

The *ab initio* model potential method. Second series transition metal elements

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The *ab initio* core method potential model (AIMP) has already been presented in its nonrelativistic version and applied to the main group and first series transition metal elements [J. Chem. Phys. **86**, 2132 (1987); **91**, 7011 (1989)]. In this paper we extend the AIMP method to include relativistic effects within the Cowan–Griffin approximation and we present relativistic Zn-like core model potentials and valence basis sets, as well as their nonrelativistic Zn-like core and Kr-like core counterparts. The pilot molecular calculations on YO, TcO, AgO, and AgH reveal that the *4p* orbital is indeed a core orbital only at the end part of the series, whereas the *4s* orbital can be safely frozen from Y to Cd. The all-electron and model potential results agree in 0.01–0.02 Å in R_e and 25–50 cm^{−1} in $\bar{\nu}_e$ if the same type of valence part of the basis set is used. The comparison of the relativistic results on AgH with those of the all-electron Dirac–Fock calculations by Lee and McLean is satisfactory: the absolute value of R_e is reproduced within the 0.01 Å margin and the relativistic contraction of 0.077 Å is also very well reproduced (0.075 Å). Finally, the relative magnitude of the effects of the core orbital change, mass–velocity potential, and Darwin potential on the net relativistic effects are analyzed in the four molecules studied.

I. INTRODUCTION

In previous papers,^{1,2} we have presented the *ab initio* model potential method (AIMP) for valence-electron molecular calculations. In the method, which makes use of valence orbitals showing the correct nodal structure, (i) the atomic core (local) Coulomb and (nonlocal) exchange and projection operators are obtained directly from the all-electron atomic core orbitals, and (ii) the atomic valence basis set is optimized according to the variational principle. As it does not make use of any *valence* reference orbitals, it can be applied to obtain complete-ion potentials, which turns it into a useful tool to represent, as well, crystal lattices in solid state calculations.³

We have presented the nonrelativistic core model potentials and valence basis sets for the main group elements up to Xe in Ref. 1, and for the first series transition metal elements in Ref. 2, together with pilot molecular calculations.

It is now well known that the relativistic effects on the second series transition metal elements, not being enormous, are not negligible. These effects are often taken into account in valence electron calculations (both in model potential⁴ and pseudopotential methods^{5–8}) through the use of one-component approaches (Cowan–Griffin like). Reviews on this subject are available in the literature.^{7,9,10}

In this paper, we extend the AIMP method to include relativistic effects within the Cowan–Griffin approximation¹¹ in a manner proposed in Ref. 12, so that an *explicit* representation of the valence mass–velocity and Darwin relativistic potentials is used (in contrast with other one-component model potential⁴ or pseudopotential methods^{5–8}) and, therefore, the physical effects of these relativistic terms may be visible. We present core-*4p* (Kr-like) nonrelativistic

and core-*3d* (Zn-like) nonrelativistic and Cowan–Griffin-relativistic potentials and valence basis sets for the second series transition metal elements, of which recent tabulations of parameters exist for other model potential methods,¹³ as well as for pseudopotential methods.¹⁴

Finally, we show the results of all-electron, AIMP, and Cowan–Griffin–AIMP Hartree–Fock–Roothaan atomic and molecular calculations (YO, TcO, AgO, and AgH) performed in order to assess the quality of the potentials and basis sets and to decide upon a proper choice of core–valence partition and basis set structure for molecular calculations, so that the objective of reproducing the all-electron results if the same kind of wave function and valence basis set is used can be reached. We also present the analysis of the contributions to the net relativistic effect (core change, mass–velocity potential, and Darwin potential) on the equilibrium distance of the four molecules. In the case of AgH, we compare the relativistic effect on R_e with that corresponding to the all-electron calculation by Lee and McLean.¹⁵

II. METHOD

The nonrelativistic version of the AIMP method, as applied to the valence electrons of a molecule, has already been described in Refs. 1 and 2. In the Cowan–Griffin relativistic extension of the AIMP method, the one-electron contributions to the MP Hamiltonian for the valence electrons of a molecule result from the addition of the mass–velocity and Darwin potentials to the nonrelativistic ones:^{2,12}

$$h(i) = -\frac{1}{2} \Delta_i - \sum_j \frac{Z^j - Z_{\text{core}}^j}{r_{ij}}$$

$$+ \sum_I [V_{\text{coul}}^I(i) + V_{\text{exch}}^I(i) + V_{\text{MV}}^I(i) + V_{\text{DW}}^I(i) + P^I(i)], \quad (1)$$

where I runs over the nuclei.

The mass-velocity and Darwin potentials, $V_{\text{MV}}^I(i)$ and $V_{\text{DW}}^I(i)$, are local operators defined as¹²

$$V_{\text{MV,DW}}^I(i) = \sum_k V_{\text{MV,DW}}^k(i), \quad (2)$$

where $V_{\text{MV,DW}}^k(i)$ is the mass-velocity or the Darwin potential associated to the k th atomic orbital,^{11,12} and k runs over the valence orbitals of atom I .¹² A nonlocal spectral representation of the same type as the one used for the exchange potential^{1,2} is used for these operators, so that

$$V_{\text{exch}}^I(i) + V_{\text{MV}}^I(i) + V_{\text{DW}}^I(i) \simeq \sum_I \sum_{m=-l}^l \sum_{a,b} |alm;I\rangle A_{kab}^I \langle blm;I|, \quad (3)$$

where the $\{|alm;I\rangle\}$ are the spherical primitive Gaussian-type functions in the molecular basis set which are centered on I , and the coefficients A_{kab}^I are the elements of the matrix

$$A^I = (S^I)^{-1} V_{\text{EMD}}^I (S^I)^{-1}, \quad (4)$$

where

$$S_{ij}^I = \langle i;I | j;I \rangle, \\ V_{\text{EMD},ij}^I = \langle i;I | V_{\text{exch}}^I + V_{\text{MV}}^I + V_{\text{DW}}^I | j;I \rangle, \quad (5)$$

$|i;I\rangle$, $|j;I\rangle$ being functions of the set $\{|alm;I\rangle\}$.

In order to obtain all the potentials and basis sets of the method one proceeds as follows. First, an all-electron Cowan-Griffin-Hartree-Fock calculation is performed for each atom I , from which the numerical core orbitals and the numerical mass-velocity and Darwin potentials, Eq. (2), are selected. The core orbitals are used to produce the (local, radial) core Coulomb potential $V_{\text{Coul}}^I(i)$, which is approximated by an analytical form whose parameters and determined through a least-squares fitting.^{1,2} Also, the numerical core orbitals are represented by linear combinations of GTF's (using a maximum overlap criterion¹⁶) which are finally used to obtain the core projection operators $P^I(i)$,^{1,2} and to define the core exchange operators $V_{\text{exch}}^I(i)$.^{1,2} Thereby, all these three nonrelativistic operators [$V_{\text{Coul}}^I(i)$, $P^I(i)$, and $V_{\text{exch}}^I(i)$] bring already indirect relativistic effects to the molecular valence, due to the relativistic core orbital change.

Once a basis set is chosen for the molecular calculation, the spectral representation of the core exchange, mass-velocity, and Darwin potentials, Eq. (3) is obtained using Eqs. (4) and (5), so that, whatever the basis set is, it is always guaranteed that

$$\langle i;I | V_{\text{exch}}^I + V_{\text{MV}}^I + V_{\text{DW}}^I | j;I \rangle = \langle i;I | V_{\text{exch}}^I + V_{\text{MV}}^I + V_{\text{DW}}^I | j;I \rangle. \quad (6)$$

Finally, as the atomic core operators are already well defined and none of them needs to be parameterized in a valence-electron atomic calculation, the atomic valence basis set is obtained by minimization of the valence energy, so

that the atomic model potential problem mimics the one of optimization of all-electron basis sets.

We may remark here that, although the mass-velocity and Darwin potentials are local and could have been treated in the same way as the Coulomb potential, they show singularities which are difficult to represent by an analytical form. Alternatively, when their spectral representation is used as in Eq. (3), they are easily and accurately handled along the numerical integration procedure involved in Eq. (5). On the other hand, these potentials are so internal that their contribution in the molecular environment is expected to be significant only through the one-center valence integrals, whose calculation is exact in the present method.

In the Cowan-Griffin approach to the relativistic valence-electron calculations the net relativistic effects may be seen as due, first, to the indirect effects of the changes in the core orbitals, and, second, to the direct effects of the mass-velocity and Darwin potentials. In the AIMP method, the latter effects are brought *explicitly* to the molecular calculation by the $V_{\text{MV,MP}}^I$ and $V_{\text{DW,MP}}^I$ operators. This feature contrasts with relativistic versions of other effective core, model, or pseudopotential methods,¹⁰ which include the mass-velocity and Darwin effects *indirectly* through the parametrization of their potentials so as to reproduce relativistic reference all-electron results.¹⁰ As a consequence of the explicit appearance of mass-velocity and Darwin operators in the molecular model potential Hamiltonian, their separate contributions to the net relativistic effects can be calculated, thus bringing about more insight to the study of relativistic effects on molecules at the present level of approximation.

It is known that the spin-orbit interaction, not included in the Cowan-Griffin approximation, may produce important effects in molecules containing the second transition metal atoms. Although we report results without the spin-orbit effects in the present paper, work is underway to include them in molecular calculations. A precursor of the work was already published,¹² where one can see that the spin-orbit term can be handled in a similar fashion as the Darwin term as far as the spectral representation is concerned. A full theoretical exposition of the treatment of the spin-orbit interaction will soon be published elsewhere.

III. MODEL POTENTIALS, BASIS SETS, AND ATOMIC RESULTS

Core-4p (Kr-like) and core-3d (Zn-like) pseudopotentials¹⁴ and model potentials¹³ which include mass-velocity and Darwin relativistic effects into the potentials have recently been published for the second series transition metal elements. In this section we present the Cowan-Griffin-relativistic Zn-like core model potentials and their corresponding 5s,4p,4d-valence Gaussian basis sets. Although these are recommended for use in actual molecular calculations, we also present the nonrelativistic Zn-like (core-3d) and Kr-like (core-4p) model potentials and basis sets, which are useful to analyze the magnitude of the relativistic effects on the calculated properties, as well as the degree of 4p participation on the bonding.

We have used the *well-tempered* core orbitals,¹⁷ which are very close to the HF limit, in the nonrelativistic calcula-

TABLE I. Coulomb model potential parameters^a corresponding to the Cowan–Griffin-relativistic Zn-like core.

Yttrium		Zirconium		Niobium		Molybdenum	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
300200.00	0.36161043	289700.00	0.37635150	308700.00	0.37491330	315500.00	0.38413670
38340.000	0.50753727	38460.000	0.51422377	41490.000	0.50729089	41530.000	0.52783805
8044.0000	0.96748213	8271.0000	0.97145684	8990.0000	0.95613142	8885.0000	1.0002681
2116.0000	1.6465543	2213.0000	1.6399047	2416.0000	1.6160665	2373.0000	1.6719229
627.40000	2.0927883	665.20000	2.0782918	732.50000	2.0549767	714.80000	2.0956825
184.20000	3.6211706	197.00000	3.6009954	219.00000	3.4425075	215.40000	3.6365420
72.530000	4.7194938	77.600000	4.7505175	86.070000	4.8665826	86.370000	4.6901237
18.910000	5.1245000	20.400000	5.0692785	23.350000	4.6086639	23.050000	5.1128259
8.4300000	8.1992249	9.1580000	8.2866049	10.324000	8.7055327	10.582000	8.2629732
2.6610000	1.8695425	2.8550000	1.8575239	3.3360000	1.9447878	3.2760000	1.8027443
1.0059000	0.89009579	1.0905000	0.85485116	1.2363000	0.92254679	1.3044000	0.81494263
Technetium		Ruthenium		Rhodium		Palladium	
α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$	α_k	$-A_k$
309200.00	0.39446533	327700.00	0.39317233	342900.00	0.39515183	328700.00	0.41114301
42870.000	0.52223887	46000.000	0.51475457	48160.000	0.51712197	47790.000	0.52508622
9463.0000	0.98094412	10270.000	0.95982829	10757.000	0.96368997	10906.000	0.97240638
2572.0000	1.6393051	2820.0000	1.6040708	2959.0000	1.6031263	3037.0000	1.6105867
784.90000	2.0707601	864.90000	2.0683157	915.00000	2.0505859	942.80000	2.0590086
237.40000	3.5158933	258.90000	3.4573391	277.20000	3.3962405	286.30000	3.4529484
94.590000	4.8082851	102.16000	4.8910938	109.50000	4.9271672	113.69000	4.8914501
25.550000	4.8643921	28.010000	4.6412239	30.540000	4.4597899	31.490000	4.6197064
11.615000	8.5325621	12.675000	8.7473719	13.743000	8.9256436	14.424000	8.7919767
3.6460000	1.8257324	4.0190000	1.8591637	4.4000000	1.8802679	4.5340000	1.8296397
1.4626000	0.84542156	1.5761000	0.86366598	1.7146000	0.88121480	1.8175000	0.83604790
Silver		Cadmium					
α_k	$-A_k$	α_k	$-A_k$				
339100.00	0.41669021	369100.00	0.40781578				
48800.000	0.53662116	54100.000	0.51736462				
11082.000	0.99211192	12511.000	0.94368972				
3087.0000	1.6335397	3528.0000	1.5692043				
957.80000	2.0723108	1106.5000	2.0267667				
292.60000	3.5236858	338.90000	3.2642283				
117.30000	4.8276352	133.01000	5.0332102				
32.260000	4.8260876	38.590000	4.0757763				
15.067000	8.6015801	17.109000	9.2935898				
4.6500000	1.7822352	5.6730000	1.9267633				
1.9168000	0.78750224	2.1994000	0.94159100				

^a See Eq. (5) in Ref. 2.

tions, and the Cowan–Griffin–Hartree–Fock numerical core orbitals in the relativistic calculations, to generate, respectively, the numerical core Coulomb potentials, to which the parameters of the local Coulomb model potentials have been fitted. In Table I we show the local Coulomb model potential parameters corresponding to the CG-relativistic Zn-like cores. The nonrelativistic Zn-like and Kr-like core Coulomb model potential parameters are deposited in PAPS.²²

Whereas we have used directly the *well-tempered* core orbitals to construct the core projection and exchange operators of the nonrelativistic calculations, we have used a set of linear combinations of GTF's which maximizes the overlap with the numerical core orbitals in the CG-relativistic calculations. The nonlocal spectral representation parameters $A_{k,ab}^I$ [Eq. (3)] to expand the exchange, mass-velocity, and

Darwin operators are actually computed along the input processing part of the molecular calculations [Eqs. (4) and (5)]. The necessary core orbitals, mass-velocity, and Darwin potentials are available from the authors upon request.

The valence basis sets have been optimized by minimizing the valence energy following the procedure described in Ref. 18. We present in Table II the basis sets corresponding to the CG-relativistic core-3*d* calculation (see the PAPS document²² for the nonrelativistic core-3*d* and core-4*p* valence basis sets.) They show the pattern ($11_{32222}/7_{322}/6_{33}$), which is of the same type as that shown to be optimum for the main group elements¹ and for the first series transition metal elements,² and performs with the same degree of quality in the second series transition metal elements.

In Table III we show some properties of the atomic valence orbitals of the CG-relativistic Zn-like core calculation

TABLE II. 5s, 4p, 4d-valence Gaussian basis sets corresponding to the Cowan-Griffin-relativistic Zn-like core (core-3d).

Y ($4p^6 5s^2 4d^1 -^2D$)		Zr ($4p^6 5s^1 4d^3 -^5F$)		Nb ($4p^6 5s^1 4d^4 -^6D$)		Mo ($4p^6 5s^1 4d^5 -^7S$)	
exp. 5s	coeff. 5s	exp. 5s	coeff. 5s	exp. 5s	coeff. 5s	exp. 5s	coeff. 5s
11780.2662	0.00065384	12534.5414	0.00066496	13656.7183	0.00067821	14940.0069	0.00067869
1581.69839	0.00454821	1672.80424	0.00462836	1809.43728	0.00472766	1969.95797	0.00471903
332.974413	0.01479512	352.649739	0.01491487	375.367370	0.01568872	401.195672	0.01627613
32.4650695	-0.06396744	33.9408952	-0.06725853	36.7017101	-0.06476796	37.9522863	-0.07110841
14.5811121	-0.03053400	13.7957748	-0.03571432	17.9635448	-0.03452656	17.3563545	-0.03173252
5.54182585	0.12161368	6.15773318	0.13191017	7.06053734	0.08817658	6.72182947	0.13859899
2.71820263	0.16679999	2.80085901	0.18498994	3.65646686	0.20194328	3.31913157	0.18911073
0.907197762	-0.12602818	1.12319133	-0.21172274	1.06578829	-0.22167174	1.36785764	-0.21557098
0.397147199	-0.44199286	0.451729203	-0.45097476	0.494427919	-0.41642680	0.572170827	-0.44775703
0.062871887	0.72485393	0.065733701	0.74494751	0.074051050	0.73008737	0.080741388	0.71981703
0.025450320	0.44979718	0.026958382	0.41893601	0.029688040	0.43469910	0.031770005	0.44042932
exp. 4p	coeff. 4p	exp. 4p	coeff. 4p	exp. 4p	coeff. 4p	exp. 4p	coeff. 4p
770.318062	0.00626204	820.168403	0.00645540	871.080891	0.00667409	924.704567	0.00685506
176.680046	0.03967012	187.925799	0.04101424	199.466492	0.04248004	211.562838	0.04373173
54.0522429	0.09844198	57.5119071	0.10224286	61.0822841	0.10629979	64.8011398	0.10992469
8.30517594	-0.19273666	8.88077680	-0.19848005	9.45214111	-0.20711744	10.322874	-0.21545805
4.34961391	-0.23410417	4.75270131	-0.24003354	5.14569959	-0.24500903	5.55190594	-0.24813932
0.820300219	0.66534536	0.910525377	0.67530293	1.00892759	0.68474898	1.11047044	0.69161432
0.298820800	0.45126954	0.327317643	0.44490891	0.363891758	0.43764436	0.401272360	0.43279482
exp. 4d	coeff. 4d	exp. 4d	coeff. 4d	exp. 4d	coeff. 4d	exp. 4d	coeff. 4d
79.6796461	-0.01365379	87.4766079	-0.01362752	95.2093984	-0.01472309	102.967178	-0.01558474
22.2810660	-0.06537182	24.5425173	-0.06643514	26.7851449	-0.07280605	29.0552743	-0.07788954
7.26689490	-0.11401089	8.06862451	-0.11812952	8.87096074	-0.13096854	9.69215797	-0.14138588
0.854645719	0.31866073	0.967773776	0.32878415	1.11198777	0.34902455	1.26047835	0.36373377
0.286965621	0.53043774	0.320984125	0.52203903	0.381098069	0.52301213	0.443207746	0.52255657
0.088778119	0.37608206	0.096488216	0.38425298	0.117214128	0.35219260	0.139247361	0.32823507
Tc ($4p^6 5s^2 4d^5 -^6S$)		Ru ($4p^6 5s^1 4d^7 -^5F$)		Rh ($4p^6 5s^1 4d^8 -^4F$)		Pd ($4p^6 5s^1 4d^9 -^3D$)	
exp. 5s	coeff. 5s	exp. 5s	coeff. 5s	exp. 5s	coeff. 5s	exp. 5s	coeff. 5s
15850.4115	0.00069333	16917.1525	0.00066850	18024.0258	0.00065655	19143.6182	0.00064447
2073.69243	0.00483219	2197.22508	0.00466413	2323.24549	0.00458702	2452.84267	0.00449570
423.482517	0.01645708	447.469418	0.01587044	471.182855	0.01560444	496.223753	0.01528192
40.1809033	-0.07104198	42.1136456	-0.06995294	44.2395297	-0.07060209	46.6919230	-0.06818066
20.0067237	-0.02978070	20.5279218	-0.02833839	18.2329916	-0.03985876	21.0829589	-0.03327044
6.70380015	0.16068138	7.27416070	0.14712323	9.28518095	0.10749504	9.63844398	0.09587806
3.38757955	0.16925086	3.82240028	0.16107510	4.76860067	0.19138292	5.12848505	0.19037347
1.44843305	-0.23380482	1.497823475	-0.23084413	1.50877278	-0.22737821	1.66291793	-0.21599388
0.617225332	-0.42935464	0.650737763	-0.38429023	0.685153174	-0.34939262	0.738897076	-0.34001748
0.089603795	0.68815474	0.088521508	0.67239274	0.091275177	0.65387103	0.093146798	0.64114707
0.034170299	0.47350877	0.033634177	0.47527453	0.034187840	0.48747715	0.034512530	0.49326093
exp. 4p	coeff. 4p	exp. 4p	coeff. 4p	exp. 4p	coeff. 4p	exp. 4p	coeff. 4p
981.542305	0.00706067	1040.33483	0.00715149	1102.08983	0.00726836	1162.56250	0.00740512
224.314339	0.04517458	237.355925	0.04589834	251.047374	0.04679569	264.618772	0.04771538
68.6934345	0.11418263	72.6632972	0.11652112	76.8127426	0.11942489	80.9850891	0.12209085
10.5688756	-0.23088565	11.2101872	-0.23396384	11.8036872	-0.24423992	12.4718803	-0.25009835
5.90294343	-0.24841239	6.38260303	-0.24975775	6.80386691	-0.24782339	7.28442623	-0.24909431
1.22645406	0.69815279	1.32555466	0.70302549	1.43845679	0.70714665	1.55301271	0.71117789
0.453639428	0.42731969	0.481932772	0.42476801	0.523883821	0.42223970	0.566306773	0.41926251
exp. 4d	coeff. 4d	exp. 4d	coeff. 4d	exp. 4d	coeff. 4d	exp. 4d	coeff. 4d
110.911794	-0.01725209	120.225274	-0.01649033	129.145664	-0.01681894	138.306748	-0.01708038
31.3632828	-0.08711680	34.0776379	-0.08446675	36.6806282	-0.08701090	39.3568728	-0.08915482
10.5265109	-0.15904244	11.4948673	-0.15729715	12.4342250	-0.16371792	13.4025525	-0.16932397
1.44120907	0.38414727	1.56613219	0.38663330	1.72780654	0.39468819	1.89538692	0.40124768
0.539232564	0.52481890	0.559274043	0.51718983	0.621745783	0.51500753	0.686671400	0.51301841
0.184092788	0.27519335	0.175251696	0.30649965	0.195665629	0.29762940	0.217061028	0.29033881

TABLE II. (continued).

Ag ($4p^6 5s^1 4d^{10} -^2S$)		Cd ($4p^6 5s^2 4d^{10} -^1S$)	
exp. 5s	coeff. 5s	exp. 5s	coeff. 5s
20518.7576	0.00062342	21853.9859	0.00071005
2606.72686	0.00435866	2756.32757	0.00496431
524.126130	0.01489322	551.708077	0.01699357
48.3722585	-0.06985278	50.6669016	-0.08048639
18.1503520	-0.04417226	18.7257132	-0.04981317
10.0265741	0.13650541	10.2350178	0.17293228
4.85513422	0.17332172	4.77412343	0.20764320
1.90540673	-0.21700202	2.30791002	-0.23452406
0.792355078	-0.33363248	0.928496395	-0.41489234
0.094683496	0.62802013	0.120852304	0.66011365
0.034768884	0.50018728	0.043704482	0.48822877
exp. 4p	coeff. 4p	exp. 4p	coeff. 4p
1224.63380	0.00753393	1291.79120	0.00768313
278.575791	0.04856124	293.449018	0.04961997
85.2836700	0.12454851	89.7989154	0.12778631
13.1491515	-0.25636850	13.7617489	-0.27195177
7.77386076	-0.24918153	8.16959841	-0.24472951
1.67104585	0.71449123	1.80674425	0.71933834
0.609777321	0.41694449	0.671231599	0.41284902
exp. 4d	coeff. 4d	exp. 4d	coeff. 4d
147.700857	-0.01730358	157.042192	-0.01814366
42.1017332	-0.09105234	44.8325831	-0.09607942
14.3971750	-0.17437782	15.3950791	-0.18479539
2.06877596	0.40679009	2.27686900	0.41614776
0.754732186	0.51126127	0.860131528	0.51075031
0.240166827	0.28349105	0.289845470	0.25577412

TABLE III. Valence energy, projection energy, orbital energies, and radial expectation values for the second series transition metal elements, corresponding to the Cowan-Griffin-relativistic Zn-like core calculations. The all-electron results (second entry) correspond to numerical Cowan-Griffin-Hartree-Fock calculations. All numbers in atomic units.

	$E(\text{val})$	$E(\text{proj})$	$-\epsilon(5s)$	$-\epsilon(4p)$	$-\epsilon(4d)$	5s			4p			4d		
						$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
Y $s^2 d^1 -^2D$	-23.810617	0.000566	0.19978 0.20132	1.30337 1.30505	0.23061 0.23152	0.295 0.298	4.231 4.211	20.470 20.293	0.900 0.899	1.461 1.462	2.441 2.451	0.530 0.530	2.495 2.513	7.575 7.770
Zr $s^1 d^3 -^5F$	-30.308867	0.001102	0.21394 0.21696	1.40097 1.40486	0.23619 0.23901	0.307 0.312	4.062 4.035	18.859 18.643	0.953 0.952	1.386 1.387	2.199 2.208	0.564 0.565	2.368 2.386	6.887 7.081
Nb $s^1 d^4 -^6D$	-37.926673	0.001532	0.22550 0.22874	1.57543 1.57948	0.28422 0.28732	0.324 0.331	3.862 3.836	17.086 16.891	1.010 1.009	1.312 1.313	1.970 1.977	0.636 0.637	2.099 2.111	5.389 5.509
Mo $s^1 d^5 -^7S$	-46.775346	0.002140	0.23427 0.23762	1.74752 1.75164	0.33917 0.34236	0.339 0.346	3.707 3.683	15.786 15.608	1.066 1.063	1.247 1.248	1.782 1.788	0.702 0.703	1.898 1.906	4.387 4.465
Tc $s^2 d^5 -^6S$	-56.769672	0.001704	0.23886 0.24098	2.06376 2.06568	0.51423 0.51553	0.352 0.355	3.586 3.568	14.817 14.681	1.129 1.126	1.181 1.182	1.594 1.598	0.803 0.805	1.641 1.643	3.217 3.241
Ru $s^1 d^7 -^5F$	-68.159243	0.002065	0.23448 0.23859	2.13750 2.14325	0.38926 0.39369	0.351 0.357	3.587 3.557	14.877 14.650	1.176 1.173	1.137 1.138	1.480 1.484	0.814 0.815	1.646 1.653	3.304 3.361
Rh $s^1 d^8 -^4F$	-81.008407	0.002356	0.23383 0.23814	2.33481 2.34118	0.42410 0.42897	0.356 0.361	3.547 3.515	14.595 14.347	1.229 1.226	1.090 1.091	1.361 1.365	0.868 0.869	1.546 1.551	2.910 2.957
Pd $s^1 d^9 -^3D$	-95.403439	0.002782	0.23333 0.23778	2.53589 2.54280	0.46131 0.46652	0.359 0.365	3.514 3.479	14.359 14.092	1.282 1.278	1.048 1.048	1.257 1.260	0.921 0.921	1.458 1.464	2.589 2.629
Ag $s^1 d^{10} -^2S$	-111.471050	0.003346	0.23246 0.23695	2.73825 2.74553	0.50605 0.51147	0.362 0.367	3.489 3.453	14.198 13.915	1.335 1.330	1.009 1.010	1.165 1.168	0.972 0.973	1.381 1.385	2.317 2.350
Cd $s^2 d^{10} -^1S$	-129.037681	0.004246	0.27783 0.28129	3.11619 3.12000	0.71891 0.72116	0.407 0.412	3.111 3.090	11.242 11.101	1.396 1.390	0.967 0.967	1.068 1.071	1.054 1.055	1.263 1.266	1.916 1.931

TABLE IV. Excitation energy from the lowest states of the $5^1 4d^{n+1}$ configurations to the lowest states of the $5s^2 4d^n$ and $4d^{n+2}$ configurations. All the basis sets have a single splitting in the s and d symmetries and include one d -diffuse function (Ref. 19). The AIMP results correspond to the Zn-like core calculations. All numbers in eV.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
$5s^2 4d^n$ configurations									
Numerical all-electron nonrelativistic HF	-0.42	0.40	1.24	2.89	-0.20	1.42	2.19	3.01	4.91
Nonrelativistic AIMP	-0.49	0.46	1.32	2.98	-0.26	1.49	2.28	3.11	5.05
Numerical all-electron CG-relativistic HF	-0.75	0.01	0.80	2.37	-0.75	0.74	1.40	2.09	3.86
CG-relativistic AIMP	-0.80	0.06	0.87	2.45	-0.79	0.82	1.50	2.22	4.03
Numerical all-electron CG-relativistic effect	-0.33	-0.39	-0.44	-0.52	-0.55	-0.68	-0.79	-0.92	-1.05
AIMP CG-relativistic effect	-0.31	-0.40	-0.45	-0.53	-0.53	-0.67	-0.78	-0.89	-1.02
$4d^{n+2}$ configurations									
Numerical all-electron nonrelativistic HF	2.31	2.11	1.17	3.92	2.43	1.69	0.95	-0.75	
Nonrelativistic AIMP	2.41	2.17	1.25	3.97	2.59	1.77	1.01	-0.70	
Numerical all-electron CG-relativistic HF	2.57	2.45	1.61	4.36	2.94	2.24	1.54	-0.10	
CG-relativistic AIMP	2.65	2.49	1.65	4.39	3.06	2.29	1.58	-0.06	
Numerical all-electron CG-relativistic effect	0.26	0.34	0.44	0.44	0.51	0.55	0.59	0.65	
AIMP CG-relativistic effect	0.24	0.32	0.40	0.42	0.47	0.52	0.57	0.64	

and their comparison with the corresponding all-electron CG-HF results.

In Table IV we present the results of nonrelativistic and CG-relativistic $5s-4d$ excitation energies calculated in order to assess the ability of the method to reproduce the behavior of the all-electron results, (i) when an important deformation of the valence orbitals takes place, and (ii) when the relativistic effects are taken into account. As it can be observed, the size of the error is acceptable both for the one-electron and the two-electron excitations. Moreover, the errors in the CG-relativistic and in the nonrelativistic calculations are systematically close, so that the relativistic effect on the excitation energies is calculated better than the excitation energies themselves.

IV. MOLECULAR CALCULATIONS

The results of RHF molecular calculations carried out in order to test, first, the performance of the method in molecules containing second series transition metal elements, and second, its ability to represent genuine relativistic effects, are

presented in this section. We present equilibrium distances R_e and vibrational frequencies $\bar{\nu}_e$ for the ground states of YO, TcO, AgO, and AgH, calculated using the potentials and basis sets already described (for O those of Ref. 1). We compare the nonrelativistic results with those of equivalent all-electron calculations using basis sets whose valence part has a similar quality. In the case of AgH we compare our relativistic results with those of all-electron Dirac-Fock calculations.¹⁵ The molecular basis sets used are described in Table V and the results are presented in Table VI.

First of all, the nonrelativistic calculations corresponding to Kr-like cores, MP-4p, and Zn-like cores, MP-3d, using the same basis set as in the all-electron calculation, AE, reveal that the 4p orbital is a true core orbital only at the end part of the row, as it happened before with the 3p orbital in the first series transition metal elements.² So, whereas freezing the Ag 4p orbital in AgO still provides very close results to the all-electron ones, it rises the errors to 0.03 Å in R_e and 50 cm⁻¹ in $\bar{\nu}_e$ in TcO, and to the unacceptable values of 0.16 Å in R_e and 180 cm⁻¹ in $\bar{\nu}_e$ in YO. On the other hand, the good results of all the Zn-like core calculations support the

TABLE V. Basis sets used in the molecular calculations on YO, TcO, AgO, and AgH.^a

Basis set label	Y, Tc, Ag	O	H
AE	(433321/4331*/421)	(521/41)	
(32...)	(322211/3221*/321)	(41/41)	(411/1*1*)
MP	(10,1/521*/51)	(41/41)	(411/1*1*)

^a The AE basis sets and all the polarization functions were taken from Refs. 18 and 20.

systematic freezing of the 4s orbitals (and, of course, of the 3d orbitals). It is for this reason that we propose the use of the MP-3d potentials and basis sets in actual molecular calculations.

The MP-3d results keep close to the AE ones when the AE basis sets are substituted by the (32...) basis sets, which are the model potential basis sets showing a contraction scheme that provides a high flexibility in the inner parts and, so, a high degree of core–valence orthogonality. When the basis set is finally contracted (basis set MP) the results still keep within the limits of 0.01–0.02 Å in R_e , and 40 cm^{−1} in $\bar{\nu}_e$.

We have also performed CG-relativistic RHF calculations using the (32...) valence basis sets and the final contracted MP basis sets. It can be observed that the effects upon contraction are almost the same as in the nonrelativistic calculations. This means that the relativistic effects are not affected by contraction of the basis sets: They shorten the bond length by 0.05 Å in AgO, by 0.02 Å in TcO, and they rise it in YO by 0.01 Å. Their effect on the vibrational frequency is also opposite in YO, where it is slightly lowered, than in TcO and AgO, where it is slightly raised.

In the AgH molecule we can compare our CG-relativistic R_e using the flexible basis set (32...) with that of the all-

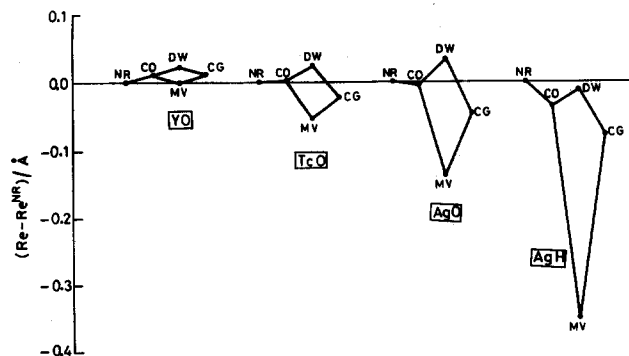


FIG. 1. Analysis of the relativistic effects on the equilibrium distance of YO, TcO, AgO, and AgH. NR: nonrelativistic calculation; CO: the CG-relativistic core orbitals are used, but the mass-velocity and Darwin potentials are omitted; MV: CO, and the mass-velocity potential is included; DW: CO, and the Darwin potential is included; CG: Cowan-Griffin calculation: CO, and the mass-velocity and Darwin potentials are included.

electron Dirac–Fock calculation of Lee and McLean¹⁵ using an STO basis set: both results are 1.697 Å. This coincidence is most probably accidental and we should still think of a range of error of 0.01 Å. What is, perhaps, more important is that our nonrelativistic result is also the same as McLean's,²¹ 1.774 Å, meaning that the relativistic contraction of 0.077 Å is very well reproduced. Upon contraction of the basis sets (basis set MP) the absolute values of R_e are still calculated within the 0.01 Å range and the relativistic contraction of R_e becomes 0.075 Å, more precise than the absolute values of R_e themselves.

Finally, we present in Fig. 1 the results of the analysis of the contributions to the relativistic effects on R_e considered in this work, namely, the *indirect* effects of the changes in the core orbitals, and the *direct* effects of the mass-velocity potential and the Darwin potential. Always referred to the nonrelativistic result, we present the results of the calculations in

TABLE VI. Calculated values of R_e and $\bar{\nu}_e$ for the ground states of YO, TcO, AgO, and AgH.

Molecule	Calculation	$R_e/\text{Å}$ Basis set			$\bar{\nu}_e/\text{cm}^{-1}$ Basis set		
		AE	(32...)	MP	AE	(32...)	MP
YO	Nonrelativistic AE	1.810			923		
	Nonrelativistic MP-4p	1.650			739		
	Nonrelativistic MP-3d	1.803	1.815	1.828	915	891	883
	CG-relativistic MP-3d		1.825	1.840		883	873
TcO	Nonrelativistic AE	1.770			821		
	Nonrelativistic MP-4p	1.741			773		
	Nonrelativistic MP-3d	1.768	1.774	1.775	810	834	843
	CG-relativistic MP-3d		1.754	1.752		884	900
AgO	Nonrelativistic AE	2.149			465		
	Nonrelativistic MP-4p	2.142			470		
	Nonrelativistic MP-3d	2.146	2.157	2.160	467	454	457
	CG-relativistic MP-3d		2.111	2.116		463	468
AgH	Nonrelativistic AE ^a	1.774			1444		
	DF-relativistic AE ^b	1.697					
	Nonrelativistic MP-3d		1.774	1.782		1468	1490
	CG-relativistic MP-3d		1.697	1.707		1603	1623

^a Reference 21, using an STO basis set.

^b Dirac–Fock calculations with an STO basis set, Ref. 15.

which the CG-relativistic core orbitals are used but the mass-velocity and Darwin potentials are omitted (CO), followed by the results when either the mass-velocity (MV) or the Darwin (DW) potential is added, and, finally, the fully CG-relativistic result (CG). We observe that the relative size of the effects is both atom and molecule dependent. In YO, for instance, the decrease on R_e caused by the mass-velocity potential is compensated almost completely by the increase due to the Darwin potential, the final effect being that ascribable to the change in the core orbitals. In AgO, on the other hand, the effect of the core orbital change is null, and the reduction on R_e comes from a balance of the mass-velocity and Darwin effects, in favor of the former. When the Ag atom is in AgH, however, the effect of the core change is significant. Finally, the effect of the mass-velocity and Darwin operators is not, in general, additive; for instance, in AgH, adding the Darwin potential to the Hamiltonian that excludes the mass-velocity potential (CO→DW) produces a slight increase on R_e by 0.02 Å, whereas adding it to the Hamiltonian that already includes the mass-velocity potential (MV→CG) produces a much higher increase on R_e , 0.27 Å.

V. CONCLUSIONS

In this paper we extend the AIMP method to include relativistic effects within the Cowan-Griffin approximation and we present core model potentials and valence basis sets for the second series transition metal elements. The results of pilot molecular calculations on YO, TcO, and AgO reveal that the 4*p* orbital is indeed a core orbital only at the end part of the series, whereas the 4*s* orbital can be safely frozen from Y to Cd. As a consequence, we recommend the use of the relativistic Zn-like core model potentials and basis sets in actual molecular calculations. The nonrelativistic Zn-like core and Kr-like core potentials and basis sets are useful to study the size of the relativistic effects and the 4*p* participation on the bonding.

The applicability of the frozen (Zn-like) core approximation and the quality of the MP-3*d* potentials are such that the molecular results are almost the same in the AE and MP-3*d* calculations if the AE basis set is used. Upon substantial reduction of the molecular basis set the MP-3*d* results agree with those of AE calculations with similar quality in the valence part of the basis set in 0.01 to 0.02 Å in R_e , and 25 to 50 cm⁻¹ in $\bar{\nu}_e$.

The Cowan-Griffin-like approach to the relativistic effects used in the AIMP method reproduces fairly well both the absolute value of R_e in AgH and its relativistic reduction as calculated in the all-electron Dirac-Fock calculation of Lee and McLean.¹⁵ Finally, the characteristics of the meth-

od allow for an analysis of the contributions to the net relativistic effect on R_e of the core orbital changes and the mass-velocity and Darwin potentials. These effects are atom and molecule dependent and are not, in general, additive.

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