. Harmonic frequencies

The harmonic frequencies from the all-electron calculations are given in Table 5 with the experimentally-derived values. The values of ω_e for CH_4 and SnH_4 are given by Gray and Robiette [56] and Halonen et al. [62] respectively; for SiH_4 and GeH_4 the harmonic frequencies are derived from the experimental fundamental frequencies in the following manner. The ratio of the values of $\omega_e x_e$ for CH and CH_4 was used to scale $\omega_e x_e$ for SiH to obtain a value for SiH_4. This value was scaled by the ratio of ν for SiH_4 and the heavier members of the series to obtain a value of $\omega_e x_e$ for the heavier members. The values of ω_e were then obtained by adding $2\omega_e x_e$ to the experimental fundamental frequencies. The values obtained for GeH_4 and SnH_4 agree well with the values quoted by Almlöf and Fægri [39], but the value for SiH_4 is somewhat higher. Calculating the frequency for SiH_4 from the force constant they quote gives a value equal to the fundamental frequency; thus we expect the value given here to be closer to the true harmonic frequency. The value predicted by this procedure for SnH_4 was within 2 cm^{-1} of the value given by Halonen et al., so we expect our procedure to be accurate to at least 5 cm^{-1} for SiH_4 and GeH_4.

The relativistic corrections to the frequencies obtained from the DHF calculations are smaller than those calculated by the PT approach, except for CH_4. Since the values are so small, particularly for the first three members of the series, it is uncertain how much reliability can be placed on them, due both to the incompleteness of the basis sets and to the fitting methods used to obtain the force constants. However, the quartic fit to eight points that was finally used for CH_4 gave energies that differed from the input values by less than $10^{-8} E_h$; we therefore expect this fit to be reliable. For SiH_4, the relativistic correction is negative: there is a subtle balancing of direct and indirect relativistic effects which causes a cancellation. Such effects have been seen in other properties: for example, in numerical atomic DHF calculations on the Group IV atoms, the integrated small component valence electron density is smaller for Si than for C or Ge, but the mixing of the $^1S_0$ and $^3P_0$ CSFs in the ground state increases monotonically down the group [65].

The relativistic corrections obtained here by PT are much smaller than those reported by Almlöf and Fægri [39]. The discrepancies may be explained by differences in the basis sets and the methods used to obtain the force constants. First, their basis sets were constructed differently. Where we used a general contraction for the core, they used a segmented contraction in which only the inner parts of the $1s$ and $2p$ core functions were contracted. Their basis included the $3s$ and $4p$ contaminants from the d and f functions while ours did not. The linearly-dependent functions thus introduced were eliminated by canonical orthonormalization. The s and p space they used was larger than ours, but the d and f space was smaller. Second, the force constants were obtained from a quadratic fit in r, which we found to give consistently higher values. A quartic fit to their original data gave a small reduction in the force constant. Calculations on SnH_4 without the added d function ($\zeta = 0.17$) gave a value of the frequency which was higher by about 1%. It may well be that, with the smaller d and f space used for Pb, the core in their calculations is a little too compact, leading to a shorter bond length, a higher frequency, and an overestimate of the relativistic corrections.

Harmonic frequencies from RECP calculations for GeH_4, SnH_4 and PbH_4 are given in Table 6, with the HF and DHF values included for comparison. Despite the inculsion of relativistic effects in the RECPs, the only values that are greater than the nonrelativistic values are the full core value for PbH_4 and the semi-core value for GeH_4 with the second set of RECPs [11], and the value for GeH_4 is substantially overestimated. Since the largest relativistic correction to the frequency is 27 cm^{-1} for PbH_4, and the RECP frequencies deviate from the DHF value by up to 38 cm^{-1} for PbH_4, 32 cm^{-1} for SnH_4 and 22 cm^{-1} for GeH_4, it would be impossible to draw any conclusions about relativistic effects on the frequencies based on the current RECP calculations.

C. Spin-orbit splitting and bonding

The spin-orbit splitting of the valence t_2 orbital, which is the bonding orbital involving the np orbital on the heavy atom, is given in Table 7, and compared with the atomic spin-orbit splitting. The magnitude of the splitting at r_e is about two-thirds of the atomic splitting. For PbH_4, the addition of two tight p functions increases the splitting by about $2\frac{1}{2}\%$: it is these numbers which are reported in Table 7. The spin-orbit splitting increases as r decreases around r_e. The gradient of the splitting at r_e is also reported. The spin-orbit splitting is varying quite rapidly in this region. Although for PbH_4 the splitting does not appear to have a large effect on the structure (see below), this may not always be the case.

The effect of relativity on the bonding of heavy elements has been discussed by a number of authors. Briefly, for diatomic molecules, $s\sigma$ bonds are strengthened due to the direct relativistic effects on the s orbitals, whereas $p\sigma$ and $p\pi$ bonds are weakened by admixture of $p\pi^*$ and $p\sigma^*$ orbitals respectively, due to the spin-orbit interaction. However, $p_{1/2}$ and $p_{3/2}$ spinors with $m_j = 1/2$ are in the same double group irreducible representation (irrep), and may mix to form spinors which are purely bonding or antibonding — known as relativistic hybridization. The energy cost is a fraction of the spin-orbit splitting energy of the atomic p orbital, and is reflected in a reduced bond energy D_e. Schwerdtfeger et al. [63] discuss the bonding in the lead hydrides in terms of sp and relativistic hybridization and orbital contraction or expansion. While this is appropriate for the linear hydrides, and for PbH_2 which has C_{2v} symmetry and therefore only one double-group irrep for describing spin-$\frac{1}{2}$ particles, for PbH_4, which has tetrahedral symmetry, the two spin-orbit components of the $6p$ orbital belong to different double-group irreps, the $6p_{1/2}$ to Γ_7 and the $6p_{3/2}$ to Γ_8. Relativistic hybridization is therefore symmetry forbidden.

Spin-orbit interaction thus has an influence on the bonding in PbH_4 which is different from the linear molecules discussed previously. The doubly-degenerate γ_7 orbital, whose principal component from the Pb atom is the $6p_{1/2}$ orbital, involves all three components of the nonrelativistic t_2 orbital in equal amounts, giving a

symmetric charge distribution; the γ_8 orbital, involving the $6p_{3/2}$ orbital from Pb and which is quadruply degenerate, gives two different charge distributions: one more extended along the z-axis, and one more spread out in the xy-plane. (The H atoms are placed at the corners of a cube; the x, y and z axes are the two-fold axes of the point group.) As in the case of linear molecules, a promotion energy is required to get the electrons into the $6p_{3/2}$ orbital for bond formation. For the group IV atoms it is 4/3 of the spin-orbit splitting. Considering the ground state of Pb to consist of a single $6p_{1/2}^2$ CSF, the promotion energy amounts to 2.0 eV; with a more realistic two-CSF function, with 7.5% of the density in the $p_{3/2}$ orbital and 92.5% in the $p_{1/2}$, the promotion energy is 1.7 eV. Both spin-orbit components of the p orbital give rise to totally bonding molecular orbitals: there is no antibonding character in the occupied spinors. The strength of the bonds will therefore be influenced by the relativistic contraction or expansion of the p orbital components. The $6p_{3/2}$ expands only slightly, so the effect on the bonding will be small. The $6p_{1/2}$ orbital contracts; the effect on the bonding will depend on the size of the contraction. If the contraction is large, the $6p_{1/2}$ orbital may act as an inert pair and contribute little to the bonding, just as for the s orbital contraction. In this case, the overall bonding energy would decrease. If the contraction is not too large, the bonds will be strengthened, as for the s orbital in $s\sigma$ bonds. The decrease in bond energy due to the cost of promotion would then be offset by the increased bond strength. In a similar way, the remaining bonding orbital, the a_1 orbital in the single group, γ_6 in the double group, which involves the $6s$ orbital of Pb, will be either strengthened or weakened, depending on the strength of the relativistic contraction. There are therefore two major contributions to the relativistic correction to the bonding energy: the promotion cost from the $6p_{1/2}$ to the $6p_{3/2}$ for bond formation and the extent of orbital contraction or expansion, which will determine whether the bond is weakened or strengthened.

Where the balance of these effects lies is hard to assess. For Pb the contraction of the $6s$ is quite large, but the $6p_{1/2}$ contraction is relatively small. The $6s$ contraction is therefore likely to result in weaker bonding. The calculations in which two tight p functions were added to the basis set affected the valence spin-orbit split-

ting by a few percent, but made no significant difference to the bond length or the force constant, implying that these properties are relatively insensitive to the spin-orbit splitting. However, the change in the spin-orbit splitting was small, and its presence or absence may have a larger effect. Our PT calculations indicate that the spin-orbit splitting increases the bond length and reduces the harmonic frequency by a small amount, suggesting that the $6p_{1/2}$ orbital has contracted sufficiently to start behaving as an inert pair and weaken the bond somewhat. If the bond involving the $6p_{1/2}$ were strengthened, the energy gained would help overcome some of the repulsion due to the expanded $6p_{3/2}$ orbital and draw the hydrogen atoms inward.

D. Basis set effects.

In order to ensure that the results obtained are reasonably well converged with respect to the basis set, we have performed a number of calculations to assess the effect of augmenting the basis sets on the heavy atoms and on hydrogen. Most of these were done nonrelativistically, although some were checked with the DHF code to ensure that there were no substantial differential relativistic effects on the properties due to changes in the basis.

For PbH_4, nonrelativistic calculations were done to assess the effects of adding diffuse s and p functions, a second, more diffuse d polarization function, a third, diffuse d function and an f polarization function with exponent 0.3 on the Pb atom, using the H atom s basis without scaling the exponents, and replacing the p polarization function by two functions with exponents 1.25 and 0.45. The s, p and d functions were added to the Pb basis in an even-tempered series with a ratio of 2.5. The results are summarized in Table 8. Similar calculations were done using the Hay and Wadt [2] RECP (results not reported). It was found that, with the supplied basis [2] uncontracted, the same changes to the bond lengths were obtained as in the nonrelativistic calculations, except for the addition of an f function, where a larger contraction of 0.003 Å was obtained. Frequency corrections were also similar for changes in the spd basis, differing from the nonrelativistic values by at most 2 cm^{-1}. With the sp basis contracted either (2,1) or fully contracted, a much larger

sensitivity to the addition of other functions was noted. Replacing the valence basis with the basis from the all-electron calculations resulted in the same bond length and a frequency different by only 1.5 cm^{-1}. We conclude that the basis sets used in the all-electron and the RECP calculations are indeed equivalent. In the all-electron calculations, we also checked the effect on the bond length and frequencies of uncontracting the next outermost s, p and d functions from the core orbitals, and found it to be negligible. We are therefore confident that the contraction of the core orbitals does not significantly affect the molecular properties. The effect of adding two tight p functions in the DHF calculations was also assessed, and found to have negligible impact on the bond length and harmonic frequency, though it increased the valence spin-orbit splitting by $2\frac{1}{2}\%$.

For SnH$_4$ the effect of adding one d polarization function, adding a second d and adding an f function were assessed both relativistically and nonrelativistically. The results are summarized in Table 9. Although the corrections are *not* identical in both cases, the differential relativistic effect was found to be only a fraction of the total relativistic correction. The differential effect on the bond length was much smaller than that on the frequency: less than 1% change compared to 15%.

Differential relativistic effects on the corrections to the bond length and harmonic frequency on improving the basis were also noted for CH$_4$. Since the values of these quantities are small in the first place, it is not surprising that changes in the basis make changes in the relativistic corrections, but it serves to illustrate the need for high quality basis sets in order to get accurate results. Though in absolute terms the relativistic corrections to the properties converge faster than the properties themselves as the basis is increased, it appears that a small basis is not sufficient to get an accurate estimate of the relativistic corrections to molecular properties for light atoms. The frequency obtained by PT remained smaller than the DF value when a more diffuse basis was used for H, suggesting that the underestimation of the relativistic correction by PT is real rather than an artifact of the calculation.

For SiH$_4$, on the other hand, the addition of the second d function had very little differential effect – about 1% on the relativistic corrections to r_e, ω_e

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and the spin-orbit splitting. While this result may appear anomalous, it should be considered that there are important differences between C and Si which may have an effect. The core in C is smaller than in Si, and has only s-type functions where Si has both s- and p-type functions; as a result the bonding electrons may penetrate the core in CH_4 more and thus be more influenced by relativistic effects, despite the greater nuclear charge of Si.

The basis set investigations indicate that while the present results are not at the basis set limit they are not far from it. For PbH_4 the basis set limit for the bond length is probably 0.005 Å longer than the tabulated value, and the frequency 20 − 25 cm^{-1} lower. Differential basis set effects appear to be an order of magnitude smaller than the basis set effects themselves on the bond length, and a factor of 3 or 4 smaller on the harmonic frequency. They tend to increase the relativistic corrections to the properties. The relativistic correction to the bond length for PbH_4 should be accurate to 0.0005 Å and the frequency to 5 cm^{-1}.

E. Omission of (SS|SS) integrals.

Since the (SS|SS) integrals contribute to the total energy only to $\mathcal{O}(c^{-4})$, and since the contribution of the small component density is localized near the nucleus, it may be possible to omit this class of integral from the calculations without significantly affecting the calculated molecular properties. We have checked the effect of this omission for PbH_4, and found that the bond length decreased by 0.0003 Å, and the frequency increased by 0.2 cm^{-1} — differences which are of the same size as those arising from the core basis set deficiencies. While it is always important to ensure that these effects are small, the fact that they have proved small in this case provides grounds for confidence that for many systems it may be possible to omit the (SS|SS) integrals, thus making it possible either to use larger basis sets or to reduce the CPU time used.

VII. CONCLUSIONS

We have calculated the equilibrium bond lengths and harmonic frequencies of the Group IV tetrahydrides using a new molecular all-electron Dirac-Hartree-Fock program. The relativistic corrections to these quantities are not very sensitive to the details of the basis sets, provided these are of good quality. In particular, the corrections are not sensitive to slight deficiencies in the core region which arise from the use of basis sets optimized in nonrelativistic calculations. Also, for the systems studied, it was found possible to omit the (SS|SS) integrals without adversely affecting the calculated properties.

Comparisons with first-order perturbation theory, which includes here only the mass-velocity and Darwin terms in the relativistic Hamiltonian, show agreement to within 0.002Å in the relativistic correction to the bond length, but an overestimation of the relativistic correction to the harmonic frequency by about 50% for the heavier members of the series — largest for PbH_4 at 18 cm^{-1}. The comparisons indicate that spin-orbit effects have little influence on the bond lengths. The RECP [2,11] results show poorer agreement with the DHF results for the heavier members of the series, giving bond lengths that differ by up to 0.03Å, and harmonic frequencies underestimated by 20 − 40 cm^{-1}. The differences are due to deficiencies in the RECPs and not in the treatment of relativistic effects.

The sensitivity of the bond lengths and harmonic frequencies to the details of the RECP model should perhaps serve as a warning in the use of RECPs, that it is necessary at some point to calibrate them, and that agreement with atomic data may not be a sufficient test of their validity. The differences between the DHF results and the PT results for the light members of the series should also serve as a warning in the use of PT with only the mass-velocity and Darwin terms included. Spin-orbit effects may be more important, and the relativistic modification of the wave function may also have a significant effect on the relativistic corrections to the properties of interest. On the other hand, the current DHF calculations do not include all terms of $\mathcal{O}(c^{-2})$, but since the omitted term, the Breit interaction, contributes mostly in the atomic core regions, its effect on valence properties is

likely to be small. Further program development is required before this point can be investigated.

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Table 1. Basis set information for Group IV atoms.

	Basis set	Relative error in E (ppm)[a]	
		Nonrel.	Rel.
C	$(11s\,6p) + 2d \rightarrow [5s\,4p\,2d]$	15	17
Si	$(13s\,9p) + 2d \rightarrow [5s\,4p\,2d]$	12	15
Ge	$(15s\,12p\,7d) + 1d \rightarrow [6s\,5p\,3d]$	6	14
Sn	$(17s\,13p\,9d) + 1d \rightarrow [7s\,6p\,4d]$	5	32
Pb	$(20s\,16p\,11d\,7f) + 1d \rightarrow [8s\,7p\,5d\,1f]$	2	82

[a] $[E(\text{numerical}) - E(\text{basis})] / E(\text{numerical})$

Table 2. Bond length r_e (a_0) and total energy (E_h) of XH_4 molecules from quartic fit to all-electron DHF calculations.

	r_e	Total energy
CH_4	2.0446	-40.228306
SiH_4	2.7912	-291.876761
GeH_4	2.8826	-2099.808310
SnH_4	3.2237	-6178.262267
PbH_4	3.2920	-20914.069813

Table 3. Bond length r_e and relativistic correction to the bond length $\Delta^{rel}r_e$ for XH_4 molecules (Å) from all-electron calculations.

	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
r_e					
HF	1.082	1.478	1.532	1.727	1.815
Pert.	1.082	1.477	1.524	1.706	1.741
DHF	1.082	1.477	1.525	1.706	1.742
Expt.	1.086[a]	1.475[b]	1.520[b]	1.700[b]	—
$\Delta^{rel}r_e$					
Pert.	−0.00009	−0.00084	−0.0081	−0.0202	−0.0748
DHF	−0.00013	−0.00066	−0.0070	−0.0206	−0.0733

[a] Gray and Robiette, Ref. 56.
[b] Estimate (see text).

Table 4. Comparison of bond lengths r_e (Å) of GeH_4, SnH_4 and PbH_4 predicted by various ECPs with HF and DHF values.

	GeH_4	SnH_4	PbH_4
HF	1.532	1.727	1.815
ECP 1[a]	1.531	1.699	1.717
ECP 2[b], full core	1.516	1.689	1.739
ECP 2[b], semi-core	1.516	1.703	1.768
ECP 3[c]		1.715	1.743
PP-CI [d]			1.732, 1.739
DHF	1.525	1.706	1.742

[a] Hay and Wadt RECP, ref 2.

[b] Hurley et al., Ross et al., Lajohn et al. RECP, Ref. 11.

[c] Pelissier, unpublished (Thesis, 1984), taken from Ref. 39.

[d] Schwerdtfeger et al. pseudopotential CISD, Ref. 63. First value excludes, second value includes spin-orbit terms.

Table 5. Harmonic frequency ω_e and relativistic correction to the harmonic frequency $\Delta^{rel}\omega_e$ of the breathing (a_1) mode of the XH_4 molecules in cm^{-1} from all-electron calculations.

	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
ω_e					
HF	3160	2349	2276	2059	1968
Pert.	3160	2349	2281	2073	2017
DHF	3160	2348	2279	2069	1995
Expt.	3025[a]	2246[b]	2168[b]	1955[c]	—
$\Delta^{rel}\omega_e$					
Pert.	−0.05	+0.51	+4.6	+14	+49
DHF	+0.08	−0.04	+3.0	+10	+27

[a] Gray and Robiette, ref 56.
[b] Estimated, see text.
[c] Halonen et al, ref. 62.

Table 6. Comparison of harmonic frequencies ω_e (cm^{-1}) of GeH$_4$, SnH$_4$ and PbH$_4$ predicted by various ECPs with DHF values.

	GeH$_4$	SnH$_4$	PbH$_4$
HF	2276	2059	1968
ECP 1[a]	2262	2037	1967
ECP 2[b], full core	2272	2050	1980
ECP 2[b], semi-core	2311	2057	1957
DHF	2279	2069	1995

[a] Hay and Wadt RECP, Ref. 2.
[b] Hurley et al., Ross et al., Lajohn et al. RECP, Ref. 11.

Table 7. Valence spin-orbit splittings $\Delta\epsilon$ of X atoms and XH_4 molecules in cm^{-1} and gradient of molecular spin-orbit splitting $-\partial\Delta\epsilon/\partial r$ in $cm^{-1}\mathring{A}^{-1}$.

X	C	Si	Ge	Sn	Pb
Atom	63	253	1472	3609	12176
Molecule	42	171	995	2354	8227
$-\partial\Delta\epsilon/\partial r$	27	175	1008	2293	8160

Table 8. Basis set effects on the bond length and breathing mode harmonic frequency of PbH$_4$. Corrections to r_e are given in Å, corrections to ω_e in cm^{-1}.

Basis set change	Δr_e	$\Delta \omega_e$
Diffuse s, p	+0.0005	−2.0
2nd polarization d	+0.003	−14.8
Diffuse d	+0.0002	−1.4
Polarization f	−0.001	+9.6
More diffuse s basis on H	+0.001	−5.8
2nd p on H	+0.001	−7.4
s, p and d uncontracted	+0.00005	+0.04

Table 9. Basis set effects on the bond length and harmonic frequency of SnH_4. Corrections to r_e are given in Å, corrections to ω_e in cm^{-1}.

Basis set change	Change in r_e		Change in ω_e	
	Nonrel.	Rel.	Nonrel.	Rel.
First d	+0.0051	+0.0045	−32.3	−28.4
Second d	+0.0031	+0.0026	−14.8	−14.2
f	−0.0006	−0.0008	+6.3	+8.3

Figure Caption

Fig. 1. Differences between numerical and finite basis radial 1s functions for Pb.
L: Large component difference; S: Small component difference; NR: nonrelativistic
difference.