

Recent Progress in Atomic and Chemical Group Effective Potentials

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Recent progress on atomic and chemical group effective potentials is presented. The reviewed effective potentials follow a shape-consistent extraction technique from *ab initio* data, within a scalar relativistic approximation. Two types of averaged relativistic effective core potentials are considered: the correlated ones where a part of the correlation energy is included in the effective potential, and the polarized ones for which only the core polarization effects are taken into account. In addition spin–orbit polarized pseudopotentials have been extracted, and the effects of the core polarization are tested on the atomic spectroscopy of iodine. Finally a very recent chemical group effective methodology is presented, reducing the number of both electrons and nuclei explicitly treated. Chemical transferability is investigated, and test calculations on a cyclopentadienyl effective group potential are presented.

1. INTRODUCTION

Due to the increasing performance of the computers as well as the progress of theoretical methods, the size of molecules that can be treated theoretically is also increasing and nowadays systems of chemical or even biochemical interest can be tackled. In the range of the theoretical progress we especially underline the implementation of crucial approximations such as the reduction of electrons and nuclei in order to keep the only ones which play a role in chemical processes. Moreover, relativistic effects have to be considered when heavy elements are concerned, but with specific approximations in order to not spoil the correlation treatment. Several solutions have been proposed, and the most popular one is the pseudopotential or effective core potential (ECP) method, which has nodeless orbitals as solutions.^{1–3} This method has been successfully applied on various problems such as spectroscopic studies of molecules containing heavy elements (see, for example, refs 4 and 5) or chemical reactivity of actinides (see for example refs 6, and 7). The main advantage of using ECPs is to give the possibility of avoiding the basis functions to describe the core orbitals, and this is taken into account to increase the valence basis set. However, one needs to define, for perturbational treatments, specific pseudooperators which have to mimic the action of the true one and which in general lead to efficient computational treatments. This feature has been clearly demonstrated for the spin–orbit operator.^{8,9} Nevertheless, ECP methods lead to an overestimation of the valence correlation energy due to the nodeless inner part of the pseudoorbitals.^{10,11}

In ECP methods, relativity can be included within three different approximations, namely four-component,¹² two-component^{13,14} or one-component (see, for example, ref 1).

As the aim of this paper is to focus on the recent progress made by the Toulouse group, we only consider in the following the latter approximation in the frame of which our methods have been developed and where two pseudopotentials intervene: averaged relativistic effective potentials (AREPs) and specific spin–orbit relativistic effective potentials (SOREPs) adapted to the previous ones. Two distinct types of ECPs are published in the literature differing in the extraction procedure. The first one considers that the atomic ECP should reproduce observables such as the energy differences between the lowest excited states and the ground state as well as the first ionization potentials and the electron affinity. This method has been proposed by the Stuttgart–Dresden group^{15,16} and is often called the *energy-adjusted* extraction method. The second one defines the ECPs by solving an eigenvalue problem. Indeed, as the solution of the ECP should be a nodeless pseudoorbital, the ECP is constructed in such a way that the pseudoorbital has the same valence part as the true atomic orbital and that the corresponding monoelectronic energy is the one coming from the all-electron atomic reference calculation. This method has been successively proposed by Durand and Barthelat,¹⁷ Christiansen et al.¹⁸ or Hay and Wadt¹⁹ and is called in contrast with the previous one the *shape-consistent* extraction method.

During the past decade, the Toulouse group worked on reducing the number of electrons in the calculation with the aim of the lowest possible loss of correlation effects, following the Durand–Barthelat technique. For the main group elements, large-core ECPs have been extracted and core–valence correlation can be accounted for by including a core polarization potential which was first proposed by Müller et al.²⁰ and improved by a *l*-dependent formulation by Fourcraut et al.²¹ Nevertheless, this method is not longer valid when transition metal compounds are considered and so far, small-core ECPs that include all *n*-shell and (*n* – 1)-shell electrons as valence are usually used for this type of problem. However, Mahé et al.²² recently proposed, for

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the right part of the transition metal row, to use large-core ECPs that include the core–valence and a part of the dynamic correlation. The main steps of the extraction procedure, based on a mixing of shape- and energy-consistent methods, are described in the following section and in more detail in ref 22. This method has been successfully applied to the description of the CuX and Cu_2X structures.²³ As a part of the valence dynamic correlation is included in the ECP, this method is basis set and method dependent but leads to excellent results at very low computational cost. At the same time, Maron et al.²⁴ proposed a method taking into account, in the extraction process, the electrostatic and spin–orbit polarization of the core electrons. Indeed, this later method, based on a pure shape-consistent procedure, considers the parameters to be fitted from multiconfigurational Dirac–Fock reference calculations. This method, which takes care of the influence of electrons in different orbitals, is described in the following section, and more details can be found in ref 24. These new AREPs have been tested on atomic and molecular spectroscopic properties of the halogens.

Within the framework of scalar relativistic calculations the AREPs used at the SCF step have to be completed by spin–orbit relativistic effective potentials (SOREPs). These SOREPs are used either at the configuration interaction (CI) step in a double group CI (DGCI) framework, or at the end of the whole process in a two-step effective Hamiltonian-based method. We have used in this work the last one, with the CIPSO method.²⁵ The discussion on the consequences on the spin–orbit coupling of the use of one or the other of these SOCI methods is out of the scope of this paper, and extensive details can be found in ref 26. Let us, however, underline that a two-step effective Hamiltonian-based SOCI method like CIPSO where the full Hamiltonian matrix is expressed in the bases of states rather than determinants is naturally well adapted to problems where spin–orbit (SO) coupling can be considered as a perturbation compared to electrostatic contributions. If the SO coupling is very large—which is the case of iodine chosen as an example in section 2—some spin–orbit polarization effects coming from outer determinants (not present in the states under consideration) could be missing. One possible way to recover most of these effects is to compute the SO matrix elements on the basis of natural orbitals rather than the canonical ones. Indeed, natural orbitals containing the effects of all the monoexcitations bring the desired polarization effects as these effects essentially come from monoexcitations. Another question concerns the effects of the correlation treatment on the spin–orbit splitting. We have in fact focused our study on the effect of the size-consistency property on the atomic SO splitting. New SOREPs adapted to the different AREPs considered in this study and taking into account the core polarization effects, have been extracted for the halogen atoms. Tests have been carried out on the atomic spectroscopy of the halogen atoms, and the influence of the size-consistency property and the influence of the atomic basis set have been investigated. We present in section 2 the results for the iodine atom.

Finally, despite the use of large-core ECPs when it is possible, the treatment of molecules of chemical interest need to consider further approximations, such as simplification of the ligand (i.e., PH_3 instead of PO_3 or $\text{P}(i\text{-Pr})_3$ or use of QM/MM methods. The latter treats the real ligand with a force field method whereas in the quantum mechanical

approach the ligand is replaced by a hydrogen.²⁷ Durand et al.²⁸ proposed to replace the ligands that do not intervene directly in the chemical reaction, for example, the phosphine or the cyclopentadienyl ligands in organometallic chemistry, by an effective group potential (EGP) that, as does an atomic ECP, mimics the presence of the real ligand. The extraction procedures have been improved by Alary et al.,²⁹ and this is briefly discussed in the following section. A more detailed presentation could be found in ref 30. EGPs have been extracted for various ligands and tested on different problems such as Lewis acido–basic complexes, quantum exchange coupling for organometallic complexes, or excited state calculations.

Section 2 is devoted to the description of the extraction procedures for the correlated and core polarized atomic ECPs as well as the effective group potentials, and we will restrict ourselves to underlining the main features of the methods. The performances of these methods are illustrated with some examples in section 3.

2. EXTRACTION PROCEDURES

2.1. Correlated Atomic Pseudopotentials. The method is based on the statement that, at a fixed correlated level of theory, it is possible to extract an ECP that reproduces the experimental atomic spectrum at this level of theory. In that sense, a part of the correlation energy is included in the ECP and it is considered that a monoelectronic term can mimic an essentially bielectronic term (correlation energy). Considering two electronic states, their experimental energy difference could be written in the following way:

$$\Delta E_{\text{exp}} = \Delta E_{\text{HF}} + \Delta E_{\text{correlated}}^{\text{calc}} + \Delta E_{\text{correlated}}^{\text{noncalc}} \quad (1)$$

where ΔE_{HF} is the energy difference calculated at the Hartree–Fock level, $\Delta E_{\text{correlated}}^{\text{calc}}$ is the part of the calculated correlation energy, and $\Delta E_{\text{correlated}}^{\text{noncalc}}$ is the part of the correlation energy that has to be included in the ECP. Thus, the previous equation can be written in a different way:

$$\Delta E_{\text{exp}} = \Delta E'_{\text{HF}} + \Delta E_{\text{correlated}}^{\text{calc}} \quad (2)$$

where $\Delta E'_{\text{HF}}$ corresponds to the Hartree–Fock energy difference calculated with the so-called *correlated ECP*. To ensure a transferability of the $\Delta E_{\text{correlated}}^{\text{calc}}$ term, it is necessary to use the same level of calculation and the same basis set for the extraction procedure and for the subsequent calculation. In that sense, those ECPs are method and basis set dependent.

The correlated ECP is extracted in a two-step procedure. In the first step, a Hartree–Fock ECP is calculated in order to fit the ΔE_{HF} term of eq 1. This ECP is obtained in a shape-consistent and energy-adjusted way. Indeed, the ECP is fitted on several atomic configurations (neutral and ionic) as in an energy-adjusted procedure. Among these configurations, a reference configuration is chosen (e.g., the ground state of the neutral atom) and a pseudorbital is built according to the shape-consistent procedure. A Gaussian basis set is optimized for this Hartree–Fock ECP, and the total correlation energy is calculated at the chosen level. After defining the $\Delta E_{\text{correlated}}^{\text{noncalc}}$ term, the correlated ECP is extracted using the same procedure than for the Hartree–Fock ECP.

2.2. Core Polarized Atomic Pseudopotentials. This method is based on the analysis of the perturbational development of the full Hamiltonian in terms of correlation and spin-orbit terms. According to the Lindgren and Morisson notation,³¹ the full Hamiltonian can be written as follows:

$$H_{\text{full}} = h_0 + V_{\text{corr}} + V_{\text{SO}} \quad (3)$$

where h_0 is the unperturbed Hamiltonian, V_{corr} the electronic correlation term, and V_{SO} the spin-orbit term. Restricting the double perturbation expansion to the atomic spin-orbit splitting contributing terms, it appears at the first-order level that only the spin-orbit interaction between occupied valence orbitals contributes to the spin-orbit splitting. This interaction leads to roughly 85% of the total spin-orbit splitting and is fully taken into account using large-core ECPs. At the second-order perturbation level, the terms can be divided in two classes. The first one corresponds to pure second-order spin-orbit effects and is very small in almost all cases. The second class of terms couple electronic correlation and spin-orbit interaction and can be quite important. This corresponds to the interaction (polarization) between the valence orbitals and the core orbitals. These terms lead to roughly 10% of the atomic spin-orbit splitting. Such terms cannot be taken into account when usual pseudopotentials extracted from SCF references are used in the calculation. It should be noticed that considering this last term changes the shape of the orbitals, as some polarization effects are included. Therefore, both AREPs and SO pseudopotentials should be reextracted when the reference all-electron atomic calculation includes this last term. To include core polarization effects in the atomic reference calculation, a correlation interaction or a multiconfigurational relativistic SCF calculation should be carried out. The remaining 5% of the spin-orbit splitting can be considered by including third-order contributions which correspond to the use of natural orbitals to compute the spin-orbit interaction.

The *core polarized* ECPs are extracted from multiconfigurational four-component calculations including the ground-state configuration and some single excitations from core orbitals to virtuals (polarization effects). This reference calculation produces the valence spinors and the corresponding monoelectronic energies. At this stage, only the normalized large components are kept. To obtain an AREP, an average orbital is built by applying the Landé interval rule to the two renormalized large components, and the corresponding average energy is obtained in the same way. The AREP is extracted according to the shape-consistent procedure. In the same way, the corresponding SO pseudopotential is extracted. So far, core polarized ECPs have been obtained for the halogen series (F, Cl, Br, I) and tested on atomic spectroscopy.

2.3. Effective Group Potentials. The effective group potential (EGP) method is a new method for increasing the efficiency of ab initio calculations. This method is supported by the idea that the chemical properties of a molecule are mainly controlled by a few electrons and nuclei, the rest of the molecule being composed of inactive parts. We propose, for instance, to replace a functional group such as PH_3 , NH_3 , or Cp by a fictitious system bearing only the bonding electrons. The effect of the rest of the functional group is

described by an EGP, in close analogy with core electrons and ECP in atoms. For example, we consider the case of a singly bonded spectator group: the SiH_3 fragment.

The silyl group is replaced by a pseudo silicon atom bearing one electron plus an effective potential designed for taking into account the effect of the whole fragment.

The extraction of an EGP is done in a purely ab initio way. The EGP is extracted from a reference molecule: Si_2H_6 at the HF level of theory.

In the first step, reference calculations are performed in a complete basis set and define the full Fock matrix (\mathbf{F}_1). In a second step, one of the two SiH_3 fragments inside the disilane molecule is superseded by an fictitious atom of silicon bearing one electron in a truncated basis set. Calculation with this truncated system leads to the reduced Fock matrix (\mathbf{F}_2). The difference between the Fock matrixes defines the part that should be restored by the EGP:

$$\mathbf{F}_{\text{EGP}} = \mathbf{F}_1 - \mathbf{F}_2 \quad (4)$$

The exponents of the truncated basis set on the fictitious atom supporting the EGP are optimized in order to get an adapted reduced basis set. At this stage, according to the shape-consistent procedure, all the molecular valence pseudo-orbitals are determined by calculating and diagonalizing the overlap matrix between the complete and the reduced basis set. The third step of the extraction is the definition of the EGP operator by a least-squares fit of $\|\mathbf{W}_{\text{EGP}} - \mathbf{F}_{\text{EGP}}\|^2$, where \mathbf{W}_{EGP} is a nonlocal operator defined by:

$$\hat{W}_{\text{EGP}} = \sum_n \sum_m \alpha_{nm} |g_n\rangle \langle g_m| \quad (5)$$

In the last step the obtained EGP operator is tested on the reduced system.

3. RESULTS AND DISCUSSION

In this section, we review some results obtained respectively with the correlated ECP, the core polarized ECP and with the EGP.

3.1. Molecular Results of Correlated ECP. The correlated ECPs have been extracted for some first-row transition metals as well as some main group elements such as carbon. This section is devoted to results on the singlet-triplet separation of the CH_2 molecules and on molecules containing copper, such as CuX and Cu_2X with $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$. In the following, all the molecular calculations have been carried out with the Gaussian 92 suite of programs.³² The correlated ECP and the adapted optimized basis set are listed in ref 22.

3.1.1. $^3\text{B}_1$ – $^1\text{A}_1$ Separation of CH_2 . The singlet-triplet separation of the CH_2 carbene is a problem which has been carefully investigated. It has been found that employing a correlated method with a large basis set leads to very accurate results. This example appears to be an excellent test case for the correlated ECP. A CASSCF correlated ECP have been extracted by considering the distribution of six electrons in six orbitals, namely the two σ ($2a_1, 1b_2$) orbitals, the two σ^* ($4a_1, 2b_2$) C–H orbitals, and the two singly occupied orbitals, in the triplet case, ($3a_1, 1b_1$). The two states have been optimized separately, and the geometrical parameters as well as the calculated singlet-triplet separations are

Table 1. Geometrical Parameters and Singlet–Triplet Transition of CH₂

state	parameter	HF-ECP	CASSCF-ECP	expt
³ B ₁	<i>r</i> (C–H) (Å)	1.103	1.099	1.077
	α(H–C–H) (deg)	131.3	131.3	134.0
	<i>r</i> (C–H) (Å)	1.141	1.151	1.124
¹ A ₁	α(H–C–H) (deg)	99.6	97.2	102.4
	³ B ₁ → ¹ A ₁	18.4	9.0	9.0

Table 2. Geometrical Parameters (*r_e* in Å, *ω_e* in cm^{−1} and *D_e* in eV) of CuX

molecule	parameter	HF-ECP	MP2-ECP	CCSD(T) ³³	expt
CuO	<i>r_e</i>	1.808	1.752	1.771	1.724
	<i>ω_e</i>	567	618	572	640
	<i>D_e</i>	2.49	2.50	2.70	2.89
CuS	<i>r_e</i>	2.122	2.071	2.107	2.051
	<i>ω_e</i>	386	415	385	415
	<i>D_e</i>	2.55	2.67	2.73	2.83
CuSe	<i>r_e</i>	2.229	2.183		2.108
	<i>ω_e</i>	285	305		302
	<i>D_e</i>	2.33	2.43		2.57
CuTe	<i>r_e</i>	2.418	2.380		2.349
	<i>ω_e</i>	243	258		253
	<i>D_e</i>	2.04	2.13		2.37
CuPo	<i>r_e</i>	2.501	2.465		
	<i>ω_e</i>	215	228		
	<i>D_e</i>	1.81	1.89		

presented in Table 1. In this table a comparison is made between the geometrical parameters obtained with an HF-ECP and a CASSCF-ECP as well as the experimental values.

For ³B₁, the geometrical parameters are in better agreement with the experimental ones when the correlated ECP (CASSCF-ECP) is used. However, for the ¹A₁ state, it appears that the HF-ECP leads to better results than the correlated ECP. This could be due to the fact that the correlated ECP (CASSCF-ECP) has been extracted with a least-squares procedure from the two states and is not fully optimized for a given state as are the HF-ECP ones. However, the results in that latter case are quite close for the two ECPs.

Concerning the singlet–triplet separation, the situation is somewhat different. Indeed, the HF-ECP leads to a separation which is the double of the experimental one. However, as expected, using the CASSCF-ECP improves the results and the separation is found to be in perfect agreement with the experiment.

3.1.2. CuX, Cu₂X Molecules with X = O, S, Se, Te, Po. CuX and Cu₂X molecules (with X = O, S, Se, Te, and Po) are interesting for testing the correlated ECP on transition metal compounds. The latter type of molecules exhibits a so-called metallophilic interaction between two d¹⁰ species.

A correlated ECP has been extracted for the copper atom at the MP2 level, and a shape-consistent ECP has been used for all the chalcogen (X) atoms. The ground state is found to be ²Π for CuX and ¹A₁ for Cu₂X. Ground-state properties of the CuX molecules are presented in Table 2 for the HF-ECP and the correlated ECP (MP2-ECP). We have also reported in Table 2 the results obtained by Bauschlicher et al. at the all-electron CCSD(T) level using a very large basis set for copper and chalcogen atoms. In contrast to the previous example, for the CuX molecules, the results obtained with the MP2-ECP are always in better agreement with experiment than the properties obtained with the HF-ECP. This result can be explained by the fact that in this

Table 3. Geometrical Parameters of Cu₂X

molecule	parameter	HF-ECP	MP2-ECP	MP2 ³⁴	expt
Cu ₂ O	<i>r</i> (Cu–O) (Å)	1.788	1.753	1.784	1.749
	<i>r</i> (Cu–Cu) (Å)	2.622	2.562	2.709	2.406
	α(Cu–O–Cu) (deg)	94.3	93.9	98.8	86.9
Cu ₂ S	<i>r</i> (Cu–O) (Å)	2.118	2.084		2.073
	<i>r</i> (Cu–Cu) (Å)	2.628	2.554		2.443
	α(Cu–O–Cu) (deg)	76.7	75.6		72.2
Cu ₂ Se	<i>r</i> (Cu–O) (Å)	2.229	2.200	2.200	2.197
	<i>r</i> (Cu–Cu) (Å)	2.623	2.549	2.621	2.597
	α(Cu–O–Cu) (deg)	72.1	70.8	73.1	67.2
Cu ₂ Te	<i>r</i> (Cu–O) (Å)	2.419	2.395		
	<i>r</i> (Cu–Cu) (Å)	2.639	2.554		
	α(Cu–O–Cu) (deg)	66.1	64.5		
Cu ₂ Po	<i>r</i> (Cu–O) (Å)	2.502	2.480		
	<i>r</i> (Cu–Cu) (Å)	2.624	2.537		
	α(Cu–O–Cu) (deg)	63.2	61.5		

calculation, we have only considered one state (the ground state). The results obtained with the MP2-ECP are in excellent agreement with the experimental data exhibiting a maximum deviation of 0.03 Å for the equilibrium distances, 20 cm^{−1} for the vibrational frequencies, and 0.29 eV for the dissociation energy. It should be noticed that the experimental uncertainty for the latter property (dissociation energy) is 0.15 eV. When comparing the MP2-ECP results with the all-electron CCSD(T) ones, it appears that the results obtained with the cheapest method (MP2-ECP) are systematically in better agreement with experiment than the CCSD(T) ones. The MP2-ECP appears to be in that case an excellent method to treat the chemistry of first-row transition metals. Ground-state properties of Cu₂X are presented in Table 3. In the same way as for CuX, we have reported the geometrical parameters obtained with the HF-ECP and the MP2-ECP as well as some all-electron MP2 calculations. The same kinds of results are obtained for Cu₂X as for CuX. The MP2-ECP results are in excellent agreement with experiment with a maximum deviation for the Cu₂O molecule. As for CuX results, the MP2-ECP calculations lead to results in better agreement with experiment than the all-electron ones, and we can conclude that using correlated ECP is a method of choice to treat this kind of system.

3.2. Atomic and Molecular Results of Core Polarized ECP. In this section, results on iodine atom and iodine molecule are presented. For sake of clarity we have split these results into two parts, with the first one devoted to the AREPs and the second one to the SOREPs. All the calculations have been carried out with the MOLCAS-4 package³⁵ in combination with the CIPSI³⁶ and MUPA codes^{37,38} for the correlation treatment. The spin–orbit calculations have been done with the CIPSO code.²⁵

3.2.1. Atomic and Molecular Averaged Relativistic Results. To do a comparison between the different atomic reference calculations used to extract ECPs, we have considered three different shape-consistent ECPs (Table 4).²⁴ These three ECPs have been respectively extracted from multiconfigurational four-component calculations (MCDF-ECP), Dirac–Fock four-component calculations (DF-ECP), and SCF scalar relativistic calculations (SR-ECP). We have also included results obtained with energy-adjusted ECPs (EAPP).³⁹ The experimental vertical transitions have been obtained from Moore’s tables⁴⁰ considering that approximately each considered multiplet follows Landé interval rule.

Table 4. Transition Energies (in cm^{-1}) for Iodine Atom with Different Pseudopotentials

transitions	expt ⁴⁰	EAPP ³⁹	MCDF-ECP	DF-ECP	SR-ECP
X \rightarrow (6s) ⁴ P	55 538	54 896	55 003	53 369	57 173
X \rightarrow (6s) ² P	55 923	56 659	56 981	57 161	59 164
X \rightarrow (6p) ⁴ P	63 249	63 815	63 813	64 599	65 219
X \rightarrow (6s) ² D	63 620	64 822	64 947	65 251	67 015
X \rightarrow (6p) ² D	65 975	66 706	65 839	65 643	67 968
X \rightarrow (6p) ² P	69 485	69 262	69 828	69 773	70 726

Table 5. Spectroscopic Constants for I₂ Ground State

properties	expt ⁴¹	EAPP ³⁹	MCDF-ECP	DF-ECP	SR-ECP
r_e (Å)	2.667	2.676	2.700	2.750	2.661
ω_e (cm^{-1})	214.50	229.01	213.23	220.02	234.47
$\omega_e x_e$ (cm^{-1})	0.615	0.760	1.470	1.220	1.096
D_e^a (eV)	1.56	1.30	1.30	1.22	1.48

^a Spin-orbit corrected values.

Comparing the results obtained with the three different shape-consistent ECPs, it appears that the vertical transitions are systematically improved, compared to experiment, when going from the scalar relativistic approximation to Dirac-Fock and then to multiconfigurational Dirac-Fock atomic reference calculations. The deviation of the calculated transitions from experiment is measured by the mean-square error:

$$\delta = \sqrt{\frac{1}{n} \sum_{i=1,n} (E_i^{\text{exp}} - E_i^{\text{calc}})^2} \quad (6)$$

where n is the number of considered transitions. The mean-square errors for the three different shape-consistent ECPs are respectively 727 cm^{-1} for MCDF-ECP, 1005 cm^{-1} for DF-ECP, and 2254 cm^{-1} for SR-ECP. It follows that the more complex and complete the atomic reference calculation, according to the analysis of the perturbational series summarized in section 2.2, the better is the calculated spectroscopy. Moreover, this result shows that the influence of the core polarization by spin-orbit coupling obtained from the four-component Dirac-Fock reference calculation is quite important compared to the SR-ECP result.

The mean-square error obtained for the energy-adjusted ECP is found to be 742 cm^{-1} and is close to the result found for the core polarized ECP (MCDF-ECP). This result can be explained by the fact that both methods include an essential part of the influence of the virtual atomic orbitals on the core polarization. Indeed, this is clear for the energy-adjusted procedure as the ECP is extracted in such a way that it should reproduce the excitation energy between the ground state and various chosen excited states. For the core polarized extraction method, the situation is somewhat different. The influence of the virtual orbitals is contracted on the occupied ones as in the multiconfigurational process pseudonatural orbitals are optimized according to the included excited configurations. In that sense, the occupied orbitals used to extract the core polarized ECP contain a part of the effects of the virtual orbitals.

Table 5 presents the spectroscopic constants found for the I₂ molecule for the same four pseudopotentials. These results are compared with the experimental parameters.⁴¹ The dissociation energy has been corrected to take into account

Table 6. Ground State Spin-Orbit Splitting of the Iodine Atom in cm^{-1} and Error vs Experiment in %

	expt ⁴⁰	MCDF-ECP	DF-ECP	SR-ECP
canonical orbitals	7603	7260	7280	7333
error	0	-4.5	-4.3	-3.6
natural orbitals	7603	7610	7759	8439
error	0	+0.15	+2.05	+10.99

the spin-orbit effects at equilibrium and infinite internuclear distances as already done in ref 4. The MCDF-ECP molecular results are in excellent agreement with the experiment as well as with the EAPP results.

3.2.2. Atomic Results Including Spin-Orbit Interaction. We now investigate the results obtained for the spectroscopy of the iodine atom when spin-orbit interaction is included in the calculation. In particular, it is of prime interest to test the influence of the use of natural atomic orbitals on the spin-orbit splitting as well as the influence of the correlation treatment, focusing here on the size-consistency property.

Table 6 presents the results obtained with the three spin-orbit pseudopotentials adapted to the three shape-consistent averaged ones for the ground-state spin-orbit splitting of the iodine atom. All the correlation calculations have been carried out with the (SC)²CAS-SDCI method⁴² that takes care of the size-consistency property, and with the same atomic bases set previously used. The results found with the canonical orbitals are systematically underestimated compared to the experimental value. Moreover, the results obtained with the core polarized ECP are too close to the one found with the DF-ECP that do not consider any core polarization effects. This result does not fit with the analysis proposed in section 2.2. The main problem of the canonical orbital results is that the determinantal space defining the states has been truncated according to electronic selection. Indeed, all the determinants with a weight lower than a given threshold in the CI expansion of the state are not considered in the spin-orbit calculation. That means that among all the singly excited determinants, which are important for the spin-orbit coupling, the major part are excluded from the final determinantal space. A detailed discussion of the influence of the single excitations for spin-orbit coupling can be found in ref 26. Thus, the canonical orbital results obtained with such a two-step SOCI method selecting the determinants using an electrostatic criterion suffers from the lack of some spin-orbit contributions. The situation is different when natural orbitals are considered. Indeed, the natural orbitals diagonalize the density matrix and the effect of all the single excitations is contained in these orbitals, so that the results are less affected by the truncation of the determinantal space. The results are in perfect agreement with the analysis done in section 2.2. Indeed, the best ground-state splitting is obtained with the core polarized ECP. This result is in excellent agreement with experiment and the error versus experiment is found to be 0.15%.

The influence of the quality of the correlation treatment has been investigated, and the results are presented in Table 7. We have in particular investigated the possibility of using the DDCI expansion⁴³ that only considers the double excitations which at least include one active orbital (the double excitations involving two inactive orbitals are excluded). For this comparison of correlation treatments, all

Table 7. Transition Energies (in cm^{-1}) for Iodine Atom Calculated with the MCDP-ECP at Various Level of Correlation

transitions	expt ⁴⁰	DDCI	CAS-SD	(SC) ² CAS-SD
$^2\text{P}_{3/2}(5s^25p^5)$	0	0	0	0
$^2\text{P}_{1/2}(5s^25p^5)$	7 603	7 615	7 615	7 610
$^4\text{P}_{5/2}(5s^25p^46s^1)$	54 633	54 647	54 647	54 639
$^4\text{P}_{3/2}(5s^25p^46s^1)$	61 819	61 761	61 761	61 756
$^4\text{P}_{1/2}(5s^25p^46s^1)$	60 896	60 840	60 840	60 832
$^2\text{P}_{3/2}(5s^25p^46s^1)$	56 012	56 027	56 027	56 017
$^2\text{P}_{1/2}(5s^25p^46s^1)$	63 186	63 235	63 235	63 227

Table 8. Geometrical Parameters of the $\text{AH}_3\text{--NH}_3$ Adducts Calculated at the DFT Level

A	$R(\text{A--N})$ (Å)	$R(\text{A--H})$ (Å)		$\alpha(\text{H--A--N})$ (deg)	
		$\text{AH}_3\text{--NH}_3$	$\text{AH}_3\text{--N}^\#$	$\text{AH}_3\text{--NH}_3$	$\text{AH}_3\text{--N}^\#$
B	1.700	1.219	1.222	104.0	103.5
Al	2.090	1.606	1.606	99.4	98.5
Ga	2.195	1.586	1.586	98.5	97.7
In	2.378	1.754	1.753	97.4	96.3
Tl	2.622	1.735	1.734	95.0	94.1

the calculations have been carried out with the core polarized ECP (MCDP-ECP) and with natural orbitals. The results are in excellent agreement with the experimental data, and the considered correlation methods lead to satisfactory splitting values. However, it is interesting to note that the CAS-SD and DDCI expansion lead to exactly the same results. This can be explained by the fact that the active space in both calculations includes all the 5p orbitals and leaves only the 5s orbital as inactive orbital. The double excitations from the latter orbital seem to be insignificant for the spin-orbit calculation. In the same way, the influence of the size consistency correction is rather small (5 cm^{-1}). We conclude that the lack of size-consistency does not significantly affect the quality of the splitting results, and that a relatively cheap method, such as DDCI, is a good choice to obtain satisfactory spectroscopic results.

3.3. Chemical Group Effective Potentials (EGP). We present some characteristic results found with the EGPs on systems of chemical interest. All the calculations have been carried out with a modified version of the Gaussian package.³² The first part of this section is devoted to transferability tests and the second part is devoted to a transition metal complex calculation.

3.3.1. Chemical Transferability. An EGP has been extracted for the amino ligand (NH_3) from the reference complex ($\text{BH}_3 - \text{NH}_3$). The system has been reduced to a nitrogen atom with two electrons on a hybrid sp orbital. This EGP have been tested on the geometrical parameters of the adducts $\text{AH}_3\text{--NH}_3$ with $\text{A} = \text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Tl}$. Table 8 presents the results found at the DFT level for the whole series with and without using an NH_3 EGP. In the following, $\text{N}^\#$ will refer to the NH_3 EGP.

One can see from Table 8 that the results found with the NH_3 EGP are in excellent agreement with the one found with the explicit NH_3 . Of course, the results found for the $\text{BH}_3\text{--NH}_3$ adduct are very similar with and without $\text{N}^\#$, but the chemical transferability is proved by the high accuracy of the EGP results vs the reference ones. The maximum deviation for the $R(\text{A--H})$ bond length is found to be 0.003 Å for the boron adduct. The same kind of result is obtained at another level of theory as presented in ref 29.

Table 9. Geometrical Parameters of the $(\text{CpIrH}_3\text{PH}_3)^+$ Complexes Calculated at the DFT Level

parameter	ref calculations	EGP	expt
IrH_a	1.586	1.579	1.591
IrH_b	1.590	1.578	1.583
IrH_c	1.590	1.578	1.588
Ir--P	2.373	2.376	2.273
P--H_d	1.438	1.438	
$\text{H}_a\text{--Ir--H}_b$	62.04	63.01	64.7
$\text{H}_a\text{--Ir--H}_c$	114.19	113.47	114.4

3.3.2 Test of the Cyclopentadienyl EGP: $(\text{CpIrH}_3\text{PH}_3)^+$.

An EGP has been extracted in order to simulate the cyclopentadienyl ligand (Cp). As the cyclopentadienyl is bound to a metal with a π -system, the reduced system will be made with one electron in a p orbital on each carbon atom of the cyclopentadienyl backbone. The number of electrons explicitly treated is then reduced to 32 electrons (vs 52 electrons with an explicit cyclopentadienyl ligand) for the $(\text{CpIrH}_3\text{PH}_3)^+$ complex. As in the previous section, Table 9 presents a comparison of the geometrical parameters found with and without a Cp EGP ($\text{Cp}^\#$). The results have been obtained at both the HF and DFT levels, and we present in Table 9 only the DFT results.

The results obtained with the $\text{Cp}^\#$ are in excellent agreement with respect to those obtained from the reference calculation. Indeed, the maximum deviation from both results is found to be 0.008 Å for the iridium-hydride bond lengths. This excellent agreement between both results is important because the computational time is highly decreased when $\text{Cp}^\#$ is used. Indeed, one geometry optimization step is performed in 1 min with the $\text{Cp}^\#$ whereas 1 h is needed with the explicit cyclopentadienyl ligand. Moreover, the EGP results compare well with the experimental parameters, with a maximum deviation of 0.013 Å for the Ir--H_a bond length.

4. CONCLUSION

We have summarized the recent progress on atomic and chemical group effective potentials made by the Toulouse group. All these effective potentials have been derived with the help of a shape-consistent extraction procedure. The atomic effective potentials are defined in a scalar relativistic scheme in order to keep the possibility of the best correlation treatment which is possible. Averaged relativistic effective core potentials are derived in such a way that they include the main polarization effects on the core, and test calculations are presented for the spectroscopy of the iodine atom and ground-state properties of the iodine molecule. We have extracted spin-orbit relativistic effective potentials using the same atomic reference data as for the averaged pseudo-potentials. We have verified on the ground ^2P state of the iodine atom that taking into account the core polarization effects in the reference atomic data significantly improves the results. Finally, an effective group potential methodology was developed, supported by the idea that some chemical properties of a molecule depend only on a few nuclei and electrons. This technique allows us to reduce the number of electrons and nuclei explicitly treated in an ab initio calculation without spoiling the description of the electronic structure of the molecule. Chemical transferability is demonstrated, and test calculations on a cyclopentadienyl EGP exhibit very good results on molecules of chemical interest.

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