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Fully relativistic pseudopotentials for alkaline atoms: Dirac–Hartree–Fock and configuration interaction calculations of alkaline monohydrides

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Abstract. Fully relativistic four-component energy-adjusted pseudopotentials and corresponding valence basis sets have been derived for the alkaline atoms Li through Cs, treating them as one-valence electron systems. Core-valence correlation effects are accounted for by a core-polarization potential, deviations of the core–nucleus repulsion from a point charge model by a suitable correction. The results of Dirac–Hartree–Fock and configuration interaction calculations are presented for atomic properties not used in the pseudopotential adjustment, i.e. electron affinities and dipole polarizabilities, as well as for the spectroscopic constants of the ground states of the alkaline monohydrides. The analytic form of the cut-off function for the electric field in the core-polarization term and its effects on atomic and molecular properties is discussed.

Key words: Pseudopotentials – Core-polarization potentials – Dirac–Hartree–Fock – Alkaline atoms – Alkaline hydrides

1 Introduction

During the last few years much progress has been made in the development of fully relativistic electronic structure methods for molecules. Besides a relatively large number of molecular Dirac–Hartree–Fock–Roothaan (DHFR) all-electron calculations based on the Dirac–Coulomb, Dirac–Coulomb–Gaunt or Dirac–Coulomb–Breit Hamiltonian [1–6] also subsequent Møller–Plesset perturbation theory [7], multi-reference configuration interaction (MRCI) [8] and single-reference coupled cluster (CCSD) [9] calculations have been performed. Currently, due to the high requirements of disk space and central processing time, these calculations appear to be limited to systems containing one or two heavy and a few additional light atoms at most. At the all-electron level, computationally less demanding alternatives to the straight-forward DHFR treatment are the so-called (stationary) direct perturbation theory developed by Kutzelnigg [10] related to earlier work of Rutkowski [11] or variationally stable one- and two-component Hamiltonians as the Douglas–Kroll–Heß (DKH) operator [12–14]. In the framework of density functional calculations, the (scaled) zeroth- and first-order regular

Hamiltonians devised by van Lenthe et al. [15], partly based on earlier work by Chang et al. [16] and Heully et al. [17], appear to be quite promising.

The early attempts of Hellmann and Gombás in 1935 [18, 19] to reduce the computational effort of quantum chemical calculations by means of a restriction to the valence electron system evolved into today's modern pseudopotential (PP) [20], effective core potential (ECP) [21] and model potential (MP) [22] approaches. In today's routine work, the computational savings occur at the integral evaluation and self-consistent field (SCF) steps of a Hartree–Fock–Roothaan (HFR) calculation as well as at the integral transformation step of a subsequent configuration interaction (CI) calculation. However, more important than the computational savings in the uncorrelated valence-only calculations appears to be the fact that PPs can be generated to implicitly account for the major relativistic effects resulting from the mass–velocity, Darwin and spin–orbit terms in the Pauli approximation, i.e. relativity may be included rather accurately in formally nonrelativistic quantum chemical calculations by means of the so-called quasi-relativistic one- or two-component PPs. In 1981, Ishikawa and Malli [23] proposed the introduction of fully relativistic, i.e. four-component, PPs into the DHF formalism. They presented test calculations at the finite difference DHF level for atoms with up to three explicitly treated valence electrons. Shukla and Banerjee [24] recently proposed a fully relativistic effective Hamiltonian formalism for the valence shell and presented DHFR results for several light atoms.

In many cases, the restriction to a small valence electron system in correlated calculations is not possible due to the large contributions of core–valence electron correlation effects to atomic and molecular properties. A very efficient treatment of core–valence correlation effects in all-electron calculations was proposed by Meyer and coworkers [25] in terms of a core-polarization potential (CPP). The method was successfully adapted by Fuentealba and coworkers [26] for PP calculations of the cations of the alkaline hydrides and dimers. Thereafter, the PP + CPP scheme has been applied by the Stuttgart group to a wide range of atoms, molecules and also solids, cf. e.g. [27–32]. An alternative treatment of core–valence correlation effects based on perturbation theory has been proposed by the Toulouse group [33] and applied to KH and CsH [34]. Recently, the same group proposed to use a l-dependent cut-off function in the CPP formulation proposed by Meyer et al. and applied it to LiH [35].

The current work describes the systematic generation of fully relativistic four-component *ab initio* PPs for the alkaline metals Li through Cs by means of a least-squares adjustment to a multitude of valence energies obtained from atomic finite difference DHF calculations including the Breit interaction as a perturbation. Corresponding valence basis sets satisfying kinetic balance of the upper and lower components have been created by adjustment to the numerical radial spinors. Semiempirical CPPs have been determined to reproduce the core–valence contributions to the experimental ionisation potentials of the atoms. For molecular calculations, core–nucleus repulsion curves have been obtained from the electrostatic potential of finite difference DHF calculations for the core-electron systems and the corrections of the core–nucleus interaction with respect to a point-charge model have been extracted. As applications, atomic properties not used for the PP and CPP generation, i.e. the electron affinity and the dipole polarizability of the alkaline atoms, as well as the spectroscopic constants of the alkaline hydrides have been calculated at the DHF + CI level. The results are compared to experimental data as well as to those of selected previous theoretical studies. Since for the heavier alkaline hydrides KH, RbH and CsH only a single reliable relativistic all-electron calculation exists (CsH [36]), we performed HFR and Møller–Plessett perturbation theory to second order (MP2) calculations based on the scalar relativistic Douglas–Kroll–Hess (DKH) Hamiltonian using large uncontracted basis sets. For the lighter molecules LiH and NaH we rely on the nonrelativistic work of Meyer and Rosmus [37] and Langhoff et al. [38].

It is assumed that the findings concerning the core definition in the PP scheme and the treatment of core–valence correlation effects with a CPP are independent of the relativistic (four-component) treatment of the valence electron system used here, e.g. similar conclusions would result from a corresponding quasi-relativistic (one- or two-component) study. Alkaline elements have been chosen for this study since they as well as their diatomic compounds have been used as model systems in numerous investigations of the reliability of valence-only methods, e.g. [39].

2 Method

The molecular valence model Hamiltonian (in atomic units) used in this work is based on a modified Dirac–Coulomb Hamiltonian

$$\mathscr{H} = \sum_i [c^2(\beta_i - I) + c\boldsymbol{\alpha}_i \boldsymbol{p}_i] + V_{PP} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{\lambda<\mu} \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}}. \tag{1}$$

i and j are electron indices, whereas λ and μ denote core or nucleus indices. Q_λ is the charge of the core or nucleus λ. The Breit interaction was omitted since it was found to be negligible for the systems investigated here in valence-only test calculations at the uncorrelated level. For the present work we choose a core charge of one for the alkaline atoms, i.e. the neutral atoms were treated as one-, the neutral monohydrides as two-valence electron systems. β_i and $\boldsymbol{\alpha}_i$ are the four Dirac matrices acting on the i-th electron, I denotes the 4×4 identity matrix. For the velocity of light c, a value of 137.03598956 a.u. was used. In case of valence-only calculations V_{PP} is a pseudopotential (PP) consisting of three terms:

$$V_{PP} = V_{DHF} + V_{CPP} + V_{CCRC}. \tag{2}$$

The molecular Dirac–Hartree–Fock (DHF) pseudopotential V_{DHF} is assumed to be a sum over atomic pseudopotentials

$$V_{DHF} = \sum_{\lambda, i} V^{\lambda}_{DHF}(i) \tag{3}$$

for which a semilocal ansatz is made

$$V^{\lambda}_{DHF}(i) = -\frac{Q_\lambda}{r_{\lambda i}} + \sum_{l,j,k} A^{\lambda}_{ljk} \exp(-a^{\lambda}_{ljk} r^2_{\lambda i}) P^{\lambda}_{lj}. \tag{4}$$

P^{λ}_{lj} is a projection operator onto spinor spherical harmonics at center λ

$$P^{\lambda}_{lj} = \sum_{m=-j}^{j} |\lambda ljm\rangle \langle \lambda ljm|. \tag{5}$$

The PP parameters A_{ljk} and a_{ljk} have been adjusted to the ionisation potential, electron affinity and excitation energies of low-lying electronic states derived from all-electron finite-difference DHF calculations including the Breit interaction by perturbation theory. A spherical, uniformly charged finite nucleus was used. The all-electron calculations have been carried out with the RELAMC code written by Desclaux [40], whereas a modified version of the program system GRASP [41] was used for the valence-only calculations. Despite the adjustment to energies, the shape of the pseudo-spinors also agrees well with the one of the spinors from all-electron calculations in the valence region, cf. e.g. Figs. 1 and 2 for the large and small components of the lowest S and P states of Cs.

The first term of the core-polarization potential (CPP) used here follows the work of Fuentealba et al. [26], which was adapted from the all-electron formulation given by Müller et al. [25], whereas the second term introduces a short-range correction to be specified later.

$$V_{CPP} = -\frac{1}{2}\sum_{\lambda}\alpha_{\lambda} f_{\lambda}^2 + \sum_{\lambda, i} V^{\lambda}(i). \tag{6}$$

α_λ is the dipole polarizability of the core which was taken from the coupled DHF results of Johnson and Kolb [42]. f_λ corresponds to the electric field at core λ due to the other nuclei or cores and all valence electrons. Since the multipole expansion breaks down when a charge, i.e. an electron or another core or nucleus, significantly penetrates the polarizable core, the electric field is multiplied by a cut-off function

$$f_{\lambda} = -\sum_{i}\frac{r_{i\lambda}}{r_{i\lambda}^3}(1 - \exp(-\delta^{\lambda} r_{i\lambda}^2))^{n_c} + \sum_{\mu \neq \lambda} Q_{\mu}\frac{r_{\mu\lambda}}{r_{\mu\lambda}^3}(1 - \exp(-\delta^{\lambda} r_{\mu\lambda}^2))^{n_c}. \tag{7}$$

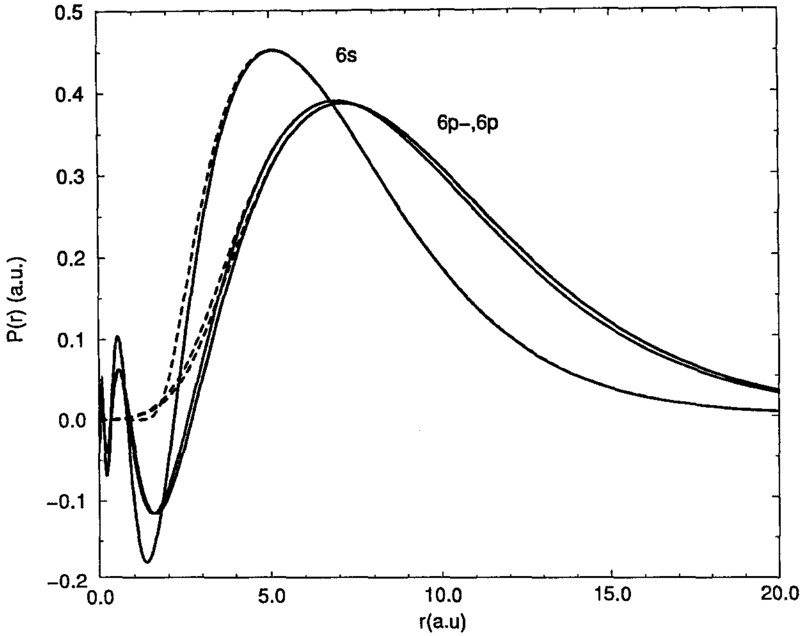

Fig. 1. Upper components of the 6s and 6p radial spinors from all-electron (solid line) and pseudopotential (dashed line) calculations for the ^2S and ^2P states of Cs (6p- denotes $6p_{1/2}$, whereas 6p denotes $6p_{3/2}$)

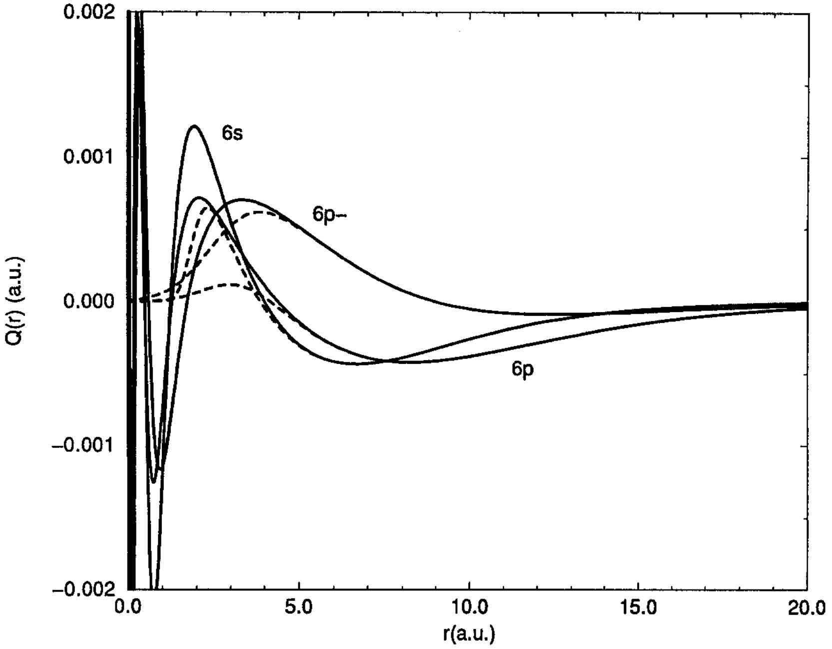

Fig. 2. Lower components of the 6*s* and 6*p* radial spinors from all-electron (solid line) and pseudopotential (dashed line) calculations for the ^2S and ^2P states of Cs (6*p*- denotes $6p_{1/2}$; whereas 6*p* denotes $6p_{3/2}$; the peaks of the all-electron curves have been truncated for small values of *r*)

In order to overcome deficiencies in the short-range part of the CPP in the original form used by Fuentealba et al. or Meyer et al., a local correction potential in the form of a single gaussian has been added

$$V^{\lambda}(i) = C^{\lambda}\exp(-\gamma^{\lambda}r_{i\lambda}^2). \tag{8}$$

Three different forms of CPPs have been used in the present work. The corresponding results for the atoms and molecules will be discussed below. Form I is defined by $n_e = n_c = 1$ and $C^{\lambda} = 0$. This form is closest to the ansatz used by Fuentealba et al. [32], who omitted the cut-off function for the nuclear part of the electric field, i.e. $n_c = 0$. We note here in passing that Fuentealba et al. also omitted the core–nucleus repulsion correction terms in his calculations on the alkaline hydrides. Form II, which will be shown to be superior to form I, is characterised by $n_e = n_c = 2$ and $C^{\lambda} = 0$. In contrast to form I, the individual contributions to the electric field vanish for $r_{i\lambda} \to 0$ and $r_{\mu\lambda} \to 0$. The most successful form III applied here results from form II by inclusion of the local potential, i.e. $n_e = n_c = 2$ and $C^{\lambda} \neq 0$. The CPP is supposed to account for static core polarization effects as well as for core–valence correlation effects. In view of the second aspect, we adjusted the cut-off parameter γ^{λ} to reproduce the experimental ionisation potential of the atom [43].

The penetration of an atomic core by another nucleus or core results in a deviation from the simple point charge repulsion which significantly affects molecular results for large cores. The necessary core–core repulsion corrections (CCRC) may be assumed to be expressible as a sum of pairwise interactions between cores and cores or nuclei

$$V_{CCRC} = \sum_{\lambda<\mu} V_{CCRC}^{\lambda\mu}. \tag{9}$$

In the case of core–core interaction corrections, the individual terms in this sum have to be calculated pointwise from all-electron or small-core PP molecular calculations for interacting frozen atomic cores. When only the core–nucleus repulsion correction is needed, as in the present work, it may easily be derived from the electrostatic potential of the core by subtraction of the point charge Coulomb contribution. In the present work, the electrostatic potential was taken from finite difference DHF calculations for the alkaline cation in its ground-state configuration. For convenience in subsequent molecular calculations, e.g. for automatic geometry optimisations, the repulsion correction curves may be approximated with good accuracy by exponential functions

$$V_{CCRC}^{\lambda\mu} = B^{\lambda\mu} \exp(-a^{\lambda\mu} r_{\lambda\mu}). \tag{10}$$

The valence basis sets used here for the PP calculations have been obtained following the prescriptions given in an earlier work of Mark [44]. Finite basis set expansions were fitted to the radial parts of the upper and lower components of the $ns_{1/2}$, $np_{1/2}$ and $np_{3/2}$ spinors ($n = 2, 3, 4, 5$ for Li, Na, K, Rb, Cs) obtained from finite difference calculations performed with the program GRASP [41]. A weight function of the form $1/r$ was used in the least squares fit. The expansions for different angular quantum numbers as well as for large and small components were constrained to have common exponents in order to save disk space in subsequent molecular calculations. Basis sets of the size ($8s\,5p\,1d$) for the large components have been created for hydrogen and the alkaline atoms. The small component basis set was chosen to fulfill the kinetic balance condition [45]. The valence energies obtained with the finite basis sets are O (10^{-4} a.u.) higher than those derived from finite difference calculations.

The PP calculations have been carried out on a workstation (40 MB core, 1 GB disk) with a strongly modified version of the four-component DHFR + CI programs developed by Mark et al. [46], which were based on the corresponding two-component codes by Hafner and Schwarz [47], Esser et al. [48] and Esser [49]. The integral routine for CPPs has been obtained from Schwerdtfeger et al. [50]. Kramers symmetry is partly exploited at the SCF level using the quaternionic matrix diagonalisation routines of Rösch [51] and assumed to be kept at the integral transformation and CI steps [49, 48]. The work presented here uses a modified lobe-based integral code originally written by Ahlrichs [52]. For large-scale all-electron DHFR calculations the ARGOS integral part of the COLUMBUS program system [53] has been adapted. Second-order perturbation theory (PT2) as well as a correlation energy density functional module has been added. Due to the use of bit operations the limitations of the program are currently 2×256 and 128 spinors at the DHFR and CI/PT2 levels, respectively. The CI/PT2 code can be used in a direct or conventional mode, the largest CI expansions so far performed on I_2 comprised up to a few million determinants [54].

Due to the lack of relativistic all-electron calculations for some of the heavier alkaline hydrides, we performed (nonrelativistic and) relativistic all-electron calculations for KH, RbH and CsH using the scalar relativistic Douglas–Kroll–Hess Hamiltonian [12, 13]. We used large uncontracted and partly energy-optimized basis sets which yield for the atom energies close to the HF limit in nonrelativistic HFR calculations (energies in atomic units, K ($19s14p$) HFR: -599.164601, HF: − 599.164787; Rb (22*s*17*p*9*d*) HFR: − 2938.356680, HF: − 2938.357454; Cs (25*s*20*p*12*d*) HFR: − 7553.932644, HF: − 7553.933658). These basis sets were further augmented by diffuse functions and polarization functions when necessary yielding final basis sets of the following sizes: K (20*s*16*p*8*d*), Rb (23*s*18*p*13*d*), Cs (25*s*21*p*16*d*4*f*). For reasons of comparison with the valence-only calculations we used the H (8*s*5*p*1*d*) basis set described above. The calculations have been carried out with the TURBOMOLE direct HFR and MP2 code [55] modified for DHK calculations by inclusion of routines written by Hess [56].

All parameters for pseudopotentials, core-polarization potentials, core–nucleus repulsion correction as well as the basis sets are available from the author upon request.

3 Results and discussion

The results of atomic pseudopotential (PP) and corresponding all-electron calculations are summarized in Tables 1–5. Only results for the form III of the core-polarization potential (CPP) are included. The spin-orbit averaged finite difference all-electron Dirac–Hartree–Fock + Breit excitation energies (AE, DHF) agree with the corresponding PP results (PP, DHF) within a few wavenumbers (Table 1), i.e. the largest error is 25 cm^{-1} and occurs for Cs $7s^1\ {}^2S$. The small optimized valence basis sets can only describe the lowest $ns^1\ {}^2S$ and $np^1\ {}^2P$ states sufficiently accurate. The basis set errors in the ${}^2P$ term energy are at most 50 cm^{-1}. The inclusion of core–valence correlation effects by means of a CPP brings the PP results into reasonable agreement with the experimental values [43], both at the finite difference (PP + CPP, DHF) and the finite basis set (PP + CPP, DHFR) level. The errors due to the PP and CPP are smaller than 100 cm^{-1}, the largest error due to the finite basis set is less than 70 cm^{-1}.

In Table 2 the corresponding fine-structure splittings are listed. The PP itself yields results with an accuracy of much better than 1 cm^{-1} (PP, DHF vs. AE, DHF), whereas the finite basis set introduces errors of up to 10 cm^{-1} (PP, DHFR vs. PP, DHF). Core–valence correlation effects increase significantly the splitting of the *P* states, an effect that is reliably accounted for by the CPP. However, for the *D* states the results are even qualitatively wrong for Cs. The magnitude of the splitting between the inverted ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states is increased instead of reduced or inverted back to usual order. For atoms this appears to be the only failure of the CPP ansatz used in the current work. It is unlikely that it can be remedied without removing the restriction to a non-*lj*-dependent CPP.

Table 3 gives the ionisation potentials of the alkaline atoms. The PP errors are 0.001 eV or less (PP, DHF vs. AE, DHF), the basis set errors 0.005 eV or less (PP, DHFR vs. PP, DHF). We note that the cut-off parameter in the CPP has been adjusted to the experimental ionisation potential, i.e. by means of adjustment the entries in the columns PP + CPP, DHF and Exp. have to agree.

The electron affinities of the alkaline atoms are summarized in Table 4. They have been used as reference data in the PP adjustment at the DHF level. The agreement between finite difference all-electron and PP results is 0.002 eV or better (PP, DHF vs. AE, DHF). A diffuse *s* function was added to the large component (8*s*5*p*1*d*) basis sets. The basis set errors are 0.006 eV or less in uncorrelated calculations (PP, DHFR vs. PP, DHF). When a CPP is added to the Hamiltonian the PP CI results agree with the recommended experimental values by Hotop and Lineberger [57] better than 0.01 eV for Li through K. Probably, due to limitations

Table 1. Low-lying spin–orbit averaged $ns^1\ ^2S \rightarrow ml^1\ ^2L$ excitation energies (cm^{-1}) for the alkaline metals from finite difference all-electron (AE) and pseudopotential (PP) Dirac–Hartree–Fock (DHF) calculations. Corresponding pseudopotential Dirac–Hartree–Fock–Roothaan results obtained with finite basis sets (DHFR) and inclusion of core-polarization effects (CPP) are compared to experimental data (Exp.)

	ml	AE DHF	PP DHF	PP DHFR	PP + CPP DHF	PP + CPP DHFR	Exp.
Li	3*s*	26893	26882		27205		27206
	4*s*	34647	34638		35017		35012
	2*p*	14853	14847	14838	14921	14911	14904
	3*p*	30630	30625		30937		30925
	3*d*	30896	30890		31292		31283
	4*d*	36232	36226		36633		36623
	4*f*	36234	36225		36627		36630
Na	4*s*	24585	24574		25738		25740
	5*s*	31851	31844		33197		33201
	3*p*	15963	15958	15964	16937	16942	16966
	4*p*	28941	28935		30258		30271
	3*d*	27767	27762		29167		29173
	4*d*	33112	33107		34543		34549
	4*f*	33127	33121		34581		34589
K	5*s*	19018	19008		21057		21027
	6s	25090	25083		27473		27451
	4*p*	11451	11445	11447	13056	13056	13024
	5*p*	22427	22421		24735		24714
	3*d*	19677	19672		21532		21535
	4*d*	25220	25214		27421		27397
	4*f*	25569	25564		28139		28128
Rb	6*s*	17764	17749		20169		20134
	7*s*	23531	23525		26338		26311
	5*p*	10840	10838	10800	12783	12721	12737
	6*p*	21062	21059		23793		23767
	4*d*	17530	17527		19365		19355
	5*d*	23237	23235		25746		25702
	4*f*	23791	23791		26807		26792
Cs	7*s*	15931	15907		18564		18536
	8*s*	21254	21246		24343		24317
	6*p*	9525	9529	9529	11635	11572	11548
	7*p*	18922	18925		21928		21886
	5*d*	13815	13819		14537		14558
	6*d*	20109	20111		22708		22615
	4*f*	21184	21194		24498		24472

Exp.: experimental values from [43]

in the basis sets, the errors for Rb and Cs are somewhat larger, i.e. 0.012 eV and 0.025 eV, respectively. For hydrogen a CI electron affinity of 0.741 eV was calculated compared to an experimental value of 0.754 eV. The PP DHF result of −0.324 eV is also close to the corresponding all-electron result of −0.329 eV.

Table 2. Fine-structure splittings $E(nl^1_{l+1/2}\,{}^2L_{L+1/2}) - E(nl^1_{l-1/2}\,{}^2L_{L-1/2})$ of the alkaline metals (cm^{-1}). For an explanation of abbreviations cf. Table 1. Only splittings larger than 0.25 cm^{-1} are included

	nl	AE DHF	PP DHF	PP DHFR	PP + CPP DHF	PP + CPP DHFR	Exp.
Li	2*p*	0.24	0.24	0.24	0.37	0.31	0.34
Na	3*p*	15.3	15.3	15.4	17.3	17.3	17.2
	4*p*	5.0	5.1		5.6		5.6
K	4*p*	45.9	45.9	46.1	58.0	58.0	57.7
	5*p*	15.7	15.7		18.6		18.8
	3*d*	– 2.7	– 2.7		– 6.0		– 2.3
	4*d*	– 1.7	– 1.7		– 3.4		– 1.1
Rb	5*p*	180.0	180.0	180.9	235.0	235.6	237.6
	6*p*	62.8	62.8		75.9		77.5
	4*d*	– 13.4	– 13.4		– 35.8		– 0.4
	5*d*	– 6.3	– 6.3		– 13.7		3.0
Cs	6*p*	399.1	399.0	403.4	543.1	543.0	554.1
	7*p*	142.0	142.1		175.8		181.0
	5*d*	– 27.0	– 27.0		– 57.7		97.6
	6*d*	– 1.2	– 1.3		– 3.1		42.9

Exp.: experimental values from [43]

Table 3. Ionization potentials (eV) of the alkaline atoms. For an explanation of abbreviations cf. Table 1

	AE DHF	PP DHF	PP DHFR	PP + CPP DHF	PP + CPP DHFR	Exp.
Li	5.343	5.342	5.338	5.390	5.388	5.390
Na	4.958	4.957	4.957	5.138	5.138	5.138
K	4.021	4.020	4.020	4.339	4.342	4.339
Rb	3.800	3.800	3.795	4.176	4.171	4.176
Cs	3.478	3.478	3.476	3.893	3.886	3.893

Exp.: experimental values from [43]

Table 4. Electron affinities (eV) of the alkaline atoms. CI denotes configuration interaction calculations. For an explanation of other abbreviations cf. Table 1

	AE DHF	PP DHF	PP DHFR	PP + CPP CI	Exp.
Li	– 0.122	– 0.120	– 0.126	0.622	0.618
Na	– 0.103	– 0.102	– 0.104	0.542	0.548
K	– 0.078	– 0.077	– 0.077	0.495	0.502
Rb	– 0.069	– 0.069	– 0.070	0.474	0.486
Cs	– 0.062	– 0.060	– 0.064	0.447	0.472

Exp.: experimental results from [57]. A diffuse *s* function has been added to calculate the DHFR and CI values

Table 5. Dipole polarizabilities (Å^3) of the alkaline atoms. For an explanation of abbreviations cf. Table 1

	PP + CPP DHFR	Exp.
Li	24.9	24.3
Na	24.2	23.6
K	43.3	43.4
Rb	46.8	47.3
Cs	59.9	59.6

Exp.: recommended experimental values from [58]

The dipole polarizabilities of the neutral alkaline atoms have been calculated with the finite field method. Field strengths of 10^{-5}–10^{-4} a.u. have been applied. The theoretical values are listed together with the recommended experimental values by Miller and Bederson [58] in Table 5. The relative errors are in the range between -1.1% (Rb) and $+2.5\%$ (Na), their absolute value being always less than 1 Å^3. For H the theoretical value of 0.68 Å^3 almost coincides with the recommended value of 0.67 Å^3.

The results of DHFR + CI calculations of the alkaline hydrides using the four-component PPs, CPPs, valence basis sets and core–nuclear repulsion corrections are summarized in Tables 6 (bond lengths), 7 (binding energies), 8 (vibrational constants) and 9 (dipole moments). The all-electron HFR + MP2 results obtained with the scalar relativistic DKH Hamiltonian are also included. The number of previous theoretical studies of alkaline hydrides available from literature is too large to be summarized here. Reviews have been published by Stwalley et al. [59]. We will only compare our work to the most rigorous nonrelativistic all-electron coupled electron-pair approximation (CEPA) calculations by Meyer and Rosmus [37] for the lighter systems LiH and NaH, the nonrelativistic all-electron coupled-pair functional (CPF) calculations by Langhoff et al. [38] for NaH, KH, RbH and CsH as well as the scalar relativistic DKH + MRCI calculations of CsH by Carnell et al. [36]. Further comparison will be made to the PP CI calculations by Fuentealba et al. [32].

The numerical stability of the results was tested for CsH. The correction of the basis set superposition error by means of the counterpoise method [60] resulted in negligible changes of the spectroscopic constants, e.g. $\Delta R_e = 0.0002$ Å, $\Delta D_e = -0.002$ eV and $\Delta\omega_e = -0.2\ \mathrm{cm}^{-1}$ at the CI level. The core–nucleus repulsion correction for a two-valence-electron molecule CsH near the equilibrium distance is approximately 20% larger when it is derived for the Cs$^+$ core taken from the neutral Cs atom instead of the bare cation itself. However, the spectroscopic constants are only slightly affected, e.g. $\Delta R_e = 0.007$ Å, $\Delta D_e = -0.007$ eV and $\Delta\omega_e = -0.4\ \mathrm{cm}^{-1}$ at the DHFR level.

Let us first turn to the discussion of the different forms of the CPP used in the PP Dirac–Hartree–Fock–Roothaan and configuration interaction calculations. CPP I yields satisfactory results for the light molecules, however it leads to too short bond lengths and too high binding energies for the heavy systems. The errors with respect to experiment for CsH are $\Delta R_e = -0.170$ Å, $\Delta D_e = 0.177$ eV and $\Delta\omega_e = 11\ \mathrm{cm}^{-1}$. Improved results are obtained with CPP II, e.g. the errors for CsH are partly reduced to $\Delta R_e = -0.104$ Å, $\Delta D_e = 0.100$ eV and $\Delta\omega_e = 65\ \mathrm{cm}^{-1}$.

Table 6. Bond lengths R_e (Å) of the alkaline monohydrides from all-electron (AE) and pseudopotential (PP) calculations in comparison to experimental values (Exp.)

Method	Ref.	LiH	NaH	KH	RbH	CsH
PP + CPP I, DHFR + CI		1.591	1.864	2.214	2.258	2.324
PP + CPP II, DHFR + CI		1.591	1.864	2.219	2.281	2.390
PP + CPP III, DHFR + CI		1.588	1.865	2.223	2.311	2.448
Exp.	[59]	1.596	1.887	2.240	2.367	2.494
AE DKH, HFR				2.307	2.446	2.601
AE, HFR				2.310	2.459	2.590
AE DKH, MP2 (2)				2.310	2.455	2.624
AE, MP2 (2)				2.313	2.467	2.612
AE DKH, MP2 (10)				2.247	2.380	2.507
AE, MP2 (10)				2.250	2.394	2.498
AE DKH, MP2 (18/28)				2.246	2.379	
AE, MP2 (18/28)				2.250	2.393	
AE DKH, MRCI	[36]					2.548
AE, CPF	[38]		1.890	2.257	2.397	2.529
AE, CEPA	[37]	1.599	1.891			
PP + CPP, HFR + CI	[32]	1.593	1.879	2.275	2.387	2.524
PP + CPP I, HFR + CI		1.591	1.883	2.220	2.326	2.440

CI: configuration interaction; DHFR: Dirac–Hartree–Fock–Roothaan; HFR: Hartree–Fock–Roothaan; DKH: scalar relativistic Douglas–Kroll–Hess Hamiltonian; MP2 (n): Møller–Plessett perturbation theory to second order for *n* valence electrons; MRCI: multi-reference configuration interaction; CPF: coupled-pair functional; CEPA: coupled electron-pair approximation

Table 7. Binding energies D_e (eV) of the alkaline monohydrides. For abbreviations cf. Table 6

Method	Ref.	LiH	NaH	KH	RbH	CsH
PP + CPP I, DHFR + CI		2.491	1.990	1.858	1.888	2.011
PP + CPP II, DHFR + CI		2.491	1.990	1.855	1.863	1.934
PP + CPP III, DHFR + CI		2.495	1.990	1.852	1.835	1.847
Exp.	[59]	2.516	1.972	1.832	1.808	1.834
AE DKH, MRCI	[36]					1.752
AE, CPF	[38]		1.92	1.79	1.75	1.86
AE, CEPA	[37]	2.48	1.92			
PP + CPP, HFR + CI	[32]	2.44	1.91	1.68	1.64	1.67
PP + CPP I, HFR + CI		2.499	1.949	1.825	1.785	1.857

Finally, CPP III leads to the best results with errors for CsH of $\Delta R_e = -0.046$ Å, $\Delta D_e = 0.013$ eV and $\Delta \omega_e = -6\ \mathrm{cm}^{-1}$. We attribute this to the considerably better description of the atomic D states obtained with CPP III, as it is obvious from the excitation energies of Cs listed in Table 10. Whereas the *s* and *p* levels are well described by all three CPPs, CPP I and II appear to be too attractive especially for the *d* levels. The local short-range correction potential is able to correct for this deficiency, however only at the spin–orbit averaged level. We note that the analytical form of the CPP cut-off function appears to be important for the heavier alkaline elements which have $(n-1)d$ and/or $(n-2)f$ valence orbitals besides the *ns* and *np* valence orbitals.

Table 8. Vibrational constants ω_e (cm^{-1}) of the alkaline monohydrides. For abbreviations cf. Table 6

Method	Ref.	LiH	NaH	KH	RbH	CsH
PP + CPP I, DHFR + CI		1390	1167	989	925	902
PP + CPP II, DHFR + CI		1391	1170	995	927	956
PP + CPP III, DHFR + CI		1386	1180	991	939	885
Exp.	[59]	1405	1172	987	937	891
AE DKH, HFR				983	909	837
AE, HFR				968	902	851
AE DKH, MP2 (2)				977	904	834
AE, MP2 (2)				960	896	847
AE DKH, MP2 (10)				984	941	888
AE, MP2 (10)				994	931	902
AE DKH, MP2 (18/28)				984	941	
AE, MP2 (18/28)				994	931	
AE DKH, MRCI	[36]					896
AE, CPF	[38]		1163	968	913	848
AE, CEPA	[37]	1402	1172			
PP + CPP, HFR + CI	[32]	1393	1162	954	893	837
PP + CPP I, HFR + CI		1391	1163	961	912	881

Table 9. Dipole moments μ_e (D) of the alkaline monohydrides. For abbreviations cf. Table 6

Method	Ref.	LiH	NaH	KH	RbH	CsH
PP + CPP I, DHFR + CI		5.84	6.30	7.98	7.98	7.74
PP + CPP II, DHFR + CI		5.84	6.30	7.99	8.09	8.15
PP + CPP III, DHFR + CI		5.84	6.30	7.99	8.12	8.53
Exp.	[63]	5.88	6.40			
AE DKH, MRCI[a]	[36]					9.15
AE, CPF[b]	[38]		6.43	8.14	8.51	8.89
AE, CEPA	[37]	5.84	6.47			
PP + CPP, HFR + CI	[32]	5.87	6.48	8.59		9.84

[a] Value calculated from the data given in [36] for the AE DKH, MRCI equilibrium distance; the corresponding value for the PP + CPP III, DHFR + CI equilibrium distance is 8.70 *D*

[b] The values for NaH, KH and RbH correspond to μ_0 rather than to μ_e.

Table 10. Errors (eV) with respect to experimental data in spin–orbit averaged $6s^1\ ^2S \rightarrow nl^1\ ^2L$ excitation energies of Cs

nl	CPP I	CPP II	CPP III
7*s*	0.001	0.002	– 0.001
6*p*	0.010	0.010	0.008
7*p*	0.004	0.004	0.000
6*d*	– 0.354	– 0.173	– 0.007
7*d*	– 0.080	– 0.040	0.004

We now turn to the results obtained by Fuentealba [32] with semiempirical energy-adjusted scalar relativistic PPs. The ansatz used by Fuentealba [32] corresponds to CPP I, however the cut-off term for the core and nuclear contributions as well as the core–nucleus repulsion correction were omitted. According to our test calculations for CsH, the neglect of the cut-off factor in the core and nuclear part of the electric field leads to the changes $\Delta R_e = 0.027$ Å, $\Delta D_e = -0.017$ eV and $\Delta\omega_e = 13\ \mathrm{cm}^{-1}$. The neglect of the core–nucleus repulsion correction reduces the equilibrium distance by 0.06 Å, increases the binding energy by 0.04 eV and the vibrational constant by 60 cm^{-1}. In addition, the results are affected by the choice of the basis sets. Fuentealba et al. use $(8s6p2d)/[6s4p2d]$ basis sets for the alkaline metals with rather diffuse d functions. For example, adding a tight d function (exponent 0.48) to the two diffuse d functions (exponents 0.03, 0.12) for Cs leads to a bond length contraction of 0.055 Å, an increase of the binding energy of 0.073 eV and of the vibrational constant of 16 cm^{-1}. Additional differences arise from the smaller $(5s2p)/[3s2p]$ basis set on H used by Fuentealba et al. Using the PP + CPP parameters of Fuentealba together with optimized basis sets, core–nucleus repulsion correction and applying the form I for the CPP, an overall improvement of the results of [32] for the binding energies and vibrational constants of the heavier molecules KH, RbH and CsH is observed. However, the bond lengths turn out to be too short, the errors being of similar magnitude as those of the DHFR + CI results with CPP III. The form of the cut-off factor is of minor importance in the scheme of Fuentealba, since his PP parameters for $l \leqslant 1$ were determined directly by fitting to experimental energies for a fixed CPP determined for $l = 0$, i.e. a clear distinction between an *ab initio* PP and a semiempirical CPP is lost for $l \leqslant 1$. Errors due to the form of the CPP are compensated by adjustment of the PP. The dipole moments of the heavier monohydrides KH and CsH published by Fuentealba et al. (the value for RbH was not given) are significantly larger than both the all-electron results of Langhoff et al. [38] and Carnell et al. [36] as well as our PP results. This is most probably due to the neglect of the contribution of the polarizable alkaline core to the dipole moment, a correction term which is not implemented into the program package used by Fuentealba. According to our calculations, this term reduces the dipole moment of CsH by about 1.8 D near the equilibrium distance, i.e. the value of 9.84 D published by Fuentealba would be brought into reasonable agreement to the present results of 7.74 D and 8.15 D obtained with forms I and II of the CPP, respectively. It should be noted that due to the steep slope of the dipole moment with respect to the bond lengths (approximately 1 a.u./bohr) the influence of bond length differences on dipole moments is nonnegligible.

We finally come to the discussion of the all-electron calculations. To our knowledge no high quality relativistic *ab initio* calculations exist for the whole series. Both the nonrelativistic CEPA results of Rosmus and Meyer [37] and the nonrelativistic CPF results of Langhoff et al. [38] are in good agreement with exprimental data as well as with our results. For the heavier molecules this is due to small relativistic effects as it is obvious from our nonrelativistic and scalar relativistic results. For CsH a relativistic MRCI study by Carnell et al. [36] based on the DKH Hamiltonian exists. The calculated CsH bond length is about 0.05 Å too long, probably due to an incomplete inclusion of core–valence correlation effects. We studied the effect of core–valence correlation in MP2 calculations of KH, RbH and CsH with 2, 10 and 18 (KH) or 28 (RbH) correlated electrons. Since the MP2 code only works for closed-shell systems we were not able to derive binding energies. From Tables 6 and 8 it is seen that correlation of 10 electrons, i.e. the binding orbital and the underlying $(n-1)s$ and $(n-1)p$ shells of the alkaline metal is sufficient to obtain beside valence also the largest part of the core–valence correlation contributions.

The accuracy of the PP approximation for very large cores was recently investigated for In treated as a three-valence-electron atom [61]. For InCl (Cl was treated at the all-electron level) similar errors occurred as for the heavier alkaline hydrides in the present investigation, i.e. the bond lengths were consistently too short. However, excellent accuracy is obtained when a smaller core is used for In [62]. In case of the alkaline atoms an inclusion of the $(n-1)s$ and $(n-1)p$ shells in the valence electron system would probably further improve the results. If core–valence correlation effects (e.g. for the fine structure of D states) can accurately be accounted for such PPs by a CPP or if the highest core orbitals have to be correlated explicitly has to be investigated in the future. The results of a preliminary study of KF (K was treated as a one-valence electron atom, whereas all the electrons were explicitly included for fluorine) suggest that calculations with energy-adjusted model potentials (retaining the correct nodal structure of the valence orbitals) overestimate the bond length by almost the same amount as energy-adjusted PPs (leading to radially nodeless valence orbitals) underestimate it [62]. One may conclude that the question whether the correct nodal structure in valence orbitals is important or not is still not fully settled. Investigations of these problems are currently carried out in the Stuttgart group.

4 Conclusions

Fully relativistic four-component pseudopotentials can be generated without problems concerning the nodal structure of the pseudospinors using the method of energy-adjustment, although the theoretical justification to do this is somewhat dubious. From a practical point of view the four-component pseudopotentials generating nodeless pseudospinors do not offer higher accuracy than the traditional quasirelativistic two-component pseudopotentials, however, they might be useful for modelling the crystal environment in cluster studies within the four-component Dirac–Hartree–Fock scheme with regards to computational savings (in comparison to a full treatment of neighbouring atoms/ions) and to accuracy (in comparison to a point-charge approximation for neighbouring ions). Irrespective of the question whether four-component pseudopotentials are useful, it has been shown that the one-valence-electron approximation for the alkaline elements is not suitable to give highly accurate results. Unsolved problems result from the different radial extent of ns and np compared to $(n-1)d$ or $(n-2)f$ valence orbitals and the too attractive effect of the core-polarization potential on the latter functions.

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