

Relativistic *ab initio* model potential calculations including spin–orbit effects through the Wood–Boring Hamiltonian

Luis Seijo^{a)}

Departamento de Química Física Aplicada, C-14, Universidad Autónoma de Madrid, 28049 Madrid, Spain

(Received 29 November 1994; accepted 22 February 1995)

Presented in this paper, is a practical implementation of the use of the Wood–Boring Hamiltonian [Phys. Rev. B **18**, 2701 (1978)] in atomic and molecular *ab initio* core model potential calculations (AIMP), as a means to include spin–orbit relativistic effects, in addition to the mass-velocity and Darwin operators, which were already included in the spin-free version of the relativistic AIMP method. Calculations on the neutral and singly ionized atoms of the halogen elements and sixth-row *p*-elements Tl–Rn are presented, as well as on the one or two lowest lying states of the diatomic molecules HX, HX⁺, (X=F, Cl, Br, I, At) TIH, PbH, BiH, and PoH. The calculated spin–orbit splittings and bonding properties show a stable, good quality, of the size of what can be expected from an effective potential method. © 1995 American Institute of Physics.

I. INTRODUCTION

It is well known that relativistic effects have to be included in order to undertake reliable theoretical studies on molecules or solids including heavy atoms,¹ and that a balance between accuracy and economy, which is necessary in order to be able to perform practical, massive relativistic *ab initio* calculations, has been attained by means of the use of effective core potential (ECP) methods.^{2–4} All of the ECP methods incorporate the contributions of the major relativistic effects into the effective core potential, in an approximate manner. Some of them, the pseudopotential methods,^{5–9} rely on a pseudo-orbital transformation and handle valence orbitals without the internal nodes; other, so-called effective core potential methods¹⁰ and model potential methods,^{11–14} use valence orbitals with internal nodes which are an approximation to the all-electron ones.

The recent availability of efficient Dirac–Hartree–Fock (DHF) codes and of four-component configuration interaction codes is leading to systematic fully relativistic all-electron calculations on molecules which provide a standard for monitoring the performance of relativistic ECP methods.^{15–22} In this respect, although a conclusion has been reached that several sets of spin-free pseudopotentials did not show a consistent quality going down the group IV of the Periodic Table,²⁰ it has recently been shown that the *ab initio* model potential method (AIMP) (Refs. 13 and 14) closely resembles the DHF results down a group of the Periodic Table.²³

One of the advantages of the relativistic ECP methods is their ability to include spin–orbit effects, very often simultaneously to correlation effects, at a reasonable cost, not too much larger than the corresponding nonrelativistic correlated calculations. Several methods have been proposed to take into account the spin–orbit interactions within the ECP methods.^{24–29} Some of them, related to the pseudopotential methods, have already been used for a number of years in molecular calculations.^{2,3} However, calculations including spin–orbit effects within model potential methods are only

limited to the one by Klobukowski,³⁰ in which the scaled Zr^{−3} spin–orbit operator proposed by Wadt²⁴ was used.

In this paper it is presented the first practical implementation of the method firstly described in Ref. 29 for including spin–orbit effects in atomic and molecular calculations, by means of the use of the Wood–Boring Hamiltonian^{31,32} within the AIMP method.³³ The previous stage of the AIMP method, CG-AIMP,^{13,14} already included a model potential representation of the spin-free relativistic mass–velocity and Darwin operators as proposed by Cowan and Griffin,³² both at the SCF and CI levels. Here, the spin–orbit effects are handled by means of a model potential representation of the one-electron spin–orbit operator of Wood and Boring,³¹ which is included at the double-group CI level.²⁸ For brevity, the method will be called WB-AIMP. It is to be noted that this is a natural extension of the spin-free relativistic CG-AIMP method in order to include spin–orbit effects, since the Wood–Boring Hamiltonian³¹ and the Cowan–Griffin one³² differ, essentially, in the spin–orbit contribution. The potentiality of the Wood–Boring one-electron spin–orbit Hamiltonian, in which two-electron contributions are implicit, has been discussed;^{31,34,35} its superiority over the explicit inclusion of two-electron contributions by means of the method of Blume and Watson³⁶ has been recently pointed out.^{9(c)} Other theoretical frameworks handling relativistic effects, and, in particular, spin–orbit interactions, can be chosen as a basis for a relativistic AIMP approach by using the AIMP main idea of taking useful equations and substituting some target operators by representations of them, either local or nonlocal; in this respect, good results have been obtained using the no-pair Hamiltonian of Hess³⁷ and the mean-field approximation for generating a one-electron spin–orbit no-pair operator.³⁸

For this work, WB-AIMP spin–orbit operators for group VIIA elements F–At and for the sixth row main group elements Tl–Rn have been obtained, and the results of calculations in atoms and in the low lying states of the diatomic molecules HX, HX⁺, (X=F, Cl, Br, I, At) TIH, PbH, BiH, and PoH (bond lengths, vibrational frequencies, dissociation energies, ionization potentials, and spin–orbit splittings) are presented. In this way, the performance of the method can be

^{a)}E-mail: ARTI@vm1.sdi.uam.es

monitored both in a group and in a row of the Periodic Table. The comparison of the results with experiments reveals that the ability of the WB-AIMP method to represent spin-orbit effects at a reasonable cost is very satisfactory.

An outline of the method is presented in Sec. II, the results of atomic calculations in Sec. III, and the results of molecular calculations in Sec. IV. The conclusions appear in Sec. V.

II. METHOD

In this section, the basic equations of the method^{13,29} are summarized and the practical details of the implementation are shown. The details of the spin-free relativistic method CG-AIMP for molecules are presented in Sec. II B, and those of the spin-dependent method WB-AIMP are presented in Sec. II C. They are based, respectively, on the Cowan–Griffin and Wood–Boring equations for atoms; these are summarized in Sec. II A.

A. Wood–Boring and Cowan–Griffin equations for atoms

The radial function of the large component of the Dirac solution for one electron in a local, central potential $V(r)$, G_k , fulfills the equation (in Rydberg units)³¹

$$\left[-\frac{d^2}{dr^2} + \frac{k(k+1)}{r^2} + V(r) + V_{MV,k} + V_{DW,k} + V_{SO,k} \hat{l}\hat{s} \right] G_k = \epsilon_k G_k, \quad (1)$$

where $k=l$ for $j=l-1/2$ and $k=-(l+1)$ for $j=l+1/2$, and the mass-velocity, Darwin, and spin-orbit operators read

$$V_{MV,k} = -\frac{\alpha^2}{4} (\epsilon_k - V)^2,$$

$$V_{DW,k} = -\frac{\alpha^2}{4} B_k \frac{dV}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right),$$

$$V_{SO,k} = \frac{\alpha^2}{2} B_k \frac{1}{r} \frac{dV}{dr},$$

and

$$B_k = \left[1 + \frac{\alpha^2}{4} (\epsilon_k - V) \right]^{-1},$$

α being the fine-structure constant.

Neglecting the spin-orbit operator and converting the differential Darwin operator into a local potential, Cowan and Griffin³² proposed the approximate equation,

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) + V_{MV,nl} + V_{DW,nl} \right] G_{nl} = \epsilon_{nl} G_{nl}, \quad (2)$$

where

$$V_{MV,nl} = -\frac{\alpha^2}{4} (\epsilon_{nl} - V)^2, \quad (3)$$

$$V_{DW,nl} = -\frac{\alpha^2}{4} B_{nl} \frac{dV}{dr} \left(\frac{1}{G_{nl}} \frac{dG_{nl}}{dr} - \frac{1}{r} \right), \quad (4)$$

$$B_{nl} = \left[1 + \frac{\alpha^2}{4} (\epsilon_{nl} - V) \right]^{-1}.$$

Cowan and Griffin³² proposed to add these $V_{MV,nl}$ and $V_{DW,nl}$ operators to the nonrelativistic Hartree–Fock operator, F_{NR} , in atoms, leading to a set of coupled equations,

$$(F_{NR} + V_{MV,nl} + V_{DW,nl}) R_{nl} = \epsilon_{nl} R_{nl}, \quad (5)$$

which can be solved self-consistently, using numerical procedures in which boundary conditions at the nucleus are imposed. In this case, V is the Hartree–Fock one-electron potential and a local approximation must be adopted for it in order to perform the derivatives leading to V_{MV} and V_{DW} ; the $X\alpha$ local approximation has been adopted here. It must be noted that, unlike Cowan and Griffin calculations,³² this local exchange approximation is used here only for the purpose of generating V_{MV} and V_{DW} , not for the rest of the one-electron operator, where the nonlocal Hartree–Fock exchange is used.

After solving Eq. (5), the numerical orbitals can be used to generate the one-electron spin-orbit operators,³¹

$$V_{SO,nl} \hat{l}\hat{s} = \frac{\alpha^2}{2} B_{nl} \frac{1}{r} \frac{dV}{dr} \hat{l}\hat{s}, \quad (6)$$

useful in Eq. (1), if the k -dependency of $V_{SO,k}$ is approximated by an l -dependency.

B. Spin-free CG-AIMP method for molecules

The spin-free Cowan–Griffin relativistic version of the AIMP method, which may be called CG-AIMP, is a scalar approximation which keeps the structure of the *ab initio* non-relativistic calculations, both at the SCF and CI levels. In this approximation, the one-electron contribution to the valence Hamiltonian of atom I is (in Hartree units)

$$h_{CG-AIMP}^I(i) = -\frac{1}{2} \Delta_i - (Z^I - Z_{core}^I)/r_i + V_{CG-AIMP}^I(i), \quad (7)$$

$$V_{CG-AIMP}^I(i) = V_{Coul}^{I,MP}(i) + V_{exch}^{I,MP}(i) + V_{MV}^{I,MP}(i) + V_{DW}^{I,MP}(i) + P^I(i). \quad (8)$$

Its components are the following:

- (1) The Coulomb core model potential,

$$V_{Coul}^{I,MP}(r_i) = \sum_k \frac{A_k^I \exp(-\alpha_k^I r_i^2)}{r_i}, \quad (9)$$

where the parameters $\{A_k^I, \alpha_k^I\}$ are determined through least-squares fitting to the genuine core Coulomb operator (including $-Z_{core}^I/r_i$) corresponding to the Cowan–Griffin core orbitals obtained from Eq. (5).

- (2) The core exchange model potential plus the relativistic mass-velocity and Darwin model potentials, which are the spectral representation of the genuine operators on the primitive basis set of atom I ,

$$V_{\text{exch}}^{I,\text{MP}} + V_{\text{MV}}^{I,\text{MP}} + V_{\text{DW}}^{I,\text{MP}} = \hat{\Omega}(V_{\text{exch}}^I + V_{\text{MV}}^I + V_{\text{DW}}^I)\hat{\Omega}, \quad (10)$$

where $\hat{\Omega}$ is the projection operator of the space defined by the nonorthogonal basis set $\{|alm;I\rangle\}$, of spherical primitive Gaussian-type functions of atom I ,

$$\hat{\Omega} = \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |alm;I\rangle (\mathbf{S}^I)_{l;ab}^{-1} \langle blm;I|, \quad (11)$$

$$(\mathbf{S}^I)_{l;ab} = \langle alm;I | blm;I \rangle,$$

and

$$V_{\text{MV}}^I + V_{\text{DW}}^I = \sum_{nl \in \text{valence}} \hat{O}_I (V_{\text{MV},nl}^I + V_{\text{DW},nl}^I) \hat{O}_I, \quad (12)$$

with

$$\hat{O}_I = \sum_{m=-l}^{+l} |lm\rangle \langle lm|, \quad (13)$$

$V_{\text{MV},nl}^I$ and $V_{\text{DW},nl}^I$ being those of Eqs. (3) and (4), converted to Hartree units. In this way, a simple expression stands for the nonlocal model potential representing the core exchange plus the valence mass-velocity and Darwin operators,

$$\begin{aligned} V_{\text{exch}}^{I,\text{MP}} + V_{\text{MV}}^{I,\text{MP}} + V_{\text{DW}}^{I,\text{MP}} \\ = \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |alm;I\rangle A_{l;ab}^{I,\text{MP}} \langle blm;I|, \end{aligned} \quad (14)$$

where the coefficients $A_{l;ab}^{I,\text{MP}}$ are the elements of the matrix

$$\mathbf{A}^{I,\text{MP}} = (\mathbf{S}^I)^{-1} \mathbf{V}_{\text{EMD}}^I (\mathbf{S}^I)^{-1}, \quad (15)$$

with

$$V_{\text{EMD},ij}^I = \langle i | V_{\text{exch}}^I + V_{\text{MV}}^I + V_{\text{DW}}^I | j \rangle, \quad (16)$$

$|i\rangle$ and $|j\rangle$ being elements of the set $\{|alm;I\rangle\}$. This $\mathbf{V}_{\text{EMD}}^I$ matrix is lm -blocked and the V_{MV}^I and V_{DW}^I operators within an lm -block only include the outermost $V_{\text{MV},nl}^I$ and $V_{\text{DW},nl}^I$ operators [Eq. (3)] of that block. If more than one atomic orbital with the same value of l is to be included in the valence of a given atom, then $|R_{nl}\rangle (V_{\text{MV},nl}^I + V_{\text{DW},nl}^I) \langle R_{nl}|$ could be used instead of $(V_{\text{MV},nl}^I + V_{\text{DW},nl}^I)$, but this is not the case in any of the calculations presented in this paper. This prescription, together with the angular projection of Eq. (12), guarantees that, say, $V_{\text{MV},nl}^I$ does not act on atomic orbitals of atom I other than nl .

(3) The core projection operator,

$$P^I = \sum_{c \in \text{core}} (-2\epsilon_c^I) |\phi_c^I\rangle \langle \phi_c^I|, \quad (17)$$

where ϵ_c^I and ϕ_c^I are the core orbital energies and functions of atom I obtained in the atomic Cowan-Griffin-Hartree-Fock calculation, Eq. (5). For simplicity, in Eq. (17) orthonormal analytical Gaussian orbitals are used

which result from maximizing the overlap with the original numerical core orbitals.

Within the CG-AIMP approximation, the basis set for the valence of atom I is optimized by minimization of its valence total energy, following the same methods applied to the optimization of all-electron atomic basis sets.^{39,40} Along this optimization, the original V_{exch}^I , V_{MV}^I , and V_{DW}^I operators are used rather than their model potential representations, $V_{\text{exch}}^{I,\text{MP}}$, $V_{\text{MV}}^{I,\text{MP}}$, and $V_{\text{DW}}^{I,\text{MP}}$, since they lead to identical results in atoms. The optimized basis set is stored in libraries, together with the core orbitals and orbital energies, the core Coulomb local potential parameters [Eq. (9)], and the numerical mass-velocity and Darwin potentials of the valence [Eqs. (3) and (4)], in order to be used in molecular calculations.

In a CG-AIMP molecular calculation using any standard analytical *ab initio* method (SCF, CASSCF, CI, ACPF, etc.) the one electron operator reads

$$h_{\text{CG-AIMP}}(i)$$

$$= -\frac{1}{2} \Delta_i + \sum_I [-(Z^I - Z_{\text{core}}^I)/r_i + V_{\text{CG-AIMP}}^I(i)]. \quad (18)$$

Here, the operators $V_{\text{Coul}}^{I,\text{MP}}$ [Eq. (9)] and P^I [Eq. (17)] are used, together with $V_{\text{exch}}^{I,\text{MP}} + V_{\text{MV}}^{I,\text{MP}} + V_{\text{DW}}^{I,\text{MP}}$ [Eq. (14)] calculated using the whole set of primitives centered on atom I in the molecular calculation. Since the coefficients of the non-local representation operators [Eq. (15)] change when a primitive is added or changed, they are calculated as a part of the input processing of every molecular calculation rather than stored in libraries; its calculation is not at all time consuming.

C. Spin-dependent WB-AIMP method for molecules

The spin-dependent Wood-Boring relativistic version of the AIMP method, which may be called WB-AIMP, results from adding to $V_{\text{CG-AIMP}}^I(i)$ [Eq. (8)] a model potential representation of the Wood-Boring one-electron spin-orbit operator [Eq. (6)].

In this paper, for practical reasons, it is chosen as a spin-orbit model potential the operator proposed by Pitzer and Winter,²⁸ so that

$$V_{\text{WB-AIMP}}^I(i) = V_{\text{CG-AIMP}}^I(i) + \sum_{nl \in \text{valence}} V_{\text{SO},nl}^{I,\text{MP}}(r_i) \hat{O}_l \hat{l} \hat{s} \hat{O}_l. \quad (19)$$

Here, the radial part is⁴¹

$$V_{\text{SO},nl}^{I,\text{MP}}(r_i) = \lambda^I \sum_k \frac{B_k^I \exp(-\beta_k^I r_i^2)}{r_i^2}. \quad (20)$$

The scaling factor λ^I is set to 1 and the parameters $\{B_k^I, \beta_k^I\}$ are determined through weighted least-squares fitting to the radial contributions to the numerical Wood-Boring spin-orbit operators [Eq. (6)] with a normalization restriction,

$$\min \left\{ \sum_i \omega_i [V_{\text{SO},nl}^{I,\text{MP}}(r_i) - V_{\text{SO},nl}^I(r_i)]^2 \right\} \quad (21)$$

$$\langle R_{nl} | V_{\text{SO},nl}^{I,\text{MP}} | R_{nl} \rangle = \langle R_{nl} | V_{\text{SO},nl}^I | R_{nl} \rangle, \quad (22)$$

TABLE I. Spin-orbit potential for Tl [Eq. (20)], with $\lambda = 1$.

$V_{SO}^{MP}(5d)$		$V_{SO}^{MP}(6p)$	
β_k	B_k	β_k	B_k
965 500.	0.246 422 88	3 129 000.	0.159 595 66
92 580.	0.340 006 69	330 400.	0.291 364 21
7 460.	0.193 677 88	38 460.	0.250 370 86
679.3	0.066 665 17	5 174.	0.136 914 27
84.42	0.022 238 32	687.4	0.060 442 31
11.854	0.007 772 19	89.31	0.023 928 08
1.808	0.001 696 86	10.696	0.008 114 21
0.2468	0.000 178 21	1.120 6	0.001 392 77

R_{nl} being the numerical atomic Cowan–Griffin–Hartree–Fock functions, Eq. (5). After some numerical experimentation, the use of r_i^4 as a weight function in a logarithmic mesh was found to be appropriated.

In atomic and molecular WB-AIMP calculations, the valence one-electron operator

$$h_{WB-AIMP}(i) = -\frac{1}{2} \Delta_i + \sum_I [-(Z^I - Z_{core}^I)/r_i + V_{WB-AIMP}^I(i)] \quad (23)$$

is used at the CI level of calculation,²⁸ which is fed with molecular orbitals obtained in a spin-free relativistic CG-AIMP calculation (usually SCF, though not necessarily).

In this approximate treatment of the spin-orbit effects in atoms and molecules, in addition to the approximations involved in freezing orbitals and representing operators, there are those of using a one-electron operator for the spin-orbit interactions and taking this operator ad hoc from the atomic Wood–Boring equations. Though not completely theoretically justified, the final form of the spin-orbit operator used is still plausible, since it is somehow related to a mean-field approximation, including an average of most of the two-electron contribution³⁶ through the use of the Hartree–Fock potential $V(r)$ [Eq. (6)]. Consequently, the atomic scaling factor λ^I is included, in an attempt to partially overcome the above approximations by using it as an empirical parameter. An empirical value for λ^I can be obtained by making the WB-AIMP atomic spin-orbit splittings to be close to the experimental ones. Values of λ^I close to 1 must be expected, and, as a matter of fact, this is what is found in the atoms studied in this paper (Sec. III). One should notice, however, that the size of the spin-orbit splittings are very often coupled to electron correlation effects and the values of λ^I can be affected by a deficient treatment of the correlation. Since this kind of parametrization of λ^I rely only on the availability of experimental atomic spectra, it is expected that values for almost all atoms can be found.

III. ATOMIC CALCULATIONS

CG-AIMP's and valence basis sets are already available for halogen atoms F–I (Ref. 14) and sixth row elements Tl–Rn.²⁵ The corresponding spin-orbit radial operators [Eq. (20)] have been obtained here and are available from the author upon request; as a showcase, the one of Tl is shown in

TABLE II. Spin-orbit corrected valence basis set for Tl. All properties in atomic units, except when indicated.

Exponent	Original coefficient	SO-corrected coefficient	Numerical
(5d orbital)			
685.880 72	0.006 861 98	0.006 903 20	
198.236 99	0.041 583 55	0.041 583 48	
71.916 786	0.092 304 94	0.092 304 79	
15.671 582	−0.101 348 56	−0.101 348 39	
9.144 742 1	−0.219 462 16	−0.219 461 79	
1.478 193 4	0.607 831 97	0.607 830 95	
0.461 619 57	0.523 405 39	0.523 404 51	
ζ (cm ^{−1}) =	6 856	6 869	6 869
$\epsilon(5d) =$	−0.824 4	−0.824 4	−0.842 7
$\langle r^{-3} \rangle =$	17.37	17.40	17.40
$\langle r^{-1} \rangle =$	0.957	0.957	0.953
$\langle r \rangle =$	1.354	1.354	1.370
$\langle r^2 \rangle =$	2.114	2.114	2.195
(6p orbital)			
5 228.566 8	0.000 886 42	0.000 648 11	
1 117.042 9	0.005 770 76	0.005 770 77	
330.964 14	0.016 037 25	0.016 037 27	
49.167 316	−0.052 107 99	−0.052 108 06	
20.929 228	−0.033 561 99	−0.033 562 03	
14.303 842	0.063 321 10	0.063 321 18	
7.321 308 2	0.108 153 39	0.108 153 53	
1.893 806 3	−0.169 539 83	−0.169 540 05	
0.917 434 61	−0.150 705 04	−0.150 705 24	
0.208 089 74	0.270 228 78	0.270 229 13	
0.082 136 63	0.549 289 49	0.549 290 21	
0.031 208 16	0.330 372 08	0.330 372 51	
ζ (cm ^{−1}) =	4 105	4 514	4 514
$\epsilon(6p) =$	−0.181 3	−0.181 0	−0.185 8
$\langle r^{-3} \rangle =$	11.39	10.30	10.58
$\langle r^{-1} \rangle =$	0.322	0.321	0.325
$\langle r \rangle =$	3.914	3.914	3.859
$\langle r^2 \rangle =$	17.92	17.92	17.42
$\epsilon(6s) =$	−0.435 3	−0.434 3	−0.449 0
valence energy =	−50.533 821	−50.533 460	

Table I. They include more terms and much higher exponents than usual pseudopotential spin-orbit operators (see, for instance, Ref. 9) as a result of requiring an accurate reproduction of the Wood–Boring radial spin-orbit operators [Eq. (6)].

Using the valence basis sets and spin-orbit operators commented above, the calculated spin-orbit coupling constants show typical errors of 10% respect to the ones calculated with the numerical atomic orbitals and spin-orbit operators. In order to improve this, the *spin-orbit corrected valence basis sets* are defined in such a way that they are still optimal for representing bonding properties (outermost parts)

TABLE III. Core definitions and valence basis set patterns.

Atom	Core	Valence	Basis set pattern
H	...	1s	(3,1,1,1/1,1)
F	[He]	2s, 2p	(3,1,1/3,1,1/1)
Cl	[Ne]	3s, 3p	(5,1,1/4,1,1/1)
Br	[Ar], 3d	4s, 4p	(7,1,1/5,1,1/3,1)
I	[Kr]	4d, 5s, 5p	(9,1,1/7,1,1/4,1,1,1)
Tl–Rn	[Xe], 4f	5d, 6s, 6p	(11,1,1/9,1,1,1/5,1,1,1/4,1)

TABLE IV. Spin-orbit splittings and excitation energies (cm^{-1}) for halogen elements F–I.

		Original basis set		SO-corrected basis set			
	Main SL	J	$\lambda=1$	$\lambda=1$	Empirical λ	Experiment ^a	Literature
(λ=0.835)							
F	2P	3/2	0	0	0	0	375 ^b
		1/2	473	483	403	404	
F ⁺	3P	2	0	0	0	0	
		1	366	374	312	342	
		0	542	553	462	491	
	1D	2	22 537	22 513	22 480	20 873	
	1S	0	45 318	45 280	45 247	44 919	
(λ=1.030)							
Cl	2P	3/2	0	0	0	0	998 ^b
		1/2	803	863	882	881	
Cl ⁺	3P	2	0	0	0	0	
		1	630	674	694	697	
		0	911	971	1 000	996	
	1D	2	13 486	13 493	13 506	11 652	
	1S	0	28 726	28 736	28 749	[27 900]	
(λ=1.080)							
Br	2P	3/2	0	0	0	0	3 963 ^c
		1/2	3 278	3 411	3 690	3 685	
Br ⁺	3P	2	0	0	0	0	
		1	2 735	2 855	3 108	3 139	
		0	3 447	3 585	3 843	3 840	
	1D	2	13 597	13 681	13 868	11 409	
	1S	0	28 094	28 206	28 455	...	
(λ=1.091)							
I	2P	3/2	0	0	0	0	7 891 ^d
		1/2	6 963	6 969	7 643	7 603	
I ⁺	3P	2	0	0	0	0	
		1	6 328	6 298	6 968	7 090	
		0	6 121	6 104	6 470	6 451	
	1D	2	14 847	14 821	15 408	13 731	
	1S	0	29 017	28 974	29 959	32 629	

^aReference 45.^bReference 7(a). Shape-consistent pseudopotential; spin-orbit operator (Ref. 27) obtained from the large components of atomic Dirac-Fock valence spinors and their eigenvalues. Spin-orbit splitting computed by first-order perturbation after a spin-free calculation.^cReference 7(b). See footnote b.^dReference 7(c). See footnote b.

but they are able to represent the spin-orbit related properties as well. Since the internal parts of the AIMP valence basis sets contain Gaussian primitives with high exponents, we achieve the above objective by changing only the innermost coefficient of a valence orbital,

$$R_{nl}^{\text{SO-corr}} = N \left(c_1^{\text{SO-corr}} \chi_1 + \sum_{i=2} c_i \chi_i \right), \quad (24)$$

where $\{\chi\}$ and $\{c\}$ are the Gaussian primitives and coefficients defining the original orbital, χ_1 is the innermost primitive, and N and $c_1^{\text{SO-corr}}$ are chosen in order to fulfill

$$\langle R_{nl}^{\text{SO-corr}} | R_{nl}^{\text{SO-corr}} \rangle = 1$$

and

$$\langle R_{nl}^{\text{SO-corr}} | V_{\text{SO},nl} | R_{nl}^{\text{SO-corr}} \rangle = \langle R_{nl}^{\text{num}} | V_{\text{SO},nl} | R_{nl}^{\text{num}} \rangle,$$

R_{nl}^{num} being the numerical Cowan-Griffin-Hartree-Fock orbital and $V_{\text{SO},nl}$ the numerical spin-orbit operator.

In Table II, the SO-corrected basis set for Tl is shown together with the original one and some atomic properties which can be compared with the numerical results. We can see that the change in the orbitals is minimal, producing only a very small loss of valence total energy, and insignificant changes in all properties except for the expected value of r^{-3} which is noticeably improved, although its original value was already acceptable. In this way, it is expected that the use of SO-corrected basis sets in atomic and molecular calculations will leave essentially unaffected all properties except those related to spin-orbit splittings. SO-corrected basis sets have been obtained for all the atoms studied here and are available from the author.

Using the CG-AIMP original and SO-corrected basis sets and the spin-orbit operators, SCF and CI calculations have been performed on a series of states of the neutral atoms and singly ionized ions of the halogen elements F–I and sixth row elements Tl–Rn. The core definitions and valence basis set patterns are presented in Table III. All the atoms

TABLE V. Spin-orbit splittings and excitation energies (cm^{-1}) for sixth row elements Tl–Rn.

		Original basis set		SO-corrected basis set				
Main SL	J	$\lambda=1$	$\lambda=1$	Empirical λ	Experiment ^a	Literature		
(λ=1.036)								
Tl	2P	1/2	0	0	0			
		3/2	8 457	7 473	7 795	7 793	7 424 ^b 7 654 ^c	
(λ=1.090)								
Pb	3P	0	0	0	0			
		1	8 328	6 847	7 754	7 819	6 615 ^c	
		2	11 914	10 289	11 289	10 650	10 195 ^c	
	1D	2	24 079	20 868	22 832	21 458	20 561 ^c	
	1S	0	32 709	29 545	31 475	29 467	29 939 ^c	
Pb ⁺	2P	1/2	0	0	0	0		
		3/2	15 781	13 479	14 903	14 081	14 038 ^b	
(λ=1.12)								
Bi	4S	3/2	0	0	0	0		
		2D	3/2	12 442	11 265	12 105	11 419	11 884 ^c
		5/2	17 350	15 729	16 907	15 438	16 537 ^c	
	2P	1/2	23 538	21 933	23 096	21 661	23 243 ^c	
		3/2	35 196	31 341	34 189	33 165	32 755 ^c	
Bi ⁺	3P	0	0	0	0	0		
		1	13 356	10 958	12 752	13 324		
		2	18 073	15 508	17 424	17 030		
	1D	2	35 742	30 727	34 472	33 936		
	1S	0	46 627	41 697	45 361	44 173		
Po	3P	2	0	0		0		
		1	19 002	15 136		16 831	16 345 ^c	
		0	8 262	7 868		7 514	7 927 ^c	
	1D	2	25 214	21 488		21 679	22 694 ^c	
	1S	0	49 647	42 028		42 718	44 278 ^c	
Po ⁺	4S	3/2	0	0				
		2D	3/2	19 653	16 289			
		5/2	26 126	22 333				
	2P	1/2	33 890	30 094				
		3/2	54 189	45 772				
At	2P	3/2	0	0				
		1/2	26 737	21 401			21 407 ^b 21 848 ^c	
At ⁺	3P	2	0	0				
		1	27 685	21 750				
		0	10 178	9 747				
	1D	2	34 692	28 922				
	1S	0	68 470	56 696				
(λ=1.067)								
Rn ⁺	2P	3/2	0	0	0	0		
		1/2	36 159	28 667	30 904	30 895	31 350 ^b	

^aReference 45.^bReference 7(d). See footnote b in Table IV.^cReference 9(c). Energy-adjusted pseudopotential; spin-orbit operator obtained by fitting to atomic spin-orbit splittings calculated at the all-electron Wood-Boring level. Transition energies computed in a CIDBG(SD) calculation of the type used in this work.

show a double splitting of the valence, extended with one d -polarization function from Ref. 40. One diffuse p -function for anion from Ref. 42 has been added to F and Cl; in Br, I, and Tl–Rn, a triple splitting of the p function is performed rather than adding extra p primitive, since the outermost exponent is very small. A d -orthogonality function¹³ is added to Br and an f -orthogonality function is added to Tl–Rn; the last one is singly splitted. The calculations have been performed with the ECPAIMP program⁴³ and COLUMBUS suite of programs.⁴⁴

Tables IV and V show the results of the excitation energies calculated at the double group CI level,²⁸ correlating the outermost s and p electrons, including all single and double excitations from the corresponding p^n complete-active-space multireference, CIDBG(SD). Generally speaking, the spin-orbit splittings obtained with the original basis sets are within a 10% error with the experiments, and this is improved by the use of the SO-corrected basis sets, in what is our strictly *ab initio* calculation ($\lambda=1$). Fluorine is an exception to these comments, in consistency with a larger relative

TABLE VI. Ionization potentials (eV) for halogens F–I and sixth row elements Tl–Rn. Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets.

	CG-AIMP SCF		WB-AIMP CIDBG(SD) ^a			Experiment ^c
	A	B	A	B		
				$\lambda=1$	Empirical λ^b	
F($^2P_{3/2}$)→F ⁺ (3P_2)	15.78	15.79	16.85	16.86	16.86	17.42
Cl($^2P_{3/2}$)→Cl ⁺ (3P_2)	11.83	11.83	12.35	12.35	12.35	13.01
Br($^2P_{3/2}$)→Br ⁺ (3P_2)	10.76	10.76	11.22	11.21	11.21	11.84
I($^2P_{3/2}$)→I ⁺ (3P_2)	9.61	9.61	9.89	9.94	9.92	10.454
Tl($^2P_{1/2}$)→Tl ⁺ (1S_0)	4.96	4.95	6.00	5.89	5.92	6.106
Pb(3P_0)→Pb ⁺ ($^2P_{1/2}$)	6.61	6.59	7.30	7.08	7.14	7.415
Bi($^4S_{3/2}$)→Bi ⁺ (3P_0)	8.31	8.29	6.92	7.08	6.94	7.287
Po(3P_2)→Po ⁺ ($^4S_{3/2}$)	7.25	7.22	7.82	7.90	7.90 ^d	8.43
At($^2P_{3/2}$)→At ⁺ (3P_2)	9.12	9.09	8.68	8.89		(9.59) ^e
Rn(1S_0)→Rn ⁺ ($^2P_{3/2}$)	11.06	11.02	10.18	10.38	10.30	10.746

^a*ns* and *np* electrons are correlated, see the text.
^bSee Tables IV and V.
^cReference 45.
^d $\lambda=1$.
^eInterpolated from Tl to Rn.

weight of the two-electron spin-orbit terms not included in a mean-field approximation.³⁶ λ [Eq. (20)] was used as an empirical parameter to further improve the agreement with the experiments. It is remarkable that all the values of λ recommended in Tables IV and V are very close to 1. Values other than the ones suggested (in parentheses,) but similar to them,

could also be acceptable. The comparison of spin-orbit splittings and transition energies with those available in the literature for the cases under study reveal that, in these cases, the precision attainable by the use of the WB-AIMP spin-orbit operators (with $\lambda=1$) and by the use, in pseudopotential calculations, of spin-orbit operators obtained from the large

TABLE VII. Bond lengths (Å). Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets. Numbers in parentheses correspond to neglecting the spin-orbit operator.

	CG-AIMP SCF		WB-AIMP CIDBG(SD) ^a			Experiment ^c
	A	B	A	B		
				$\lambda=1$	Empirical λ^b	
HF $^1\Sigma_0^+$	0.896	0.896	0.909(0.909)	0.909	0.909	0.916
HF ⁺ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	0.975	0.976	0.989(0.989)	0.989	0.989	1.001
			0.989	0.989	0.989	
HCl $^1\Sigma_0^+$	1.275	1.275	1.284(1.284)	1.284	1.284	1.275
HCl ⁺ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	1.315	1.316	1.326(1.326)	1.326	1.326	1.315
			1.326	1.326	1.326	
HBr $^1\Sigma_0^+$	1.414	1.414	1.424(1.424)	1.424	1.424	1.414
HBr ⁺ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	1.444	1.445	1.457(1.457)	1.458	1.458	1.448
			1.458	1.458	1.458	
HI $^1\Sigma_0^+$	1.603	1.603	1.616(1.614)	1.616	1.616	1.609
HI ⁺ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	1.623	1.622	1.638(1.637)	1.638	1.638	(1.62) ^d
			1.638	1.638	1.638	
HAt $^1\Sigma_0^+$	1.692	1.694	1.727(1.709)	1.724		
HAt ⁺ $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	1.708	1.710	1.750(1.729)	1.745		
			1.771	1.753		
TlH $^1\Sigma_0^+$	1.908	1.910	1.925(1.953)	1.931	1.929	1.870
PbH $^2\Pi_{1/2}$ $^2\Pi_{3/2}$	1.847	1.849	1.876(1.881)	1.879	1.878	1.839
			1.854	1.862	1.858	...
BiH $^3\Sigma_{0+}^-$ $^3\Sigma_1^-$	1.791	1.793	1.834(1.823)	1.832	1.834	1.805
			1.822	1.825	1.825	1.791
PoH $^2\Pi_{3/2}$ $^2\Pi_{1/2}$	1.739	1.742	1.781(1.762)	1.777		...
			1.767	1.766		...

^a*ns* and *np* electrons are correlated, see the text.
^bSee Tables IV and V.
^cReference 47.
^dReference 47, estimated from HF⁺, HCl⁺, and HBr⁺.

TABLE VIII. Vibrational frequencies, ω_e (cm^{-1}). Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets. Numbers in parentheses correspond to neglecting the spin-orbit operator.

	CG-AIMP SCF		WB-AIMP CIDBG(SD) ^a			Experiment ^a
	A	B	A	B		
				λ = 1	Empirical λ ^a	
HF ¹ Σ ₀ ⁺	4526	4526	4299(4299)	4299	4299	4138
HF ⁺ ² Π _{3/2} ² Π _{1/2}	3393	3392	3259(3259)	3258	3258	3090
			3258	3258	3258	
HCl ¹ Σ ₀ ⁺	3097	3095	2976(2976)	2974	2974	2991
HCl ⁺ ² Π _{3/2} ² Π _{1/2}	2766	2764	2664(2663)	2662	2662	2674
			2663	2661	2661	
HBr ¹ Σ ₀ ⁺	2745	2745	2630(2631)	2629	2629	2649
HBr ⁺ ² Π _{3/2} ² Π _{1/2}	2544	2543	2423(2424)	2422	2422	2442
			2424	2421	2421	
HI ¹ Σ ₀ ⁺	2439	2439	2331(2340)	2331	2329	2309
HI ⁺ ² Π _{3/2} ² Π _{1/2}	2337	2334	2206(2223)	2212	2210	2170
			2205	2211	2208	
HAt ¹ Σ ₀ ⁺	2259	2250	2035(2143)	2060		
HAt ⁺ ² Π _{3/2} ² Π _{1/2}	2186	2180	1951(2053)	1973		
			1739	1876		
TiH ¹ Σ ₀ ⁺	1388	1387	1329(1310)	1325	1326	1391
PbH ² Π _{1/2} ² Π _{3/2}	1645	1642	1507(1544)	1515	1507	1564
			1563	1558	1560	...
BiH ³ Σ ₀₊ ⁻ ³ Σ ₁ ⁻	1866	1863	1672(1733)	1686	1673	(1636)
			1699	1706	1699	(1669)
PoH ² Π _{3/2} ² Π _{1/2}	2084	2077	1850(1960)	1875		...
			1867	1903		...

^aSee footnotes a, b, c in Table VII.

components of atomic Dirac-Fock valence spinors and their eigenvalues,⁷ or from fitting all-electron spin-orbit splittings,⁹ is overall in the same order of magnitude.

Table VI presents the ionization potentials calculated with spin-orbit and correlation effects included through the WB-AIMP Hamiltonian and the same CIDBG(SD) wave function used for the excitation energies, as well as with the

spin-free CG-AIMP SCF method. The use of the SO-corrected basis sets leaves essentially unchanged this property, both at the SCF and CI levels, and the same is true for the use of the empirical parameter λ ; the differences shown at the CI level are due to effects of the basis set and the λ parameter on the spin-orbit splittings of the atom and ion. The final values of the ionization potentials compare favor-

TABLE IX. Dissociation energies, D_e (eV). Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets. Numbers in parentheses correspond to neglecting the spin-orbit operator.

	CG-AIMP SCF		WB-AIMP CIDBG(SD) ^a			Experiment ^a
	A	B	A	B		
				λ=1	Empirical λ ^a	
HF ¹ Σ ₀ ⁺	4.32	4.33	5.69(5.71)	5.69	5.70	6.13
HF ⁺ ² Π _{3/2}	5.63	5.64	6.92(6.92)	6.93	6.93	...
HCl ¹ Σ ₀ ⁺	3.33	3.33	4.15(4.17)	4.14	4.14	4.62
HCl ⁺ ² Π _{3/2}	3.46	3.46	4.26(4.27)	4.26	4.26	4.82
HBr ¹ Σ ₀ ⁺	2.85	2.82	3.54(3.67)	3.54	3.52	3.92
HBr ⁺ ² Π _{3/2}	2.80	2.80	3.58(3.61)	3.58	3.57	4.04
HI ¹ Σ ₀ ⁺	2.35	2.35	2.88(3.15)	2.83	2.81	3.19
HI ⁺ ² Π _{3/2}	2.17	2.17	2.85(2.96)	2.85	2.83	3.25
HAt ¹ Σ ₀ ⁺	2.09	2.08	2.01(2.91)	2.10		...
HAt ⁺ ² Π _{3/2}	1.88	1.86	2.03(2.71)	2.16		...
TiH ¹ Σ ₀ ⁺	1.70	1.69	2.32(2.41)	2.40	2.37	2.06
PbH ² Π _{1/2}	1.50	1.50	1.33(2.27)	1.48	1.39	≤1.69
BiH ³ Σ ₀ ⁺	1.25	1.25	2.09(210)	2.12	2.10	≤3.00
PoH ² Π _{3/2}	1.61	1.60	1.97(2.44)	2.07		...

^aSee footnotes a, b, c in Table VII.

TABLE X. Adiabatic ionization potentials (eV) $HX(^1\Sigma) \rightarrow HX^+(^2\Pi_{3/2})$. Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets. Numbers in parentheses correspond to neglecting the spin-orbit operator.

	CG-AIMP SCF		WB-AIMP CIDBG(SD) ^a			
	A	B	A	B		Experiment ^a
				$\lambda=1$	Empirical λ^a	
HF	14.47	14.47	15.62(15.64)	15.62	15.63	15.64
HCl	11.70	11.70	12.23(12.26)	12.23	12.23	12.75
HBr	10.80	10.80	11.18(11.33)	11.17	11.16	11.67
HI	9.79	9.80	9.92(10.24)	9.93	9.90	10.38
HAt	9.33	9.30	8.65(9.77)	8.83		...

^aSee footnotes a, b, c in Table VII.

ably with the experiments both in absolute values and in tendencies.

IV. MOLECULAR CALCULATIONS

In this section, the results of calculations on the lowest states of hydrogen halides, their singly charged cations, and the sixth row element hydrides are presented. The basis set for H (Table III) corresponds to Ref. 46; the basis sets for the rest of the atoms is the same as in the atomic calculations. Bond lengths (Table VII), vibrational frequencies (Table VIII), dissociation energies (Table IX), and adiabatic ionization potentials (hydrogen halides, Table X), have been calculated with the spin-free CG-AIMP method at the SCF level, and with spin-orbit effects included through the WB-AIMP method, using a CI wave function which includes all single and double excitations from the two σ and two π orbitals with main character s and p , from the π^n multireference, using the double group CI formalism,²⁸ WB-AIMP CIDBG(SD); the molecular orbitals were the CG-AIMP SCF ones. Adiabatic spin-orbit splittings calculated with the last method are presented as well in Table XI. Both the original

basis sets and the spin-orbit corrected basis sets have been used. In the WB-AIMP CIDBG(SD) calculations with the original basis sets, the spin-orbit effects have been estimated by switching off the spin-orbit operators ($\lambda=0$); the corresponding results appear in parentheses. In the WB-AIMP CIDBG(SD) calculations with the spin-orbit corrected basis sets, results using the values of λ obtained empirically for the atoms are presented, together with those in which no empirical information is used ($\lambda=1$).

One observes, firstly, that the use of the spin-orbit corrected basis set and of the empirical spin-orbit scaling parameter λ does not affect the molecular bonding properties and exclusively changes the spin-orbit splittings. The effects seen on the WB-AIMP dissociation energies and ionization potentials are indirect, due to their influence on the atomic and molecular spin-orbit splittings.

The overall results of the WB-AIMP CIDBG(SD) calculations using the spin-orbit corrected basis sets and the empirical values of λ show a reasonable agreement with the experiments, both in absolute values and (especially) in tendencies, with differences which are a logical consequence of

TABLE XI. Adiabatic spin-orbit splittings (cm^{-1}). Column labels A and B stand, respectively, for calculations using the original and the spin-orbit corrected basis sets.

	WB-AIMP CIDBG(SD) ^a				
	A	B		Experiment ^a	Literature
		$\lambda=1$	Empirical λ^a		
HF ⁺ ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	338	344	288	293	
HCl ⁺ ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	589	627	646	648	710 ^c
HBr ⁺ ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	2 381	2 476	2 674	2 653	2 740 ^c
HI ⁺ ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	5 010	4 989	5 443	~5 400	5 470 ^c
HAt ⁺ ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	16 040	13 675		...	
PbH ($^2\Pi_{1/2} \rightarrow ^2\Pi_{3/2}$)	7 618	6 589	7 227	(~8 000) ^b	6 380 ^a 6 846 ^e
BiH ($^3\Sigma_0^+ \rightarrow ^3\Sigma_1^-$)	4 802	3 741	4 535	4 917	3 840 ^d 5 737 ^f 4 303 ^g
PoH ($^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$)	12 632	10 565		...	10 583 ^d 9 920 ^h

^aSee footnotes a, b, c in Table VII.

^bExpected result.

^cReference 49.

^dReference 48.

^eReference 51(a).

^fReference 52(a).

^gReference 52(a).

^hReference 53.

the approximations involved in the calculation, mainly frozen core, representation of operators, one-electron ad hoc spin-orbit operator, and a limited CI expansion. Bond distances agree within expected margins, the errors (systematically positive, except for HF, HF⁺) being smaller for the lighter elements. The same is true for the vibrational frequencies, though here the discrepancies are not systematic. The dissociation energies are also acceptable; the agreement with the experimental values is more or less the same for all the molecules under study, and one may remark the results of the differential dissociation energies of the set of hydrogen halides (both neutral and first cations,) where the spin-orbit effects correct the order of HBr-HBr⁺ and HI-HI⁺, and quantitatively improve the differences between molecules. The adiabatic ionization potentials of the hydrogen halides are acceptable as well, smaller than the experimental values by 0.5 eV for all molecules except HF.

The spin-orbit effects estimated with the WB-AIMP calculation on bond lengths and vibrational frequencies are insignificant for the halides down to iodine, as expected. They are significant only for the molecules involving sixth row elements. The effects on the dissociation energies, mainly a result of the different atomic and molecular spin-orbit splittings, grow down the Periodic Table, becoming very important in the Π states of the sixth row hydrides; the molecular reduction of the spin-orbit splitting results in smaller dissociation energies. The spin-orbit splitting of the $^2\Pi$ ground state of the hydrogen halide cations HX⁺ results in a reduction of the HX ionization potentials.

The molecular spin-orbit splittings are presented in Table XI. The spin-orbit correction on the basis set (column B, $\lambda=1$), which has been designed only to make the WB-AIMP wave functions closer to the numerical theoretical reference in the very innermost part, does not necessarily bring the molecular splittings closer to the experiments, as is clear in BiH, this meaning that, in individual cases, fortunate cancellation of errors can go parallel to a slightly poorer description of the innermost parts of the wave function. Comparison of our *ab initio* (column B, $\lambda=1$) results with pseudopotential calculations in the literature,⁴⁸⁻⁵³ may lead to the conclusion, as was the case for the atoms, that the precision attainable in the spin-orbit splittings is, in overall, similar. The use of the *atomic* empirical values of λ does certainly bring the *molecular* splittings closer to the experiments. This effect of λ can be regarded as a measure of the non-mean-field two-electron spin-orbit contribution, though the λ empirical values obviously correct for other limitations of the method as well, in particular for eventual insufficient descriptions of the coupling between electron correlation effects and spin-orbit effects.

V. CONCLUSIONS

In this paper, an extension of the relativistic spin-free Cowan-Griffin based core *ab initio* model potential method¹³ is presented in order to handle spin-orbit effects in atomic and molecular valence electron calculations. The spin-orbit operators, which are included in the calculations at the CI stage, are one-electron operators representing the ones proposed by Wood and Boring for atoms.³¹ The calcu-

lations on neutral and singly ionized atoms and monohydrides of group VIIA elements and sixth row *p*-elements are very satisfactory, since the absolute results and their tendencies fall within the margins demandable to an effective core potential method. In particular, the spin-orbit splittings are very reasonable.

ACKNOWLEDGMENTS

The author is very grateful to Professor R. M. Pitzer, Columbus, for kindly providing his computer programs and his help, and to Professor S. Huzinaga, Edmonton, and Dr. Z. Barandiarán, Madrid, for their comments, their critical reading of the manuscript, and their supportive attitude. This work was partly supported by grants from Ministerio de Educación y Ciencia (DGICYT PS92-0146) and Comunidad de Madrid (AE00145/94), Spain. Partial support from the European Science Foundation is as well acknowledged.

- ¹P. Pyykkö, *Chem. Rev.* **88**, 563 (1988).
- ²K. Balasubramanian and K. S. Pitzer, *Adv. Chem. Phys.* **67**, 287 (1987).
- ³W. C. Ermler, R. B. Ross, and P. A. Christiansen, *Adv. Quantum Chem.* **19**, 139 (1988).
- ⁴O. Gropen, in *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1988), Vol. 2, p. 109, and references therein.
- ⁵L. R. Kahn, P. J. Hay, and R. D. Cowan, *J. Chem. Phys.* **68**, 2386 (1978).
- ⁶P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 270 (1985); W. R. Wadt and P. J. Hay, *ibid.* **82**, 284 (1985); P. J. Hay and W. R. Wadt, *ibid.* **82**, 299 (1985).
- ⁷L. F. Pacios and P. A. Christiansen, *J. Chem. Phys.* **82**, 2664 (1985); M. M. Hurley, L. F. Pacios, P. A. Christiansen, B. R. Ross, and W. C. Ermler, *ibid.* **84**, 6840 (1986); L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *ibid.* **87**, 2812 (1987); R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn, and P. A. Christiansen, *ibid.* **93**, 6654 (1990); R. B. Ross, S. Gayen, and W. C. Ermler, *ibid.* **100**, 8145 (1994).
- ⁸Y. Bouteiller, C. Mijoule, M. Nizan, J. C. Barthelat, J. P. Daudey, M. Pelissier, and B. Silvi, *Mol. Phys.* **65**, 295 (1988).
- ⁹M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *J. Chem. Phys.* **86**, 866 (1987); M. Dolg, H. Stoll, and H. Preuss, *ibid.* **90**, 1730 (1989); W. Küchle, M. Dolg, H. Stoll, and H. Preuss, *Mol. Phys.* **74**, 1245 (1991); *J. Chem. Phys.* **100**, 7535 (1994).
- ¹⁰C. M. Marian, U. Wahlgren, O. Gropen, and P. Pyykkö, *J. Mol. Struct. (Theochem)* **169**, 339 (1988); L. G. M. Pettersson, U. Wahlgren, and O. Gropen, *Chem. Phys.* **80**, 7 (1983).
- ¹¹M. Klobukowski, *J. Comput. Chem.* **4**, 350 (1983).
- ¹²Y. Sakai, E. Miyoshi, M. Klobukowski, and S. Huzinaga, *J. Comput. Chem.* **8**, 226 (1987); **8**, 256 (1987).
- ¹³Z. Barandiarán, L. Seijo, and S. Huzinaga, *J. Chem. Phys.* **93**, 5843 (1990).
- ¹⁴Z. Barandiarán and L. Seijo, *Can. J. Chem.* **70**, 409 (1992).
- ¹⁵Y. S. Lee and A. D. McLean, *J. Chem. Phys.* **76**, 735 (1982).
- ¹⁶S. N. Datta and C. S. Ewig, *Chem. Phys. Lett.* **85**, 443 (1982).
- ¹⁷O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort, *Theor. Chim. Acta* **81**, 405 (1992).
- ¹⁸Y. Ishikawa, G. L. Malli, and N. C. Pyper, *Chem. Phys. Lett.* **194**, 481 (1992).
- ¹⁹O. Matsuoka, *J. Chem. Phys.* **97**, 2271 (1992); O. Matsuoka, L. Pisani, and E. Clementi, *Chem. Phys. Lett.* **202**, 13 (1993).
- ²⁰K. G. Dyall, P. R. Taylor, K. Faegri, Jr., and H. Partridge, *J. Chem. Phys.* **95**, 2583 (1991); K. G. Dyall, *ibid.* **96**, 1210 (1992); **98**, 2191 (1993).
- ²¹K. G. Dyall, *J. Chem. Phys.* **98**, 9678 (1993).
- ²²L. Visscher, T. Saue, W. C. Nieuwpoort, K. Faegri, and O. Gropen, *J. Chem. Phys.* **99**, 6704 (1993).
- ²³Z. Barandiarán and L. Seijo, *J. Chem. Phys.* **101**, 4049 (1994).
- ²⁴W. R. Wadt, *Chem. Phys. Lett.* **89**, 245 (1982).
- ²⁵C. Teichteil, M. Pelissier, and F. Spiegelmann, *Chem. Phys.* **81**, 273 (1983).
- ²⁶P. Hafner and W. H. E. Schwarz, *Chem. Phys. Lett.* **65**, 537 (1979).

- ²⁷W. C. Ermler, Y. S. Lee, P. A. Christiansen, and K. S. Pitzer, *Chem. Phys. Lett.* **81**, 70 (1981).
- ²⁸R. M. Pitzer and N. W. Winter, *J. Phys. Chem.* **92**, 3061 (1988).
- ²⁹S. Katsuki and S. Huzinaga, *Chem. Phys. Lett.* **147**, 597 (1988); S. Huzinaga, *J. Mol. Struct. (Theorchem)* **80**, 51 (1991).
- ³⁰M. Klobukowski, *Chem. Phys. Lett.* **183**, 417 (1991).
- ³¹J. H. Wood and A. M. Boring, *Phys. Rev. B* **18**, 2701 (1978).
- ³²R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
- ³³S. Huzinaga, L. Seijo, Z. Barandiarán, and M. Klobukowski, *J. Chem. Phys.* **86**, 2132 (1987).
- ³⁴A. M. Boring and J. H. Wood, *J. Chem. Phys.* **71**, 32 (1979).
- ³⁵J.-L. Heully, *J. Phys. B At. Mol. Phys.* **15**, 4079 (1982); J.-L. Heully and S. Salomonson, *ibid.* **15**, 4093 (1982).
- ³⁶M. Blume and R. E. Watson, *Proc. R. Soc. London, Ser. A* **270**, 127 (1962); **271**, 565 (1963).
- ³⁷B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986); R. Samzow and B. A. Hess, *Chem. Phys. Lett.* **184**, 491 (1991).
- ³⁸C. M. Marian and U. Wahlgren (private communication).
- ³⁹H. Tatewaki and S. Huzinaga, *J. Chem. Phys.* **71**, 4339 (1979).
- ⁴⁰J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, edited by S. Huzinaga (Elsevier, Amsterdam, 1984).
- ⁴¹L. R. Kahn, P. Baybutt, and D. G. Truhlar, *J. Chem. Phys.* **65**, 3826 (1976).
- ⁴²T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1977).
- ⁴³ECPAIMP is an integral program for ECP and AIMP calculations written by L. G. M. Pettersson and L. Seijo.
- ⁴⁴COLUMBUS suite of programs (ARGOS, CNVRT, SCFPQ, LSTRN, CGDBG, and CIDBG). R. M. Pitzer (principal author). See, A. H. H. Chang and R. M. Pitzer, *J. Am. Chem. Soc.* **111**, 2500 (1989), and references therein for a description. CNVRT and LSTRN have been adapted to handle ECPAIMP integrals by L. Seijo.
- ⁴⁵C. E. Moore, *Natl. Bur. Stand. (U.S.) Circ.* 467 (1949, 1952, 1958).
- ⁴⁶S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ⁴⁷K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ⁴⁸M. Dolg, W. Küchle, H. Stoll, H. Preuss, and P. Schwerdtfeger, *Mol. Phys.* **74**, 1265 (1991).
- ⁴⁹S. Roszak, J. J. Kaufman, W. S. Koski, R. D. Barreto, T. P. Fehlner, and K. Balasubramanian, *J. Phys. Chem.* **96**, 7226 (1992).
- ⁵⁰P. A. Christiansen, K. Balasubramanian, and K. S. Pitzer, *J. Chem. Phys.* **76**, 5087 (1982); K. S. Pitzer, in *Relativistic Effects in Atoms, Molecules, and Solids*, edited by G. L. Malli (Plenum, New York, 1983), p. 403; P. Schwerdtfeger, *Phys. Scr.* **36**, 453 (1987); K. Balasubramanian and J. X. Tao, *J. Chem. Phys.* **94**, 3000 (1991).
- ⁵¹K. Balasubramanian and K. S. Pitzer, *J. Chem. Phys.* **88**, 1146 (1984); A. Chapman, J. Li, K. Balasubramanian, and S. H. Liu, *ibid.* **88**, 3826 (1988); P. Schwerdtfeger, H. Silberbach, and B. Miehl, *ibid.* **90**, 762 (1989).
- ⁵²(a) K. Balasubramanian, *J. Mol. Spectrosc.* **115**, 258 (1986); (b) D. Dai and K. Balasubramanian, *J. Chem. Phys.* **93**, 1837 (1990); (c) A. B. Alekseyev, R. J. Buenker, H. Liebermann, and G. Hirsch, *ibid.* **100**, 2989 (1994).
- ⁵³K. Sumati and K. Balasubramanian, *J. Chem. Phys.* **92**, 6604 (1990).