

Relativistic Energy-Consistent Pseudopotentials—Recent Developments

HERMANN STOLL,¹ BERNHARD METZ,¹ MICHAEL DOLG²

¹*Institut für Theoretische Chemie, Universität Stuttgart, D-70550 Stuttgart, Germany*

²*Institut für Physikalische und Theoretische Chemie, Universität Bonn, D-53115 Bonn, Germany*

Received 13 August 2001; Accepted 23 September 2001

DOI 10.1002/jcc.10037

Abstract: The direct adjustment of two-component pseudopotentials (scalar-relativistic + spin-orbit potentials), to atomic total energy valence spectra derived from four-component multiconfiguration Dirac–Hartree–Fock all-electron calculations based on the Dirac–Coulomb–Breit Hamiltonian, has been made a routine tool for an efficient treatment of heavy main-group elements. Both large-core (*nsp* valence shell) and small-core ($(n - 1)spd\ nsp$ valence shell) potentials have been generated for all the post-*d* elements of groups 13–17. At the example of lead and bismuth compounds (PbHal, BiH, BiO, BiHal (Hal = F, Cl, Br, I)), we show how small-core and large-core potentials can be combined in accurate, yet computationally economic, spin-free-state-shifted relativistic electronic structure calculations of molecular ground and excited states.

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Key words: relativistic effects; spin-orbit coupling; pseudopotentials; Pb and Bi compounds

Introduction

Historically, pseudopotentials were introduced as a computationally inexpensive means for simulating the interaction between valence electrons and (frozen) atomic cores.^{1,2} A one-center, one-electron form of the potentials was assumed, and effects due to the nonseparability of valence and core wave functions were neglected. To fully exploit computational simplifications, it turned out to be necessary to introduce a “pseudo-orbital transformation,” at the same time, which eliminates radial nodes of valence orbitals yielding pseudovalence orbitals.³ The concomitant changes of the pseudovalence wave function, with respect to the valence part of the all-electron wave function, have then to be compensated, within expectation values, by a suitably modified form of the pseudopotential. Later on, it became apparent (see, e.g., refs. 4–6) that pseudopotentials also allow in an efficient way to implicitly introduce scalar-relativistic effects into formally nonrelativistic molecular calculations, not only the indirect ones due to relativistic changes of the core but also effects directly acting on the valence electrons. It is clear again, that due to the differences between all-electron valence and pseudovalence orbitals (which mainly arise in the core region) the relativistic part of the pseudopotential must be quite different from the corresponding all-electron operators (which mainly act in the region close to the nucleus). Currently, with spin-orbit (SO) modules becoming increasingly available in quantum-chemical program packages, cf. e.g., refs. 7–12, the focus is on two-component pseudopotentials with a full ac-

count of relativistic effects. Still, a one-electron form of the potentials but dependent now on the relativistic quantum number κ (or the angular-momentum quantum numbers l, j) is assumed to serve the purpose.

Do we have a guarantee for the accuracy and reliability with which the various steps mentioned above can be accounted for by pseudopotentials? The answer is no, because pseudopotentials are generally fixed by requiring agreement to certain properties of given atomic states, at a prescribed theoretical level—there is no theorem governing the transferability to other atomic or molecular properties and/or to other theoretical levels. Everything rests on the basic idea that effects originating spatially in the core region of a given atom should be transferable, without change, to molecules. Error bars are only accessible empirically, via benchmark calculations employing the pseudopotentials and comparing to high-quality all-electron results and/or to accurate experimental data. However, there are certain notions that we can follow to improve the transferability and performance of the potentials, if desired: (a) the atomic input used for generating the pseudopotentials should include information on as many atomic states as possible that might be of relevance for chemical bonding; (b) the theoretical level used for generating the reference data should be as close as possible to that aimed at in molecular calculations with the pseu-

Correspondence to: H. Stoll; e-mail: stoll@theochem.uni-stuttgart.de

Contract/grant sponsor: Deutsche Forschungsgemeinschaft (DFG) (to B.M.)

dopotentials, i.e., valence correlation should be included to a decent degree, and the relativistic treatment should meet current standards with respect to the Hamiltonian used and the relativistic coupling within the wave function; (c) the pseudo-orbital transformation should be modeled so as to minimize the difference to the all-electron case—within the limits, of course, given by economic considerations.

Let us see how well current pseudopotential approaches meet these principles. Shape-consistent (or norm-conserving) pseudopotentials, see, e.g., refs. 13–17, rely on orbital properties (all-electron valence orbitals, suitably smoothed within the core region, and corresponding orbital energies); as such, they belong to a single atomic state and do not meet criterion (a). It may be argued that the potentials are l -dependent, and can be (and often are) adjusted to different atomic states for different angular-momentum quantum numbers, but state-averaging for a given l , although possible in principle, has been very seldom tried up to now (see, however, refs. 18 and 19). The orbital-based derivation of shape-consistent pseudopotentials implies certain limitations, too, concerning criterion (b). It is difficult to see how to incorporate correlation effects. Relativistic effects can be included at the Dirac–Hartree–Fock level, but the concomitant jj -coupling imposed on the wave function is not really very realistic over most part of the Periodic Table. Criterion (c), finally, can be well taken care of within the framework of the shape-consistent approach, as long as there is only one occupied valence orbital per l value. This is no longer the case with small-core potentials—here, the advantage of better agreement of all-electron valence and pseudovalence orbitals, with respect to their nodal structure, is (partially) compensated by the fact that the pseudopotential is usually generated from the outer-core orbitals instead of the physically more relevant genuine valence orbitals (see, however, ref. 20).

Turning now to energy-consistent pseudopotentials (cf. ref. 21), which are adjusted to total energy valence spectra, criterion (a) seems to be satisfied per construction. However, it should be mentioned that this is literally true only for scalar-relativistic potentials—the spin-orbit (SO) part of the energy-consistent pseudopotentials was fitted, up to quite recently, to SO splittings of highly charged ions without real physical significance regarding chemical bonding. Again, fulfilment of criterion (b) seems to be quite easy with energy-consistent pseudopotentials, because the total energies used as reference data are well defined at every useful theoretical level. However, up to quite recently, these potentials were adjusted at the independent-particle (Hartree–Fock, HF) level, neglecting valence correlation altogether, and (scalar-) relativistic effects were treated by an (approximate) one-component quasi-relativistic Hamiltonian (Wood–Boring²²). With regard to criterion (c), there is no direct control over the pseudo-orbital transformation with energy-consistent pseudopotentials, but the gain in accuracy with small-core pseudopotentials can be fully exploited. However, while the small-core option was early taken for d -elements (and has been commonly recognized as the only reliable option for that case, since then), small-core energy-consistent potentials for main-group elements were mostly missing up to quite recently.

In the present article, we show how recent developments lead to energy-consistent pseudopotentials much more in line with criteria (a)–(c) than before (see next section). A status report on

adjustment tools and the two-component potentials available so far (or upcoming in the near future) is given in the Implementation Section. In the Implementation and Molecular Application Sections, we proceed to discuss possibilities for efficient application of the potentials in one- and two-component molecular calculations and illustrate these points with new calculations on lead and bismuth compounds (PbX, BiX, BiO, BiH; X = F, Cl, Br, I). The Conclusion, finally, contains some ideas and prospects on future lines of progress.

Pseudopotential Adjustment

Methodological Considerations

Starting-point in any pseudopotential method is the definition of the valence Hamiltonian \mathcal{H}_{val} . We use

$$\mathcal{H}_{\text{val}} = -\frac{1}{2} \sum_i^{n_v} \Delta_i + \sum_{\lambda} V_{PP}^{\lambda} + \sum_{i < j}^{n_v} \frac{1}{r_{ij}} + \sum_{\lambda < \mu} V_{cc}^{\lambda\mu} \quad (1)$$

which is the simplest possible form, formally nonrelativistic, acting on the n_v valence electrons only (i, j are valence-electron indices), changes of the form of the operators with respect to the all-electron case being restricted to the electron-nucleus and inter-nuclei parts—the latter are replaced by the electron-core potentials, V_{PP}^{λ} , and core-core potentials, $V_{cc}^{\lambda\mu}$ (λ, μ are core indices), which are at the focus of pseudopotential theory.

For molecular pseudopotentials, it has always been a good tradition to derive the form of V_{PP}^{λ} and $V_{cc}^{\lambda\mu}$ from information on the simplest possible systems where these potentials appear, i.e., to derive V_{PP}^{λ} from atomic and $V_{cc}^{\lambda\mu}$ from diatomic information. It is important, at this point, to realize that it is only necessary to develop a theory for setting up the short-range part of V_{PP}^{λ} and $V_{cc}^{\lambda\mu}$ —the long-range part is well known and easily accessible from electrostatic considerations. The cores are spherically symmetric entities carrying charges $Q_{\lambda} = Z_{\lambda} - n_{c,\lambda}$ (where Z is the nuclear charge and n_c is the number of core electrons) but no higher static multipoles. Thus, the leading long-range terms in V_{PP}^{λ} and $V_{cc}^{\lambda\mu}$ are the monopole terms,

$$-\sum_i \frac{Q_{\lambda}}{r_{\lambda i}}, \quad + \frac{Q_{\lambda} Q_{\mu}}{r_{\lambda\mu}}, \quad (2)$$

respectively. Of course, induced multipoles of any order are possible additionally, and the leading term here is the charge-induced dipole term

$$-\frac{1}{2} \alpha_{\lambda} \vec{f}_{\lambda}^2 \quad (3)$$

where α_{λ} is the dipole-polarizability of core λ , and \vec{f}_{λ} is the field generated at the site of core λ by valence electrons and other cores. While terms like in eq. (2) are part of every pseudopotential approach, the term (3) which gives rise to the so-called core-polarization potential (CPP) has often been neglected in the past.

However, it has been shown to be important for heavy-element compounds, cf., e.g., ref. 23, and is traditionally used in connection with large-core energy-consistent pseudopotentials since nearly two decades.²¹

Turning now to the short-range parts of V_{pp}^λ and V_{cc}^λ , it is obvious that their importance is much larger in the first than in the second case. While valence electrons have finite, nonnegligible probability densities within atomic cores, core–core distances are usually so large that intercore Pauli repulsion and core–core penetration effects need not be accounted for—note, however, that changes induced by these effects amount to up to several pm for bond lengths of hydrides and oxides of sixth row post-*d* main-group elements, if large-core potentials (*nsp* valence shell) are used.^{24,25} Not only is the short-range part of V_{pp}^λ much more important than the one of V_{cc}^λ , it is also less straightforward to determine. While we can invoke the Born–Oppenheimer approximation for calculating deviations from the point-charge approximation of V_{cc}^λ , eq. (2), for pairs of (frozen) cores at fixed distances, an analogous procedure is obviously not possible in the case of V_{pp}^λ . It is true that Hartree–Fock theory provides us with an effective electron-frozen core interaction potential, but even supplemented by suitable relativistic potentials this does not serve our purpose in a theory that aims at a simplifying transformation of the short-range (core-region) part of the wave function, with respect to the all-electron case. This has led to the idea, pursued in the shape-consistent pseudopotential approach, of working backwards from smoothed pseudovalence orbitals (and corresponding orbital energies) via inversion of Hartree–Fock or Dirac–Hartree–Fock-like equations. A more general viewpoint is taken in the energy-consistent pseudopotential approach. When working back from properties of the valence-electron system in the field of the core, why not use physical observables instead of orbital properties defined only within the realm of the independent-particle picture. Properties directly accessible at every reasonable theoretical level (or from experiment) are total energies and their differences forming the valence spectrum of the atom. It is the basic idea underlying the energy-consistent pseudopotential approach that reliable and accurate potentials can be derived from these data, i.e., from the valence energies of ground and (low-lying) excited states of the neutral atom and of corresponding ions with low charge, and that *no more input data are needed*.

A remark on the quality of the atomic reference data used for deriving V_{pp}^λ is in order now, because the new generation of our energy-consistent pseudopotentials differs here from the older ones. As already mentioned earlier, scalar-relativistic valence energies were previously calculated using the quasi-relativistic Wood–Boring (WB) Hamiltonian²² and HF wave functions in *LS*-coupling; these data were supplemented by SO splittings of single-valence electron ions evaluated at the Dirac–Hartree–Fock (DHF) level. Presently, we rely on fully relativistic multiconfiguration DHF (MCDHF) data, using the Dirac–Coulomb–Breit Hamiltonian and four-component wave functions optimized (in a state-averaged way) for all relativistic states that can be derived from nonrelativistic orbital configurations. Considering the treatment of relativistic effects, this is the best we can do currently. The dominant relativistic one-particle effects are fully included. The smaller corresponding two-particle contributions are taken into account to order α^2 (α denotes the fine structure constant), similar

to the best known relativistic all-electron Hamiltonian for a many-electron system. In principle, higher-order relativistic corrections can be implicitly considered within the energy-consistent pseudopotential approach as soon as reliable and generally applicable all-electron treatments become available. Finally, the multiconfiguration wave functions provide for a realistic description of relativistic coupling from the very lightest to the superheavy elements (spanning the range from *LS*- over intermediate to *jj*-coupling). It is clear, on the other hand, that the treatment of correlation effects is still far from satisfactory. This is no serious drawback, because valence correlation—in contrast to relativity—is not meant to be incorporated into the pseudopotentials but rather is treated explicitly in valence-only molecular *ab initio* calculations. However, it would be desirable to include valence correlation effects in the atomic fitting procedure, at least for the most important electronic states, and, if possible, in combination with the computational level used routinely so far. Whereas the most important near-degeneracy effects can already be accounted for within the current implementation, the inclusion of dynamical correlation would require accurate numerical multireference configuration interaction or coupled-cluster programs for atoms, which are not yet available. Our pseudopotential approach presently is the only one that allows besides the consideration of a multitude of electronic states also the simultaneous application of several theoretical levels for each of these states in the adjustment procedure.

What is the connection now between the input reference data and the (short-range part of the) electron-core pseudopotential V_{pp}^λ to be derived from them. The connection is obvious in the case of the shape-consistent pseudopotentials—the modified (radially nodeless) valence orbitals and corresponding orbital energies can be used to invert a Fock-like equation (with Coulomb and exchange operators built from these orbitals) that contains (and can be solved for) the pseudopotential. This can be done for each set of angular momentum quantum numbers l, j separately, thus defining a semi-local potential of the form

$$V_{pp}^\lambda = - \sum_i \frac{Q_\lambda}{r_{\lambda i}} + \sum_i \sum_{l,j} V_{ij}^\lambda(r_{\lambda i}) \mathcal{P}_{ij}^\lambda, \quad (4)$$

where \mathcal{P}_{ij}^λ is the projector onto one-electron functions transforming according to the quantum numbers l, j around site λ . (Note, however, that this construction is valid only for one orbital of a given l, j set.) The situation seems to be more problematic in the case of the energy-consistent pseudopotentials, because only energies are available as input data and energies alone are not sufficient to uniquely define a potential. However, this nonuniqueness of the potential is intimately connected to the nonuniqueness of the pseudovalence wave function. Instead of explicitly fixing the short-range (core-region) part of the latter, as in the case of the shape-consistent pseudopotentials, we can fix it indirectly by a suitable choice of the short-range form of the V_{pp}^λ . We are completely free in this choice, except for the requirement that the long-range part of the pseudovalence wave function should be identical to the all-electron one, i.e., that the boundary conditions for the transition from the short-range to the long-range region are the same as in the all-electron case. Following this idea, we make

an *ansatz* for a short-range modification of each of the long-range terms in eqs. (2) and (3) as follows:

$$-\frac{Q_\lambda}{r_{\lambda i}} \rightarrow -\frac{Q_\lambda}{r_{\lambda i}} + \sum_{l,j} V_{lj}^\lambda(r_{\lambda i}) \mathcal{P}_{lj}^\lambda$$

$$V_{lj}^\lambda(r) = \sum_k B_{\lambda,lj,k} e^{-\beta_{\lambda,lj,k} r^2}; \quad (5)$$

$$\frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} \rightarrow \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} + C_{\lambda\mu} e^{-\gamma_{\lambda\mu} r_{\lambda\mu}} \quad (6)$$

and

$$-\frac{1}{2} \alpha_\lambda \tilde{r}_\lambda^2 \rightarrow -\frac{1}{2} \alpha_\lambda [\tilde{r}_\lambda^c(\tilde{r}_{\lambda i}^c, \tilde{r}_{\lambda\mu}^c)]^2,$$

$$\tilde{r}^c = \tilde{r}(1 - e^{-\delta_\lambda r^2})^{-1}. \quad (7)$$

Equation (5) is formally the same as (4)—we chose it because it is the simplest possible, physically reasonable *ansatz*—but note that there would be no problem, in our scheme, to use a more sophisticated form, involving outer-core projectors as in ref. 20, for example. The radial potentials in eq. (5) are written as an expansion in Gaussians (again the simplest possible, computationally convenient, short-range *ansatz*), with adjustable parameters $B_{\lambda,lj,k}$, $\beta_{\lambda,lj,k}$. The expansion length should be kept as small as possible so as to yield pseudopotentials and pseudovalence wave functions smooth in the core region, but, on the other hand, should contain as many parameters as needed for reproducing the reference valence spectrum to the desired accuracy. It is our experience that in most cases one- or two-term expansions are sufficient for an accuracy of adjustment between $\sim 10^{-1}$ eV (large-core pseudopotentials) and $\sim 10^{-2}$ eV (small-core pseudopotentials). The potentials V_{lj}^λ in eq. (5) are assumed to be short-range (essentially restricted to the core region), and it would seem necessary, therefore, to impose some lower threshold on the exponential parameters during the optimization, i.e. $\beta_{\lambda,lj,k} > \beta_c$. However, it is our experience that we are always able to find suitable minima in the parameter space of the $B_{\lambda,lj,k}$, $\beta_{\lambda,lj,k}$ *a posteriori*, without ever explicitly imposing such a criterion. As to eq. (6), a short-range Born–Mayer potential is used to describe deviations from the electrostatic monopole core–core repulsion. The parameters are fitted to potential curves of (frozen) bare cores evaluated in SCF all-electron or small-core pseudopotential calculations, for use with large-core pseudopotentials. Equation (7), finally, is meant to simulate static and dynamic core polarization (including core-valence correlation).^{21,26} δ_λ is a cut-off parameter for core λ which, in the simplest case, can be fitted to reproduce the core-valence correlation contribution to the ionization potential of the single-valence-electron ion.

Implementation

The MCDHF reference data for valence energies are calculated using the relativistic atomic structure program GRASP.²⁷ The calculations are done using a finite-difference scheme for solving

the radial equations, thus avoiding finite-basis-set errors. The relativistic effects are included at a four-component level, using the Dirac–Coulomb Hamiltonian, with Breit interaction evaluated to first-order perturbation theory. After a selection of the important nonrelativistic orbital configurations, a series of state-averaged MCDHF calculations is performed for all relativistic states of these configurations, with weights usually chosen according to the degeneracy of individual states, $(2J + 1)$.

For adjusting the pseudopotentials V_{PP}^λ , eq. (5), to the reference valence spectrum, calculations equivalent to the all-electron case are performed using the valence Hamiltonian \mathcal{H}_{val} , eq. (1). Again GRASP is employed but modified for the use of pseudopotentials²⁸ and in the limit $c \rightarrow \infty$ (c : velocity of light), because \mathcal{H}_{val} is formally nonrelativistic. As convergence turned out to be poor in many cases, we analytically eliminate the small component in the radial equations and determine the large component from a second-order differential equation that is numerically solved using routines taken from the MCHF program.^{28,29} The same series of state-averaged MCSCF calculations is performed as in the all-electron case, with the same weights, and first and second derivatives of individual state energies are evaluated with respect to the parameters $B_{\lambda,lj,k}$, $\beta_{\lambda,lj,k}$ of V_{PP}^λ , in the Hellmann–Feynman approximation. This information is used for improving on an initial guess for the parameters $B_{\lambda,lj,k}$, $\beta_{\lambda,lj,k}$ iteratively as follows. At each iteration step, the quality of V_{PP}^λ is characterized by

$$S = \sum_m w_m \sum_n w_{n,m} (E_{nm}^{PP} - E_{\text{val},nm}^{\text{AE}})^2 \quad (8)$$

Here, m and n denote orbital configurations and relativistic states of a given orbital configuration, respectively; E_{nm}^{PP} and $E_{\text{val},nm}^{\text{AE}}$ are the valence energies from the pseudopotential calculation with the current V_{PP}^λ and from the reference all-electron calculation, where valence energy in the latter case means total energy minus energy of the bare core; the $w_{n,m}$ and w_m are individual and configurational weights, respectively—the $w_{n,m}$ are chosen as in the all-electron calculations, and the w_m can be used for renormalization, for example, to give all the nonrelativistic orbital configurations the same total weight irrespective of their number of states. An augmented Hessian-like procedure,³⁰ based on the derivatives of E_{nm}^{PP} with respect to $B_{\lambda,lj,k}$ and $\beta_{\lambda,lj,k}$ is then adopted for obtaining a new guess of parameters yielding a smaller value of S . This leads us, over ~ 10 – 100 iteration steps, very near to the minimum value of S . However, because the above derivatives of E_{nm}^{PP} are approximate only, a line search has to be used in the final iteration steps.

So far, relativistic energy-consistent pseudopotentials adjusted along these lines are available for the fourth through sixth row main-group elements of group 13,^{31,32} groups 14, 15,³² with a small-core definition ($(n - 1)spd$ *nsp* valence shells); corresponding potentials for groups 1, 2,³³ groups 11, 12,³⁴ and groups 16, 17³⁵ are in preparation. Further small-core potentials for Fr, Ra,³³ and the superheavy elements E111–E120^{33,36,37} are also forthcoming. Work on small-core potentials for first-row transition metals is in progress,³⁸ a corresponding potential for Db (E105) has been published.³⁹ Large-core pseudopotentials (*nsp* valence shell) have been derived for the fourth through sixth row main-group elements of groups 14–17.^{25,30,32} For most of the pseudo-

potentials mentioned, energy-optimized valence basis sets have been (or are being) generated for use in molecular calculations. One-component molecular calculations, using the pseudopotentials in an averaged scalar-relativistic form, are as well possible as two-component calculations, using the full potentials including the SO part. The previously published Wood–Boring adjusted pseudopotentials usually yield results of similar quality in scalar-relativistic molecular calculations; however, the present approach based on multiconfiguration Dirac–Hartree–Fock reference data is clearly preferable when SO effects are considered.

In the present work, the *ab initio* quantum-chemical program packages MOLPRO⁹ and DGC1⁷ have been used for the molecular calculations. These calculations have been done in three stages. First, one-component calculations, neglecting SO effects, have been performed with MOLPRO, mostly with small-core pseudopotentials, extended valence basis sets and at a high correlation level [e.g., coupled cluster with single and double excitations and a perturbative account of triples (CCSD(T))]. These calculations are followed by two-component multireference configuration-interaction calculations with single excitations (MRCIS) using DGC1. At this stage, we can monitor SO effects by doing these calculations with and without the SO part of the pseudopotential. Single excitations are sufficient (i.e., yield the main contributions) because our pseudopotential SO operator is one-electronic. For reducing the computational burden, we also leave out higher polarization functions needed for describing electron correlation and sometimes even work with large-core pseudopotentials. Thus, while the calculations of the first stage aim at a good description of electron correlation at the scalar-relativistic level, the calculations of the second stage aim at describing SO effects at a low level of correlation treatment. Simply adding the SO effects determined at the second stage to the results of the first stage would essentially mean neglect of the coupling between electron correlation and SO effects. This drawback can be removed, however, at the third stage by means of a spin-free-state-shift technique.^{40,41} The idea is to use the results of the first stage as input information for the two-component MRCIS. This can be done by adding the projector

$$\sum_i |\Psi_i^{(0)}\rangle (E_i - E_i^{(0)}) < \Psi_i^{(0)}| \quad (9)$$

into the Hamiltonian of the final MRCIS calculations including the SO potential. Here, the $|\Psi_i^{(0)}\rangle$ are wave functions of low-lying states obtained in MRCIS calculations of the second stage *without* the SO potential, the $E_i^{(0)}$ are their energies, and the E_i are the corresponding well-correlated results from the one-component calculations of the first stage. Thus, the projector shifts the MRCIS energies of the “spin-free” states (i.e., the states obtained without SO coupling) to values corresponding to a better treatment of correlation. The final diagonalization, at the third stage, of the two-component MRCIS Hamiltonian matrix including the projector then amounts to evaluating SO coupling between well-correlated states. Summarizing, we need one-component (first stage) and two-component spin-free (second stage) calculations to build up the projector (9) which is used in the final two-component calculations including the SO potential (third stage). Note at this point that we are not forced to use the same pseudopotential in all

of the three stages. Use of a small-core pseudopotential is often needed at the first stage to include outer-core relaxation and correlation effects. On the other hand, SO effects are often sufficiently small for a large-core pseudopotential to provide sufficient accuracy at the second and third stage, without need to explicitly model the (computationally heavy) SO-induced orbital relaxation of the outer-core orbitals. Of course, the E_i and $E_i^{(0)}$ in eq. (9) should not be taken then as absolute valence energies but rather be taken relative to a common energy zero (e.g., the energy of the large core).

Molecular Applications

Lead Monohalides

Table 1 contains results of two-component calculations, performed by means of the two-step procedure outlined earlier, for the two lowest states ($X_1 \ ^2\Pi_{1/2}$, $X_2 \ ^2\Pi_{3/2}$) of PbF. In all cases, CCSD(T) one-component calculations are followed by spin-free-state-shifted two-component MRCIS ones. We first applied the small-core (22-valence electron) pseudopotential (PP) for Pb³² in both steps, together with the corresponding optimized (12s12p9d3f2g)/[6s6p4d3f2g] valence basis set at the CCSD(T) level, and a reduced 1f polarization set at the MRCIS one. For F, the aug-cc-pVTZ basis set^{42,43} was applied for CCSD(T) and reduced by replacing the df polarization set with the d cc-pVDZ one for MRCIS. All outer-core and valence electrons of Pb and the 2s2p valence electrons of F were correlated, but the spin-free-state shift was restricted to the valence energy, $E(\text{PbF}) - E(\text{Pb}^{4+}) - E(\text{F}^{7+})$. Only the two members of the spin-free $^2\Pi$ state were included in the shift, in these first calculations. The resulting spectroscopic constants for PbF are in good agreement with the experimental values, to 0.6 pm for r_e , 12 cm^{−1} (2%) for ω_e , and 0.04 eV for $D_e(^2\Pi_{1/2})$. Due to their large influence on the atomic asymptote SO contributions are important for D_e (−0.9 eV), but relatively small for r_e (± 0.6 pm). In accordance with experiment, the $^2\Pi_{1/2}$ bond length becomes larger than the $^2\Pi_{3/2}$ one. (The bond lengths would be the same if the SO splitting were independent of r , but with SO effects being increasingly quenched with decreasing r , a longer (shorter) r_e results for the lower (higher) state.) However, the SO effect on r_e is significantly smaller than the experimental one, and the molecular $^2\Pi_{1/2} - ^2\Pi_{3/2}$ spin-orbit splitting, T_e , is underestimated by 1200 cm^{−1} (~15%).

We now tried to improve on these results, to make them more accurate but also to achieve computational simplifications. As already mentioned, using a large outer-core + valence active space, with the small-core PP, is computationally rather demanding, especially at the two-component MRCIS level. We, therefore, tried to replace the small-core PP with a large-core (4-valence-electron) PP³² and corresponding optimized (6s6p)/[4s4p] valence basis set, supplemented by 2 d polarization functions, in the MRCIS step, while still retaining the small-core PP for the one-component CCSD(T) and the spin-free-state shifts (sc/lc-PP in Table 1). This turns out to be an excellent approximation, changes with respect to the full small-core PP treatment being −0.2 pm for r_e , +3 cm^{−1} for ω_e , +0.03 eV for D_e , and +357 cm^{−1} for T_e . On the other hand, rather large differences arise, if the large-core PP

Table 1. Results for Spectroscopic Constants of the $X_1 \ ^2\Pi_{1/2}$ and $X_2 \ ^2\Pi_{3/2}$ States of PbF, from Two-Component MRCIS Calculations with Spin-Free-State Shifts from One-Component CCSD(T) Calculations.

	$^2\Pi_{1/2}$			$^2\Pi_{3/2}$		
	r_e (Å)	ω_e (cm $^{-1}$)	D_e (eV)	r_e (Å)	ω_e (cm $^{-1}$)	T_e (cm $^{-1}$)
sc-PP						
2 conf. ^a	2.052 (2.046)	519 (526)	3.71 (4.64)	2.040	530	7060
sc/lc-PP						
2 conf. ^a	2.050	521	3.74	2.038	533	7417
3 conf. ^b	2.060	505	3.81	2.038	533	7947
4 conf. ^c	2.059	509	3.80	2.038	532	7757
lc-PP						
4 conf. ^c	1.996 (1.983)	531 (550)	4.21 (5.12)	1.975	557	7780
exp. ^d	2.058	507 ^e	3.67	2.034	533 ^e	8262 ^e

sc-PP or lc-PP denotes the kind of pseudopotential (small core or large core) used for Pb; in the sc/lc-PP case, a hybrid treatment with a small-core PP (large-core PP) at the one-component (two-component) level was employed. n conf denotes the number of reference configurations for the MRCIS, in C_{2v} double-group symmetry. Numbers in parentheses are one-component results for the $^2\Pi$ state.

^aSpin-free-state shift for $^2\Pi$.

^bSpin-free-state shifts for $^2\Pi$, $^2\Sigma^+$.

^cSpin-free-state shifts for $^2\Pi$, $^2\Sigma^+$, $^4\Sigma^-$.

^dFrom ref. 44, if not indicated otherwise.

^eFrom ref. 56.

is used throughout, at the one-component (uncontracted 6s6p4d3f2g basis) as well as two-component steps ($\Delta r_e = -6$ pm, $\Delta D_e = +0.4$ eV), making this level of approximation less recommendable.

The largest error in the small-core or hybrid small-core/large-core PP calculations described so far is, most probably, that we introduced a spin-free-state shift for the $^2\Pi$ state of interest but left out such a shift for low-lying excited spin-free states. Thus, the energy differences between ground and excited spin-free states is artificially increased leading to an underestimation of SO effects. In fact, including the $^2\Sigma^+$ state (with a Pb $p\sigma$ instead of a $p\pi$ orbital singly occupied) into the spin-free-state shift, yields additional SO contributions to $^2\Pi_{1/2}$ reducing the difference to experiment to 0.2 pm (r_e), 2 cm $^{-1}$ (ω_e), and 315 cm $^{-1}$ (T_e), while D_e is slightly overestimated now (by 0.14 eV). Adding the next higher spin-free state ($^4\Sigma^-$), within the MRCIS shift, changes very little.

The remaining differences to experiment may be compared to values of $\Delta r_e = 1$ pm, $\Delta D_e = 0.24$ eV obtained very recently by Liu et al.⁴⁵ in two-component CCSD(T) calculations for the $^2\Pi_{1/2}$ ground state of PbF, using a small-core shape-consistent PP for Pb. Their SO contributions to the spectroscopic constants ($\Delta r_e^{\text{SO}} = +1.5$ pm, $\Delta \omega_e^{\text{SO}} = -15$ cm $^{-1}$, $\Delta D_e^{\text{SO}} = -0.73$ eV) are similar to ours ($\Delta r_e^{\text{SO}} = +1.3$ pm, $\Delta \omega_e^{\text{SO}} = -17$ cm $^{-1}$, $\Delta D_e^{\text{SO}} = -0.84$ eV).

Let us next consider PbCl (see Table 2). The calculations closely follow those for PbF discussed above. An all-electron description is chosen for Cl, using the aug-cc-pVTZ basis set⁴⁶ at the CCSD(T) level and a reduced cc-pVDZ d polarization set for

the MRCIS; correlation is restricted to the Cl 3s3p valence electrons. However, we only compare here calculations with a combined small-core/large-core pseudopotential treatment for Pb to corresponding ones using the large-core pseudopotential throughout. In the first case, i.e., applying the small-core pseudopotential for the CCSD(T) spin-free-state shifts, we achieve reasonable agreement with experiment (to 2 pm for r_e , 6 cm $^{-1}$ for ω_e , 0.3 eV for D_e) already with the shift restricted to the $^2\Pi$ state only. However, as for PbF, this is due to the fact that SO effects are either small (r_e , ω_e) or mainly of atomic origin (D_e); for the large molecular $^2\Pi_{1/2}$ - $^2\Pi_{3/2}$ SO splitting of ~ 8300 cm $^{-1}$, on the other hand, our result is off by ~ 750 cm $^{-1}$. The error for the latter can be reduced again by including low-lying excited states (mainly $^2\Sigma^+$) into the spin-free-state shift of the two-component MRCIS calculations. Still, the result with four reference configurations ($^2\Pi$, $^2\Sigma^+$, $^4\Sigma^-$) is off by 400 cm $^{-1}$, and the final values for r_e and D_e are less accurate than in the case of PbF ($\Delta r_e = 2$ pm, $\Delta D_e = 0.2$ eV). Because the SO effect on r_e (2.0 pm) is equal to that obtained in two-component CCSD(T) calculations by Liu et al.⁴⁵ and the difference between the r_e values of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states is in close agreement with the experimental data, we cannot attribute the error in r_e to shortcomings of our SO treatment, it rather seems to be a basis-set error of our one-component CCSD(T) calculation. This error is overcompensated, on the other hand, if we replace the small-core pseudopotential by the large-core one. Due to this compensation, the difference of the large-

Table 2. As Table 1, but for PbCl.

	$^2\Pi_{1/2}$			$^2\Pi_{3/2}$		
	r_e (Å)	ω_e (cm $^{-1}$)	D_e (eV)	r_e (Å)	ω_e (cm $^{-1}$)	T_e (cm $^{-1}$)
sc/lc-PP						
2 conf. ^a	2.475 (2.469)	310 (313)	2.81 (3.70)	2.458	317	7526
3 conf. ^b	2.491	298	2.88	2.457	317	8084
4 conf. ^c	2.489	299	2.87	2.459	317	7874
lc-PP						
3 conf. ^b	2.441 (2.421)	313 (328)	3.07 (3.94)	2.410	334	7987
exp. ^d	2.471 ^e	304	~3.1	2.439 ^e	322	8273

^aSpin-free-state shift for $^2\Pi$.^bSpin-free-state shifts for $^2\Pi$, $^2\Sigma^+$.^cSpin-free-state shifts for $^2\Pi$, $^2\Sigma^+$, $^4\Sigma^-$.^dFrom refs. 44, 56, and 57.^e r_0 values.

core PP results to experiment (3 pm for r_e , 9 cm $^{-1}$ for ω_e , 0.05 eV for D_e) are smaller than in the PbF case.

Finally, results for PbBr and PbI are given in Table 3. The calculations done for these compounds are of the mixed small-core/large-core pseudopotential type, for Pb. For Br and I, large-core (7-valence electron) MCDHF-adjusted pseudopotentials, including CPPs at the one-component level, have been used. These pseudopotentials and the corresponding optimized (7s7p3d2f)/[5s5p3d2f] basis sets are available from the authors upon request and will also be made accessible on the Web.⁴⁷ While the full Br and I basis sets just mentioned have been used at the one-component CCSD(T) level, reduced 2d polarization sets were applied in the two-component MRCIS calculations. Our calculated results are

in reasonable agreement with available ground-state experimental data (to <10 cm $^{-1}$ for ω_e , 0.3 eV for D_e). It should be noted at this point, however, that we only included the $^2\Pi$ state in the spin-free-state shift for PbBr and PbI. (There are many states here with low excitation energies [$^2\Sigma^+$, $^4\Sigma^-$, $^4\Pi$, ...], and we encountered severe convergence difficulties when including them into the MRCIS.) Thus, the SO effects in Table 3 are certainly underestimated—we expect a SO-induced elongation of at least 2 pm (the SO effect for PbCl) for the ground-state r_e values of PbBr and PbI. This expectation is in line with findings of Liu et al.,⁴⁵ where SO effects of +2.0 and +2.3 pm were found for PbBr and PbI, respectively. The $^2\Pi_{1/2}$ – $^2\Pi_{3/2}$ SO splittings are similar (to ~250 cm $^{-1}$) in our calculations for PbBr and PbI to those obtained for

Table 3. Results for Spectroscopic Constants of the X_1 $^2\Pi_{1/2}$ and X_2 $^2\Pi_{3/2}$ States of PbBr and PbI, from Two-Component MRCIS Calculations with Spin-Free-State Shifts from One-Component CCSD(T) Calculations.

	$^2\Pi_{1/2}$			$^2\Pi_{3/2}$		
	r_e (Å)	ω_e (cm $^{-1}$)	D_e (eV)	r_e (Å)	ω_e (cm $^{-1}$)	T_e (cm $^{-1}$)
PbBr						
calc.	2.603 (2.598)	212 (214)	2.33 (3.35)	2.588	216	7577
exp. ^a		207	2.6		218	8198
PbI						
calc.	2.772 (2.770)	168 (169)	1.81 (2.97)	2.760	171	7659
exp. ^a		161	2.0		169	7969

A hybrid treatment with a small-core PP (large-core PP) at the one-component (two-component) level was employed, and 2 reference configurations with spin-free-state shift for $^2\Pi$ were used in the MRCIS. Numbers in parentheses are one-component results for the $^2\Pi$ state.

^aFrom refs. 44, 56, 59, and 59.

Table 4. Results for Spectroscopic Constants of the $X_1\ 0^+$ and $X_2\ 1\ (^3\Sigma^-)$ States of BiH, from Two-Component MRCIS Calculations with Spin-Free-State Shifts from One-Component CCSD(T) Calculations.

	$X_1\ 0^+$			$X_2\ 1$		
	$r_e\ (\text{\AA})$	$\omega_e\ (\text{cm}^{-1})$	$D_e\ (\text{eV})$	$r_e\ (\text{\AA})$	$\omega_e\ (\text{cm}^{-1})$	$T_e\ (\text{cm}^{-1})$
1 conf. ^a	1.786 (1.784)	1773 (1782)	1.92 (2.40)	1.783	1779	1285
6 conf. ^b	1.789	1760	2.35	1.784	1771	4662
10 conf. ^c	1.800	1716	2.38	1.790	1741	4328
exp. ^d	1.805	1636 1699 ^e	≤ 2.9	1.791	1669	4917

A hybrid treatment with a small-core PP (large-core PP) at the one-component (two-component) level was employed. $n\ \text{conf}$ denotes the number of reference configurations for the MRCIS, in C_{2v} double-group symmetry. Numbers in parentheses are one-component results for the $^3\Sigma^-$ state.

^aSpin-free-state shift for $^3\Sigma^-$.

^bSpin-free-state shifts for $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$.

^cSpin-free-state shifts for $^3\Sigma^-$, $^1\Delta$, $^1\Sigma^+$ $2 \times$ $^3\Pi$, $^5\Sigma^-$.

^dFrom ref. 44, unless indicated otherwise.

^eValue cited in ref. 52.

PbF and PbCl at the same level of approximation, and, in fact, all the experimental T_e values for the lead monohalides lie in the range of 7960 . . . 8270 cm^{-1} .

Bismuth Monohydride

Turning now to calculations involving bismuth, we first have to characterize Bi pseudopotentials and basis sets. In the one-component CCSD(T) treatment, we used the small-core (23-valence-electron) pseudopotential,³² together with the corresponding optimized (12s12p9d3f2g)/[6s6p4d3f2g] basis set. In the two-component MRCIS calculations, a large-core (5-valence electron) MCDHF-adjusted potential³⁰ and a (6s6p2d)/[4s4p2d] valence basis set were used, which are available from the authors upon request (or may be downloaded from the Web page⁴⁷). For hydrogen, the aug-cc-pVTZ basis^{42,43} was applied, which was truncated to a sp set in the two-component MRCIS. In the CCSD(T) as well as the MRCIS all orbitals (including the outer-core orbitals of Bi, in the small-core case) were treated as active. We performed calculations for the $X_1\ 0^+$ and $X_2\ 1$ states of BiH, both derived from the scalar-relativistic $^3\Sigma^-$ state. As can be seen from Table 4, SO effects are severely underestimated with a single-reference MRCIS and spin-free-state shift for $^3\Sigma^-$ only. This is especially apparent for the $X_1\ 0^+ - X_2\ 1$ SO splitting, T_e , which comes out too small by a factor of 4! We, therefore, added to the $\sigma^2\pi_x^1\pi_y^1$ ground-state configuration in the MRCIS further references of the type $\sigma^2\pi_x^{2-n}\pi_y^n$ and $\sigma^{*2}\pi_x^{2-n}\pi_y^n$ and introduced spin-free-state shifts for the low-lying $^1\Delta$ and $^1\Sigma^+$ states. In a final step, we tried reference configurations of the type $\sigma^2\pi_x^{2-n}\pi_y^n$, $\sigma^1\sigma^{*1}\pi_x^{2-n}\pi_y^n$, $\sigma^2\sigma^{*1}\pi_{x,y}^1$, $\sigma^1\pi_{x,y}^2\pi_{y,x}^1$ and added spin-free-state shifts for $2 \times$ $^3\Pi$, $^5\Sigma^-$. We obtain a drastic improvement of T_e , with the deviation from experiment reduced to 300–600 cm^{-1} . The calculated bond lengths for $X_1\ 0^+$, $X_2\ 1$ become accurate to 0.5 pm (although the difference between them is still somewhat to the low side).

This is slightly better than calculations with a medium-core (15-valence electron) shape-consistent potential by Christiansen and coworkers^{48,49} and Han et al.,⁵⁰ and also definitely better than previous calculations with large-core (5-valence electron) shape-consistent^{51,52} as well as WB-derived energy-consistent pseudo-potentials²⁴—there, bond lengths are off by 1–6 pm. SO effects on the ground-state bond length vary between 1.5 pm²⁴ and 1.9 pm.⁵⁰ Our final values for vibrational constants are too large by ~ 20 –80 cm^{-1} (or 1–5%, according to the experimental source), but their difference (25 cm^{-1}) well mimicks the experimental SO effect. The experimental dissociation energy is not known (only an upper limit has been given); our calculated D_e for the $X_1\ 0^+$ ground state is in the range of this limit and the previously published theoretical values of 2.1 . . . 2.3 eV.^{24,49,50}

Bismuth Monoxide

In our calculations for BiO, the Bi atom was treated as described in the previous subsection, while for O, we used the aug-cc-pVTZ basis set^{42,43} (with the polarization set reduced to the d piece of the cc-pVTZ set in the two-component MRCIS). As can be seen from Table 5, already the CCSD(T) one-component results for the “spin-free” $^2\Pi$ state are in surprisingly good agreement with the spectroscopic constants of the experimental $X_1\ ^2\Pi_{1/2}$ ground state, to 1 pm for r_e , 29 cm^{-1} (5%) for ω_e , and 0.1 eV for D_e . The good value for D_e is, of course, due to the fact that there is no (first-order) atomic SO-splitting for the 4S ground state of Bi. Little improvement is obtained by including SO interaction at the two-component level. Proceeding from the lowest level (the $^2\Pi$ state, with orbital configuration $\sigma^2\pi^4\pi^*$, in the MRCIS reference space and CCSD(T) spin-free-state shift for $^2\Pi$) to higher ones (including $\pi \rightarrow \pi^*$ excitations in the reference space, and performing spin-free-state shifts for $2 \times$ $^2\Pi$ and $^4\Pi$), only leads to small changes of the ground-state properties with respect to the one-

Table 5. As Table 4, But for the $X_1 \ ^2\Pi_{1/2}$ and $X_2 \ ^2\Pi_{3/2}$ States of BiO.

	$^2\Pi_{1/2}$			$^2\Pi_{3/2}$		
	r_e (Å)	ω_e (cm $^{-1}$)	D_e (eV)	r_e (Å)	ω_e (cm $^{-1}$)	T_e (cm $^{-1}$)
2 conf. ^a	1.927 (1.923)	724 (721)	3.36 (3.59)	1.917	698	7590
4 conf. ^b	1.919	737	3.24	1.928	701	5169
6 conf. ^b	1.923	725	3.30	1.926	705	5771
exp. ^c	1.934	692	3.47		688 ^d	7089 ^d

Numbers in parentheses are one-component results for the $^2\Pi$ state.

^aSpin-free-state shift for $^2\Pi$.

^bSpin-free-state shifts for $2 \times ^2\Pi$, $^4\Pi$.

^cFrom ref. 44, unless indicated otherwise.

^dFrom ref. 60.

component result (<0.4 pm for r_e , 16 cm $^{-1}$ for ω_e , and 0.3 eV for D_e), and the “best” results are not better than the one-component ones. The $^2\Pi_{1/2}$ – $^2\Pi_{3/2}$ excitation energy, on the other hand, turns out to be quite sensitive to the SO treatment, and does not seem to be stabilized in our “best” calculation. The problem here is the large number of spin-free excited states with similar energies that led to convergence problems, for example, when we tried to include $\pi \rightarrow \sigma^*$ and $\pi^* \rightarrow \sigma^*$ excitations into the reference space and to find corresponding CI solutions for applying spin-free-state shifts. Such problems do not arise in large-scale SOCI calculations like those performed by Buenker and coworkers for BiO⁵³ (and also for Bi halides^{54,55}); however, due to the relatively small one-particle basis sets (used in connection with a medium-core pseudopotential), the bond lengths are overestimated there by as much as 10 pm.

Bismuth Monohalides

Table 6 presents our results for BiF. The pseudopotentials and basis sets used for Bi are the same as in the two previous para-

graphs, the basis-set choice for F (aug-cc-pVTZ at the one-component level, with a reduced d cc-pVTZ polarization set at the two-component level^{42,43}) is completely analogous to that for O in BiO. The calculations are of the mixed small-core (one-component CCSD(T))/large-core (two-component MRCIS) variety. It is seen that it is essential to go beyond the single-reference level in the two-component MRCIS; neglecting to do so leads to very small SO effects on the $X_1 \ 0^+$ ($^3\Sigma^-$) ground-state properties (which are too small for r_e by an order of magnitude, e.g.) and an excitation energy T_e for the $X_2 \ 1$ ($^3\Sigma^-$) state that is not much more than 10% of the experimental T_e . It turns out that two low-lying $^1\Sigma^+$ and $^3\Pi$ states strongly mix with $^3\Sigma^-$ to form the $X_1 \ 0^+$ and $X_2 \ 1$ states. Spin-free state shifts for these states were included in MRCIS calculations with four and six reference configurations ($\sigma^2 \pi^4 \pi_x^{*2-n} \pi_y^{*n}$ plus additional $\sigma \rightarrow \sigma^*$ and $\pi^* \rightarrow \sigma^*$ excitations). Especially the admixture of $^3\Pi$ ($\pi^* \rightarrow \sigma^*$ excitations) is instrumental in reaching agreement to 0.7 pm for r_e , 14 cm $^{-1}$ for ω_e in the $X_1 \ 0^+$ ground-state spectroscopic constants, while inclusion of all states of the π^{*2} configuration ($^1\Sigma^+$ in particular) is

Table 6. As Table 4, But for the $X_1 \ 0^+$ and $X_2 \ 1$ ($^3\Sigma^-$) States of BiF.

	$X_1 \ 0^+$			$X_2 \ 1$		
	r_e (Å)	ω_e (cm $^{-1}$)	D_e (eV)	r_e (Å)	ω_e (cm $^{-1}$)	T_e (cm $^{-1}$)
1 conf. ^a	2.021 (2.020)	554 (556)	3.25 (3.85)	2.020	555	832
4 conf. ^b	2.028	549	3.79	2.019	557	6234
6 conf. ^c	2.045	527	3.95	2.026	545	6005
exp. ^d	2.052	513	3.79 3.9	2.029	543	6753

Numbers in parentheses are one-component results for the $^3\Sigma^-$ state.

^aSpin-free-state shift for $^3\Sigma^-$.

^bSpin-free-state shifts for $^3\Sigma^-$, $^1\Sigma^+$.

^cSpin-free-state shifts for $^3\Sigma^-$, $^1\Sigma^+$, $^3\Pi$.

^dFrom refs. 61–67.

Table 7. Results for Spectroscopic Constants of the $X_1\ 0^+$ and $X_2\ 1\ (^3\Sigma^-)$ States of BiCl and BiBr, from Two-Component MRCIS Calculations with Spin-Free-State Shifts from One-Component CCSD(T) Calculations.

	$X_1\ 0^+$			$X_2\ 1$		
	$r_e\ (\text{\AA})$	$\omega_e\ (\text{cm}^{-1})$	$D_e\ (\text{eV})$	$r_e\ (\text{\AA})$	$\omega_e\ (\text{cm}^{-1})$	$T_e\ (\text{cm}^{-1})$
BiCl						
calc.	2.477 (2.443)	319 (336)	3.04 (2.90)	2.452	328	6159
exp. ^a	2.472	308	3.15 ^b		327 ^c	6671 ^c
BiBr						
calc.	2.604 (2.575)	219 (228)	2.62 (2.57)	2.583	224	6150
exp. ^a	2.610	209	2.75 ^b		220 ^c	6526 ^c

A hybrid treatment with a small-core PP (large-core PP) at the one-component (two-component) level was employed, and six reference configurations with spin-free-state shift for $^3\Sigma^-$, $^1\Sigma^+$, $^3\Pi$ were used in the MRCIS. Numbers in parentheses are one-component results for the $^3\Sigma^-$ state.

^aFrom ref. 44, unless indicated otherwise.

^bFrom ref. 67 and references cited therein.

^cFrom ref. 68.

sufficient to get a reasonable $X_1\ 0^+ \rightarrow X_2\ 1\ T_e$ (to $\sim 500\ \text{cm}^{-1}$). The experimentally observed SO-induced shortening of the bond length from $X_1\ 0^+$ to $X_2\ 1$ (2.3 pm) is well described in our best calculations (1.9 pm).

Similar calculations as for BiF were done for BiCl and BiBr (Table 7). For Cl, an all-electron description with an aug-cc-pVTZ basis set⁴⁶ (reduced with respect to the polarization functions for the two-component calculations, as for F) was employed; for Br, a large-core pseudopotential description with (7s7p3d2f)/[5s5p3d2f] or (7s7d2d)/[5s5p2d] valence basis sets as for PbBr was applied. At the highest theoretical level (two-component large-core PP MRCIS with six reference configurations, with spin-free-state shifts for $^3\Sigma^-$, $^1\Sigma^+$, $^3\Pi$ from one-component small-core PP CCSD(T) calculations), we obtain a SO-induced elongation of the bond length by $\sim 3 \dots 3.5$ pm for the ground state and a differential effect of $2 \dots 2.5$ pm for the bond lengths of $X_1\ 0^+$ and $X_2\ 1$; good agreement with experiment is achieved, to 0.6 pm for r_e , 11 cm^{-1} for ω_e , 0.1 eV for D_e , while the $X_1\ 0^+ \rightarrow X_2\ 1$ excitation energy is systematically by $\sim 400 \dots 500\ \text{cm}^{-1}$ too low as in the case of BiF.

Conclusion

A review of the present status of the energy-consistent pseudopotential approach has been given. The basic idea underlying this approach, of adjusting pseudopotentials to valence spectra of low-lying atomic/ionic states relevant for chemical bonding, has been consistently implemented now at the full two-component level, i.e., scalar-relativistic and spin-orbit potentials are treated on equal footing and are determined simultaneously. Relativistic effects, to be fitted into the pseudopotentials, are treated at a high level in the atomic reference calculations, using the Dirac–Coulomb–Breit Hamiltonian and providing for a realistic description of relativistic

coupling in four-component multiconfiguration Dirac–Hartree–Fock calculations. Correlation effects, on the other hand, are still treated at a low level during the adjustment procedure. Although such effects are not intended to be fitted into the pseudopotentials, their incorporation might improve the description of the coupling between electron correlation and relativity. Using the current implementation based on the multiconfiguration Dirac–Hartree–Fock code GRASP the inclusion of the most important static correlation or near-degeneracy effects is already possible; however, the consideration of dynamical correlation effects in the adjustment procedure, for the most important states, is a topic of future investigations.

Despite the simplicity of the energy-consistent pseudopotential approach, which uses only energetic information for setting up the potentials, the resulting pseudopotentials prove to be very reliable and highly transferable, especially so in the small-core case. This has been shown in a series of benchmark calculations in the past (cf. e.g. refs. 25, 31, 32, 37, and 69), and is documented again in the test calculations of the present article, for diatomic lead and bismuth compounds (PbF, PbCl, PbBr, PbI, BiH, BiO, BiF, BiCl, BiBr) with a hybrid small-core/large-core pseudopotential treatment for the sixth-row elements and special emphasis on spin-orbit effects. Shortcomings of current quantum-chemical *ab initio* calculations with respect to one-particle basis sets, valence-correlation treatment and, in particular, treatment of SO effects, are certainly larger than inherent errors of the pseudopotentials.

Acknowledgment

The authors are grateful to Professors H.-J. Werner (Stuttgart) and R. M. Pitzer (Columbus) for providing their program packages.

References

- Hellmann, H. *J Chem Phys* 1935, 3, 61.
- Gombás, P. *Z Phys* 1935, 94, 473.
- Phillips, J. C.; Kleinman, L. *Phys Rev* 1959, 116, 287.
- Lee, Y. S.; Ermler, W. C.; Pitzer, K. S. *J Chem Phys* 1977, 67, 5861.
- Hafner, P.; Schwarz, W. H. E. *J Phys B* 1978, 11, 217.
- Kahn, L. R.; Hay, P. J.; Cowan, R. D. *J Chem Phys* 1978, 68, 2386.
- ARGOS, CNVRT, SCFPQ, LSTRN, CGDBG, CIDBG: atomic and molecular spin-orbit CI program package: Chang, A.; Pitzer, R. M. *J Am Chem Soc* 1989, 111, 2500; Tilson, J. L.; Ermler, W. C.; Pitzer, R. M. *Comput Phys Commun* 2000, 128, 128.
- COLUMBUS *ab initio* program package: Lischka, H.; Shepard, R.; Pitzer, R. M.; Shavitt, I.; Dallos, M.; Müller, T.; Szalay, P. G.; Seth, M.; Kedziora, G. S.; Yabushita, S.; Zhang, Z. Y. *Phys Chem Chem Phys* 2001, 3, 664; Yabushita, S.; Zhang, Z. Y.; Pitzer, R. M. *J Phys Chem* 1999, 103, 5791.
- MOLPRO is a package of *ab initio* programs written by Werner, H.-J.; Knowles, P. J., with contributions from Amos, R. D.; Bernhardtsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J.; Knowles, P. J. *J Chem Phys* 1988, 89, 5803; Knowles, P. J.; Werner, H.-J. *Chem Phys Lett* 1988, 145, 514; Hampel, C.; Peterson, K.; Werner, H.-J. *Chem Phys Lett* 1992, 190, 1; Knowles, P. J.; Hampel, C.; Werner, H.-J. *J Chem Phys* 1993, 99, 5219; Deegan, M. J. O.; Knowles, P. J. *Chem Phys Lett* 1994, 227, 321; Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. *Mol Phys* 2000, 98, 1823.
- RELMOL: atomic and molecular spin-orbit CI program package: Dolg, M. (unpublished).
- Lee, S. Y.; Lee, Y. S. *J Comput Chem* 1992, 13, 595; Lee, H. S.; Han, Y. K.; Kim, M. C.; Bae, C.; Lee, Y. S. *Chem Phys Lett* 1998, 293, 97.
- Vallet, V.; Maron, L.; Teichteil, C.; Flament, J. P. *J Chem Phys* 2000, 113, 1391.
- Bachelet, G. B.; Hamann, D. R.; Schlüter, M. *Phys Rev B* 1982, 26, 4199.
- Hay, P. J. *J Chem Phys* 1983, 79, 5469; Hay, P. J.; Wadt, W. R. *J Chem Phys* 1985, 82, 270; Wadt, W. R.; Hay, P. J. *J Chem Phys* 1985, 82, 284; Hay, P. J.; Wadt, W. R. *J Chem Phys* 1985, 82, 299; Hay, P. J.; Martin, R. L. *J Chem Phys* 1998, 109, 3875.
- Pacios, L. F.; Christiansen, P. A. *J Chem Phys* 1985, 82, 2664; Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J Chem Phys* 1986, 84, 6840; LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J Chem Phys* 1987, 87, 2812; Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; LaJohn, L. A.; Christiansen, P. A. *J Chem Phys* 1990, 93, 6654; Wallace, N. M.; Blaudeau, J.-P.; Pitzer, R. M. *Int J Quantum Chem* 1991, 40, 789; Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Int J Quantum Chem* 1991, 40, 829; Ross, R. B.; Gayen, S.; Ermler, W. C. *J Chem Phys* 1994, 100, 8145; Nash, C. S.; Bursten, B. E.; Ermler, W. C. *J Chem Phys* 1997, 106, 5133; Wildman, S. A.; DiLabio, G. A.; Christiansen, P. A. *J Chem Phys* 1997, 107, 9975; Blaudeau, J.-P.; Curtiss, L. A. *Int J Quantum Chem* 1997, 61, 943; Nash, C. S.; Bursten, B. E. *J Phys Chem A* 1999, 103, 402.
- Stevens, W. J.; Basch, H.; Krauss, M. *J Chem Phys* 1984, 81, 6026; Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can J Chem* 1992, 70, 612; Cundari T. R.; Stevens, W. J. *J Chem Phys* 1993, 98, 5555.
- Bouteiller, Y.; Mijoule, C.; Nizam, M.; Barthelat, J. C.; Daudey, J. P.; Pelissier, M.; Silvi, B. *Mol Phys* 1988, 65, 295.
- Maron, L.; Teichteil, C. *Chem Phys* 1998, 237, 105.
- Hartwigsen, C.; Goedecker, S.; Hutter, J. *Phys Rev B* 1998, 58, 3641.
- Titov, A. V.; Mitrushenkov, A. O.; Tupitsyn, I. I. *Chem Phys Lett* 1991, 185, 330; Mosyagin, N. S.; Titov, A. V.; Tulub, A. V. *Phys Rev A* 1994, 50, 2239; Titov, A. V.; Mosyagin, N. S. *Struct Chem* 1995, 6, 317; Tupitsyn, I. I.; Mosyagin, N. S.; Titov, A. V. *J Chem Phys* 1995, 103, 6548; Mosyagin, N. S.; Titov, A. V.; Latajka, Z. *Int J Quantum Chem* 1997, 63, 1107; Titov, A. V.; Mosyagin, N. S. *Int J Quantum Chem* 1999, 71, 359.
- Fuentealba, P.; Preuss, H.; Stoll, H.; v. Szentpály, L. *Chem Phys Lett* 1982, 89, 418; v. Szentpály, L.; Fuentealba, P.; Preuss, H.; Stoll, H. *Chem Phys Lett* 1982, 93, 555; Fuentealba, P.; Stoll, H.; v. Szentpály, L.; Schwerdtfeger, P.; Preuss, H. *J Phys B* 1983, 16, L323; Stoll, H.; Fuentealba, P.; Schwerdtfeger, P.; Flad, J.; v. Szentpály, L.; Preuss, H. *J Chem Phys* 1984, 81, 2732; Fuentealba, P.; v. Szentpály, L.; Preuss, H.; Stoll, H. *J Phys B* 1985, 18, 1287; Schwerdtfeger, P. *Phys Sci R* 1987, 36, 453; Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J Chem Phys* 1987, 86, 866; Igel-Mann, G.; Stoll, H.; Preuss, H. *Mol Phys* 1988, 65, 1321; Schwerdtfeger, P.; Silberbach, H.; Miehlisch, B. *J Chem Phys* 1989, 90, 762; Dolg, M.; Stoll, H.; Preuss, H. *J Chem Phys* 1989, 90, 1730; Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J Chem Phys* 1989, 91, 1762; Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor Chim Acta* 1989, 75, 173; Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor Chim Acta* 1990, 77, 123; Dolg, M.; Fulde, P.; Küchle, W.; Neumann, C. S.; Stoll, H. *J Chem Phys* 1991, 94, 3011; Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol Phys* 1991, 74, 1245; Kaupp, M.; v. R. Schleyer, P.; Stoll, H.; Preuss, H. *J Chem Phys* 1991, 94, 1360; Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol Phys* 1993, 80, 1431; Dolg, M.; Stoll, H.; Preuss, H. *Theor Chim Acta* 1993, 85, 441; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H.; Schwerdtfeger, P.; Pitzer, R. M. *Mol Phys* 1993, 78, 1211; Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J Chem Phys* 1994, 100, 7535; Nicklass, A.; Dolg, M.; Stoll, H.; Preuss, H. *J Chem Phys* 1995, 102, 8942; Dolg, M. *Theor Chim Acta* 1996, 93, 141; Leininger, T.; Nicklass, A.; Küchle, W.; Stoll, H.; Dolg, M.; Bergner, A. *Chem Phys Lett* 1996, 255, 274; Seth, M.; Schwerdtfeger, P.; Dolg, M. *J Chem Phys* 1997, 106, 3623; Leininger, T.; Berning, A.; Nicklass, A.; Stoll, H.; Werner, H.-J.; Flad, H.-J. *Chem Phys* 1997, 217, 19; Schautz, A.; Flad, H.-J.; Dolg, M. *Theor Chem Acc* 1998, 99, 231; Wang, Y.-X.; Dolg, M. *Theor Chem Acc* 1998, 100, 124.
- Cowan, R. D.; Griffin, D. C. *J Opt Soc Am* 1976, 66, 1010; Wood, J. H.; Boring, A. M. *Phys Rev B* 1978, 18, 2701.
- Nicklass, A.; Stoll, H. *Mol Phys* 1995, 86, 317.
- Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H.; Schwerdtfeger, P. *Mol Phys* 1991, 74, 1265.
- Dolg, M. habilitation thesis, University of Stuttgart, 1997.
- Müller, W.; Flesch, J.; Meyer, W. *J Chem Phys* 1984, 80, 3297.
- GRASP: Atomic Numerical MCDHF Program Package; Dyall, K. G.; Grant, I. P.; Johnson, C. T.; Parpia, F. A.; Plummer, E. P. *Comput Phys Commun* 1989, 55, 425.
- Dolg, M.; Metz, B. Supplementary Pseudopotential Adjustment Routines for GRASP (unpublished).
- MCHF77: Atomic Numerical MCHF Program Package; Froese Fischer, C. *The Hartree-Fock Method for Atoms—A Numerical Approach*; Wiley: New York, 1976; Dolg, M. Supplementary Pseudopotential Adjustment Routines for MCHF77 (unpublished).
- Metz, B. doctoral thesis, University of Stuttgart (in preparation).
- Metz, B.; Schweizer, M.; Stoll, H.; Dolg, M.; Liu, W. *Theor Chem Acc* 2000, 104, 22.
- Metz, B.; Stoll, H.; Dolg, M. *J Chem Phys* 2000, 113, 2563.
- Lim, I.; Schwerdtfeger, P.; Stoll, H. (unpublished).
- Figgen, D.; Stoll, H. (unpublished).
- Goll, E.; Metz, B.; Stoll, H. (unpublished).

36. Seth, M.; Schwerdtfeger, P.; Dolg, M.; Goll, E.; Stoll, H. (unpublished).
37. Dolg, M.; Stoll, H.; Seth, M.; Schwerdtfeger, P. *Chem Phys Lett* 2001, 345, 490.
38. Sheu, J.-H.; Dolg, M. (unpublished).
39. Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J Phys Chem* 1993, 97, 5852.
40. Teichteil, C.; Pelissier, M.; Spiegelmann, F. *Chem Phys* 1983, 81, 273.
41. Llusar, R.; Casarrubios, M.; Barandiarán, Z.; Seijo, L. *J Chem Phys* 1996, 105, 5321.
42. Dunning, T. H., Jr. *J Chem Phys* 1989, 90, 1007.
43. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J Chem Phys* 1992, 96, 6796.
44. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*, vol. 4: Constants of Diatomic Molecules; Van Nostrand-Reinhold: Princeton, NJ, 1979.
45. Liu, W.; van Wüllen, C.; Han, Y. K.; Choi, Y. J.; Lee, Y. S. *Adv Quant Chem*, accepted.
46. Woon, D. E.; Dunning, T. H., Jr. *J Chem Phys* 1993, 98, 1358.
47. Web database for energy-consistent pseudopotentials and corresponding valence basis sets: <http://theochem.uni-stuttgart.de/pseudopotentials>.
48. Wildman, S. A.; DiLabio, G. A.; Christiansen, P. A. *J Chem Phys* 1997, 107, 9975.
49. DiLabio, G. A.; Christiansen, P. A. *J Chem Phys* 1998, 108, 7527.
50. Han, Y. K.; Bae, C.; Son, S. K.; Lee, Y. S. *J Chem Phys* 1999, 112, 2684.
51. DiLabio, G. A.; Christiansen, P. A. *Chem Phys Lett* 1997, 277, 473.
52. Alekseyev, A. B.; Buenker, R. J.; Liebermann, H. P.; Hirsch, G. *J Chem Phys* 1994, 100, 2989.
53. Alekseyev, A. B.; Liebermann, H. P.; Buenker, R. J.; Hirsch, G.; Li, Y. *J Chem Phys* 1994, 100, 8956.
54. Alekseyev, A. B.; Liebermann, H. P.; Boustani, I.; Hirsch, G.; Buenker, R. J. *Chem Phys* 1993, 173, 333.
55. Alekseyev, A. B.; Das, K. K.; Liebermann, H. P.; Buenker, R. J.; Hirsch, G. *Chem Phys* 1995, 198, 333.
56. Ziebarth, K.; Breidohr, R.; Shestakov, O.; Fink, E. H. *Chem Phys Lett* 1992, 190, 271.
57. Ziebarth, K.; Setzer, K. D.; Shestakov, O.; Fink, E. H. *J Mol Spectrosc* 1998, 191, 108.
58. Drake, L. R.; Simons, J. W.; Oldenbourg, R. C. *J Phys Chem* 1995, 99, 11350.
59. Simons, J. W.; Oldenbourg, R. C.; Baughcum, S. L. *J Phys Chem* 1987, 91, 3840.
60. Shestakov, O.; Breidohr, R.; Demes, H.; Setzer, K. D.; Fink, E. H. *J Mol Spectrosc* 1998, 190, 28.
61. Devore, T. C.; Brock, L.; Kahlscheuer, R.; Dulaney, K.; Gole, J. L. *Chem Phys* 1991, 155, 423.
62. Jones, W. E.; McLean, T. D. *J Mol Spectrosc* 1981, 90, 481.
63. Shestakov, O.; Fink, E. H. *Chem Phys Lett* 1994, 229, 273.
64. Fink, E. H.; Setzer, K. D.; Ramsay, D. A.; Vervloet, M. *Chem Phys Lett* 1991, 179, 95.
65. Cheong, B. S.; Oberlander, M. D.; Kampf, R. P.; Parson, J. M. *J Chem Phys* 1993, 99, 5104.
66. Yoo, R. K.; Ruscic, B.; Berkowitz, J. *Chem Phys* 1992, 166, 215.
67. Devore, T. C.; Gole, J. L. *Chem Phys* 1993, 174, 409.
68. Beutel, M.; Setzer, K. D.; Shestakov, O.; Fink, E. H. *J Mol Spectrosc* 1996, 175, 48.
69. Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J Chem Phys* 1996, 105, 1052; Schwerdtfeger, P.; Brown, J. R.; Laerdahl, J. K.; Stoll, H. *J Chem Phys* 2000, 113, 7110; Dolg, M. *Mol Phys* 1996, 88, 1645; Liu, W.; Dolg, M. *Phys Rev A* 1998, 57, 1721; Liu, W.; Küchle, W.; Dolg, M. *Phys Rev A* 1998, 58, 1103; Cao, X.; Dolg, M. *J Chem Phys* 2001, 115, 7348.