

Relativistic CASSCF/CI Calculations: Applications to Transition Metal Dihydrides

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Abstract

A complete active space MCSCF (multi-configuration self-consistent field) scheme (CASSCF) using relativistic effective potentials followed by configuration interaction and relativistic CI calculations provides a very good description of the electronic states and potential energy surfaces of transition metal dihydrides. Such calculations are of considerable value not only in our understanding of the transition metal-hydrogen bonding but also in the prediction of the barrier to insert the metal atom into the H_2 bond. All-electron CASSCF/CI calculations are carried out on twelve electronic states of CoH_2 . Comparable RECP-CASSCF/CI calculations are also carried out to show that the RECP-CASSCF/CI calculations provide an accurate method for the investigation of transition metal compounds. The general method of RECP-CASSCF/CI calculations for molecules containing heavy atoms is described. The calculations on CoH_2 are compared with similar calculations on Sch_2 , YH_2 , PtH_2 , and PdH_2 . A critical comparison of all these transition metal hydrides reveals that in general the low-spin excited metal atom inserts into H_2 spontaneously while the high spin ground state atom has to surmount a large barrier.

Introduction

Electronic structure of clusters and their reactivities with molecules such as H_2 , CO, etc. is a topic of considerable activity in recent years [1–11]. Clusters of transition metal atoms are useful models of surfaces and thus the investigation of the electronic properties of such clusters could provide significant insight into the electronic properties of metal surfaces and their reactivities with molecules such as CO, H_2 , etc. Surfaces can also be modeled by a semi-infinite slab and one can adapt the band theory to discuss the electronic properties of these systems. However, such calculations have to be approximate or at a semi-empirical level [12] than more rigorous *ab initio* calculations including electron correlations.

Smalley and coworkers [1, 2] have investigated recently the reactivities of cobalt, iron, nickel, niobium clusters as a function of cluster size with D_2 , N_2 , and CO using a new fast-flow chemical reactor scheme. Their investigations have revealed dramatic size dependence of reactivities of these clusters. For example, consider the dissociative chemisorption of D_2 with Co clusters and Nb clusters. The Co atom and Co_2 molecule do not react with D_2 , Co_3 – Co_5 react completely, Co_6 – Co_9 show little or no reactivity, and clusters of larger size react well. The niobium clusters exhibit a similar behavior. The CO chemisorption also exhibits a similar size dependence. It is not

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certain whether this is a kinetic effect associated with the short lifetimes of the complex or inherent unreactivities of these species.

Theoretical study of transition metal dihydrides and their potential energy surfaces could provide very valuable information on the nature of the metal- H_2 bonding and the reactivity of the metal atom with H_2 . In an unpublished investigation, Fox, Lee and Schaefer [13] have used SCF/CI all-electron methodology to study the properties of the first-row transition metal dihydrides. Here we compare their results for CoH_2 and ScH_2 with our CASSCF/CI calculations. Siegbahn, Blomberg, and Bauschlicher [14] have carried out calculations on the bending potential energy surfaces of CoH_2 , FeH_2 , and CuH_2 with a somewhat smaller basis set in comparison to the one used here for CoH_2 .

The objective of the present investigation is to develop a comprehensive understanding of the nature of the metal- H_2 bonding and potential energy surfaces of transition metal hydrides as well as to demonstrate the use of relativistic effective core potentials in relativistic CASSCF/CI calculations. This manuscript contains both the results of new calculations on CoH_2 and comparison with results obtained before for other systems for a comprehensive understanding of the transition metal-hydrogen bonding. For CoH_2 , we present unpublished all-electron CASSCF/MRSDCI calculations using large gaussian basis sets and comparative RECP-CASSCF/MRSDCI calculations.

The general area of relativistic quantum chemistry and applications to molecules containing very heavy atoms have been reviewed by many workers before [15–23]. The readers are directed to these reviews for many details not considered in the present article.

Methods

In recent years, Ermler and coworkers [24–26] have published the averaged relativistic effective potentials and the spin-orbit operators in a gaussian expansion form for many elements in the periodic table.

Balasubramanian and coworkers [27–45] have demonstrated that RECPs, when used properly in conjunction with large-scale CASSCF/CI/RCI calculations, can yield very good results for potential energy surfaces, spectroscopic constants, dipole, and transition moments [46–48] of many molecules. We will briefly summarize the general philosophy of the relativistic CASSCF and CI methods.

Nonrelativistic CASSCF method has been discussed by Roos [49] in a recent review article. In the complete active space MCSCF method, shortly abbreviated as CASSCF, one optimizes a multiconfiguration selfconsistent field wavefunction in a complete configuration space of the most important orbitals referred to as the internal or active space. The internal space is usually chosen as the valence orbitals of the separated atoms. The active electrons are distributed in all possible ways among the chosen set of internal space of orbitals. The MCSCF wavefunction is optimized in this space. Thus, the orbitals are fully optimized in the zeroth-order most important space. The CASSCF method includes the zeroth-order correlation effects. Although the CASSCF is accurate to only this order, it provides reasonable results for many molecules in the main group. The CASSCF orbitals are normally used as the starting orbitals for more accurate CI calculations. The CASSCF method is the only method that provides reasonable start-

ing point for transition states in potential energy surfaces. For transition metal compounds due to large degree of correlation effects, CASSCF is the best way to obtain orbitals for CI calculations.

I [27] have modified nonrelativistic CASSCF scheme to include relativistic ECPS. In this method, the RECPs obtained from the Dirac-Fock numerical solutions of the atoms are averaged with respect to spin at the CASSCF stage. The RECP integrals without the spin-orbit integrals are then added to the one-electron integrals and CASSCF calculations are carried out. The CASSCF orbitals obtained this way include all relativistic effects except the spin-orbit interaction. The spin-orbit effects are obtained using the relativistic CI method and introduced as corrections to the CI energies and properties obtained without the spin-orbit term.

Configuration interaction calculations are carried out using the CASSCF orbitals. The levels of CI calculations carried out vary depending on the complexity of the problems. The best CI calculation used here is a second-order CI (SOCi) with Davidson's correction for unlinked clusters. The SOCi calculations include (a) all configurations in the zeroth-order CASSCF, (b) configurations obtained by distributing $n-1$ electrons in the internal space and one electron in the orthogonal external space in all possible ways, and (c) configurations obtained by distributing $n-2$ electrons in the internal space and two electrons in the external space in all possible ways, where n is the total number of electrons. The first-order CI (FOCI) calculations include the first two of the configuration set in the SOCi.

The dimensions of the configuration space in the SOCi and FOCI methods can be restricted by choosing the most important reference configurations from the CASSCF. In general, a list of configurations with coefficients ≥ 0.07 or 0.05 is chosen. If one allows all possible single and double excitations from such a reference list the resulting CI is labeled MRSDCI. A subset of MRSDCI that does not include the two electrons in the external space is referred to as POLCI. POLCI includes all single and some important double excitations from the reference configurations.

The CASSCF/CI calculations described are carried out by a modification of the Alchemy II codes to include relativistic effective potentials as described in reference 27. The Alchemy II codes were developed at the IBM Laboratory, San Jose, CA [50].

The relativistic configuration interaction method includes configurations that mix by both correlation and spin-orbit interactions. In the RCI scheme, a list of important configurations for both correlation and spin-orbit contamination are arrived at and then single and double excitations are allowed from these reference configurations. The spin-orbit matrix elements are transformed over MOs and added to the one electron matrix elements at the CI stage. In general, one mixes in RCI all λ -s configurations which have the same Ω symmetry and mix substantially.

RECP-CASSCF/CI calculations for many transition metal hydrides and dihydrides have been performed before. For CoH_2 , new all-electron results for both bent and linear geometries are presented. We also carried out RECP-CASSCF/CI calculations for CoH_2 with a somewhat smaller basis set to compare the geometries of the ECP and all-electron calculations.

Wachters [51] optimized all-electron (14s9p5d) gaussian basis set which is used for the cobalt atom. To the Wachter's set a diffuse d function with $\alpha_d = 0.1219$ was added, as suggested by Hay [52]. This was augmented by two sets of diffuse $4p$ type func-

tions with the exponents determined by Wachters. The 14s functions were contracted to eight functions with the contraction (6, 2, 1, 1, 1, 1, 1). More flexibility was allowed in the *p* and *d* basis in comparison to Wachter's suggested contractions. The 11*p* functions were contracted to 7*p* functions with the (4, 2, 1, 1, 1, 1) contraction. This is different from the Wachter's (4, 2, 1, 2) contraction. Similarly, the 6*d* functions were contracted to four functions with the (3, 1, 1, 1) contraction. The resulting basis set is of the type (14s11*p*6*d* | 8s7*p*4*d*). Van Duijneveldt's [53] (5s | 3s) basis was used for the hydrogen atoms augmented by a *p* function with $\alpha_p = 0.9$. The hydrogen basis exponents were multiplied by a scaling factor of 1.44. This basis set for the hydrogen atom is identical to the one used in SiH₂ calculations by Balasubramanian and McLean [54].

CASSCF calculations were carried out to generate the orbitals for CI calculations. We included five *a*₁ orbitals, two *b*₂ orbitals, one *b*₁, and one *a*₂ orbital in the active space. CASSCF calculations included about 1000 configurations. No excitations were allowed from the 1s, 2s, 2*p*, 3s, and 3*p* orbitals in the all-electron calculations, but the coefficients of these orbitals were allowed to change for all geometries.

Two types of configuration interaction calculations were carried out for the quartet states which are low-lying electronic states of CoH₂. The first CI calculation is called the Restricted First Order CI (RFOCI). The RFOCI calculations included configurations in the CASSCF with coefficients ≥ 0.07 as reference configurations. Configurations included in the RFOCI calculations are generated by distributing 11 electrons in the internal space, and ten electrons in the internal and one electron in the external spaces, respectively, in all possible ways. Then those configurations that differ by no or single internal excitation with respect to the chosen reference configurations in each of the above electronic distributions are selected and included in the RFOCI calculations. The geometries were reoptimized with RFOCI calculations. The RFOCI calculations included about 10,000 configurations. Note that the RFOCI calculations include all single and some most important double excitations from the reference configurations.

The second CI, which we call MRSDCI, included configurations in the CASSCF with coefficients ≥ 0.07 as reference configurations. All possible single and double excitations from these reference configurations were included in the MRSDCI. Thus, the MRSDCI calculations constitute a restricted second order CI. The MRSDCI calculations included about 100,000 configurations for the linear quartet states. We do not reoptimize the bond lengths at MRSDCI level. All MRSDCI calculations were carried out at the optimized CASSCF geometries.

The MOS for the saddle point of the highspin (⁴B₁) state were generated using the Co (⁴F) + H₂ initial guess. Siegbahn, Blomberg, and Bauschlicher [14] have shown that the MOS for the saddle point generated using the dissociated orbitals are slightly better than the linear CoH₂ orbitals as input guess. Our calculations on CoH₂ linear molecule show that the bond lengths calculated by Siegbahn, Blomberg, and Bauschlicher are about 0.05 Å longer than our calculated values, because they use a much smaller basis set. We applied a correction of about 0.05 Å in their calculated CASSCF bond lengths for the ⁴B₁ saddle point. Thus the saddle point calculations were carried out at 1.60 Å (Co-H bond) and 70° (H-Co-H bond angle). We carried out RFOCI and POLCI calculations followed by CASSCF. The POLCI calculations included all configurations in

the MRSDCI except the configurations generated by distributing nine and two electrons in the internal and external spaces, respectively.

Results and Discussion

All-electron, RECP and CASSCF/CI results for CoH₂

Table I shows the geometries and energies of linear and bent states of CoH₂ obtained with the all-electron CASSCF method. The ground state of CoH₂ is found to be of $^4\Phi_g$ symmetry with linear geometry. The equilibrium bond length of the ground state is 1.647 Å at the CASSCF level. The bond length we obtained using the RECPs is 1.643 Å at the CASSCF level. The corresponding value obtained by Siegbahn, Blomberg, and Bauschlicher [14] is 1.683 Å. This difference could be attributed to the smaller basis set they use. For other states in Table I ($^4\Pi_g$, $^4\Sigma_g^-(\text{II})$, $^2\Pi_g$, $^2\Sigma_g^-(\text{II})$, 2A_2 and 2B_1), even CASSCF calculations have not been carried out before. The bent doublet states reported in Table I are more stable in comparison to the corresponding linear states. The 2A_1 and 2B_1 states correlate into the $^2\Delta_g$ linear state while the 2A_2 and 2B_2 states correlate into $^2\Pi_g$. The 2A_1 and 2B_1 states are 0.387 eV and 0.597 eV more stable in comparison to the linear $^2\Delta_g$ state. The 2A_2 (bent) state is 0.689 eV more stable than the (linear) $^2\Pi_g$ state. We also attempted calculations on the 2B_2 state. Our calculations indicated that the $^2\Pi_g$ (linear) state is more stable than the (bent) 2B_2 state and the potential energy surface of 2B_2 is repulsive.

Table II shows the properties of some low-lying linear states of CoH₂ obtained using RFOCI and MRSDCI calculations. As one can see from Table II, the bond lengths

TABLE I. Properties of low-lying states of CoH₂ as obtained by all electron CASSCF.

State	$r(\text{\AA})$	θ	E^a
$^4\Phi_g$	1.647	180	-1382.45298
$^4\Sigma_g^-$	1.633	180	0.26
$^4\Pi_g$	1.651	180	0.44
$^4\Delta_g$	1.648	180	0.45
$^4\Sigma_g^-(\text{II})$	1.646	180	2.06
$^2\Delta_g$	1.632	180	2.19
$^2\Pi_g$	1.636	180	2.34
$^2\Sigma_g^-$	1.655	180	2.79
$^2\Sigma_g^-(\text{II})$	1.662	180	2.87
2B_1	1.511	105.1	1.60
2A_2	1.491	79.2	1.66
2A_1	1.535	102.6	1.81
$^4B_1^b$	1.60	70°	2.18
Co(4F) + H ₂ ^c			-0.169

^aEnergy of $^4\Phi_g$ state in hartree atomic units. The energies of other states are in eV calculated with respect to the $^4\Phi_g$ minimum.

^bThe bent 4B_1 geometry is a saddle point.

^cDissociation limit. Distance between Co and H₂ is 10.0 au.

TABLE II. Properties of quartet states of CoH₂ obtained by RFOCI and MRSDCI.

Method	State	$r_e(\text{\AA})$	E^a
RFOCI	$^4\Phi_g$	1.615	-1382.508742
RFOCI	$^4\Sigma_g^-$	1.611	0.317
RFOCI	$^4\Pi_g$	1.608	0.480
RFOCI	$^4\Delta_g$	1.642	0.546
RFOCI	$^4\Sigma_g^-(\text{II})$	1.608	1.889
RFOCI	$^4B_1^c$		1.689
RFOCI	Co(4F) + H ₂		0.089
MRSDCI ^b	$^4\Phi_g$		-1382.6150573
MRSDCI	$^4\Sigma_g^-$		0.135
MRSDCI	$^4\Pi_g$		0.210
MRSDCI	$^4\Delta_g$		0.256
MRSDCI	$^4\Sigma_g^-(\text{II})$		1.80
POLCI	Co(4F) + H ₂		-1382.510278
POLCI	$^4B_1^c$		-1382.456233

^aEnergies reported for the $^4\Phi_g$ state and POLCI calculations are in hartree atomic units. The energies of other states are in eV.

^bMRSDCI calculations were carried out at the optimized CAS geometries.

^cThe r and θ values for the saddle point are 1.60 Å and 70°.

The saddle point and dissociation limit were calculated by POLCI.

of $^4\Phi_g$, $^4\Sigma_g^-$ and $^4\Pi_g$ states shrink by 0.032 Å, 0.022 Å, and 0.037 Å, respectively, at the first-order CI levels of calculations.

Table III shows a comparison of the RECP and all-electron geometries. As one can see, the agreement is quite good. Although all-electron MRSDCI geometry optimization was not carried out comparison of RFOCI all-electron geometries with RECP-MRSDCI geometries in Table III reveals that the RFOCI geometries are quite accurate. The shortening in the bond lengths due to second order excitations is at most 0.013 Å.

The SCF/CI calculations carried out by Fox, Lee, and Schaefer [13] predict the $^4\Pi_g$ state to be the ground state. This may be attributed to a single configuration SCF cal-

TABLE III. Comparison of RECP and all-electron geometries for CoH₂.

Method	State	RECP	All-electron
CASSCF	$^4\Phi_g$	1.643	1.647
CASSCF	$^4\Sigma_g^-$	1.632	1.633
CASSCF	$^4\Pi_g$	1.643	1.651
CASSCF	$^4\Delta_g$	1.660	1.648
MRSDCI	$^4\Phi_g$	1.602	
MRSDCI	$^4\Sigma_g^-$	1.596	
MRSDCI	$^4\Pi_g$	1.606	
MRSDCI	$^4\Delta_g$	1.638	

ulation with which the orbitals were obtained. It seems that orbital relaxation effects are so large in these systems that MCSCF/CI calculations are warranted for an accurate description of the electronic states.

The barrier to insert Co into H_2 to form CoH_2 is the difference between the energies of the saddle point and dissociation limits. This is about 54 kcal/mole at the CASSCF level. However, the RFOCI and POLCI calculations yield a barrier height of 37 and 34 kcal/mole, respectively. The corresponding value reported by Siegbahn, Blomberg, and Bauschlicher [14] is 45 kcal/mole. The difference between our calculated value and their value may be attributed to a smaller basis set they use. The weakly bound doublet complexes (2A_1 , 2B_1 , and 2A_2) do not have barriers in their potential energy surfaces and thus CoH_2 in doublet bent spin states can be formed spontaneously. However, the linear and bent doublet states are separated by a barrier. All these calculated results explain the recent experimental observations by Smalley and coworkers [1], which suggest that the Co atom does not react with H_2 in dissociative chemisorption.

Tables IV and V show the weights of the CI important configurations in the CASSCF wavefunction of the linear and bent states of CoH_2 , respectively. Some of the electronic distributions with many open shells can be represented by more than one Slater determinant. As one can see from these tables, a number of configurations contribute to a significant extent in the CASSCF. The bent states except the 2B_2 state are well represented by a two-configuration SCF. For linear states, however, a MCSCF treatment seems to be necessary.

We carried out calculations of the 2A_1 state of CoH_2 in C_s symmetry also to obtain the vibrational frequencies of CoH_2 . The calculated vibrational frequencies for this state are ν_{bend} (660 cm^{-1}), ν_{asym} (1917 cm^{-1}), and ν_{sym} (1924) cm^{-1} .

The $1\sigma_g$ orbital of the linear molecule is a bonding MO formed by Co $4s$ and hydrogen orbitals. We oriented the molecule in the yz plane with the linear structure oriented along the y axis. The $2\sigma_g$ orbital is a mixture of Co $d_{2y^2 - z^2 - x^2}$ and hydrogen orbitals. The δ orbital in the a_1 block is thus $\delta_{z^2 - x^2}$. The σ_u orbital results from the mixing of Co $4p_y$ with the u -combination of hydrogen orbitals. The π_g and δ_g orbitals are nonbonding Co d orbitals. For the bent structure, the $1a_1$ orbital is a mixture of Co $4s$ and hydrogen a_1 orbitals. The $2a_1$ and $3a_1$ orbitals are $d_{2y^2 - x^2 - z^2}$ and $d_{x^2 - z^2}$ with some mixing with the hydrogen $1s$. The $1b_2$ orbital is a mixture of Co $4p_y$ and hydrogen b_2 orbitals. The $2b_2$ orbital is dominantly Co d_{yz} . The $1a_2$ and $1b_1$ orbitals are primarily Co d and are nonbonding.

The mixing of the $2\sigma_g^1\delta_g^2\pi_u^4$ and $2\sigma_g^1\delta_g^4\pi_u^2$ configurations in the CASSCF of $^4\Sigma_g^-$ leads to an overall occupancy of about $\sigma_g^1\delta_g^{2.8}\pi_g^{3.2}$. In general, the occupancies of the MCSCF δ_g and π_g orbitals tend to be closed to 3.0 for all low-lying linear states since the splitting between the nonbonding δ_g and π_g orbitals is small.

Comparison of the Electronic States of Some Transition Metal Hydrides

Table VI compares the geometries and energies of electronic states of ScH_2 and YH_2 . Table VII compares the properties of electronic states of PtH_2 with and PdH_2 without the spin-orbit term. The ScH_2 and YH_2 results are from references [34] and [55], respectively. The PtH_2 and PdH_2 results are from references [38] and [56]. The

TABLE IV. CI weights of important configurations in the CASSCF of linear states of CoH₂.

C^2 ^a	Configuration					
	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	σ_u	δ_g	π_g
0.936	2	1	0	2	3	3
			$4\Phi_g$			
0.7283	2	1	0	2	3	3
0.2534	2	2	0	2	2	3
			$4\Pi_g$			
0.577	2	1	0	2	2	4
0.402	2	1	0	2	4	2
0.004	1	1	1	2	2	4
			$4\Sigma_g^-$			
0.982	2	2	0	2	3	2
			$4\Delta_g$			
0.570	2	1	0	2	4	2
0.402	2	1	0	2	2	4
0.004	1	2	0	2	4	2
0.003	1	1	1	2	4	2
0.003	1	1	1	2	2	4
0.002	1	0	2	2	2	4
			$4\Sigma_g^-(II)$			
	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	σ_u	δ_g	π_{xg}
0.831	2	2	0	0	3	2
0.0681	2	2	0	2	3	1
0.0231	2	2	0	2	3	2
0.0231	2	2	0	2	3	0
			$2\Delta_g$			
0.523	2	1	0	2	4	1
0.156	2	1	0	2	2	2
0.127	2	2	0	2	3	2
0.127	2	2	0	2	3	0
			$2\Sigma_g^-$			
0.295	2	1	0	2	2	2
0.230	2	2	0	2	3	1
0.228	2	1	0	2	4	1
0.114	2	2	0	2	3	2
0.114	2	2	0	2	3	0
0.065	2	1	0	2	2	2
			$2\Sigma_g^-(II)$			
	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	σ_u	δ_g	π_g
0.685	2	1	0	2	3	3
0.202	2	0	0	2	4	3
0.049	2	2	0	2	4	1
0.045	2	2	0	2	2	3
			$2\Pi_g$			

^aSum of the squares of the Slater determinants corresponding to the electronic distribution shown.

TABLE V. CI weights of leading configurations in the CASSCF of bent states of CoH₂.

C^2	Configuration							
	$1a_1$	$2a_1$	$3a_1$	$4a_1$	$1b_2$	$2b_2$	$1b_1$	$1a_2$
2A_1								
0.893	2	2	1	0	2	0	2	2
0.029	2	2	1	0	0	2	2	2
0.016	2	2	1	0	1	1	2	2
2A_2								
0.871	2	2	2	0	2	0	2	1
0.033	2	2	2	0	0	2	2	1
0.021	2	2	1	0	2	1	1	2
0.020	2	2	1	1	1	1	2	1
0.013	2	2	2	0	1	1	2	1
2B_1								
0.861	2	2	2	0	2	0	1	2
0.031	2	2	2	0	0	2	1	2
0.025	2	2	1	0	2	1	2	1
0.016	2	2	2	0	1	1	1	2
0.015	2	2	1	1	1	1	1	2
2B_2								
0.448	2	2	2	0	2	1	2	0
0.351	2	2	2	0	2	1	0	2
0.166	2	1	1	0	2	1	2	2
0.018	2	2	1	0	2	2	1	1
$^4B_1^a$								
0.805	2	2	1	1	2	0	1	2
0.094	2	2	1	1	0	2	1	2
0.063	2	2	1	1	1	1	1	2

^aSaddle point.

YH₂ molecule forms a very stable bent 2A_1 minimum while ScH₂ forms only a shallow bent minimum. The YH₂ 2A_1 bent minimum is about 31 kcal/mole more stable than the Y + H₂ separated species while ScH₂ $^2\Sigma_g^+$ linear state is only 5 kcal/mole more stable than Sc + H₂. The barrier to insert the metal atom into the H₂ bond is about 36 kcal/mole for the Sc atom in comparison to 23 kcal/mole for Y in the 2A_1 surface. Thus the Yttrium atom is likely to be more reactive than Sc with H₂. The saddle points for both ScH₂ and YH₂ occur at somewhat small angle. The linear electronic states of ScH₂ ($^2\Sigma_g^+$, $^2\Pi_g$, and $^2\Delta_g$) are much more closely spaced in comparison to the corresponding electronic states of YH₂.

In comparing ScH₂, YH₂, and CoH₂ we find that the *M-H* bond lengths for the bent (doublet) states are shorter than the corresponding linear states. Of course, the high spin electronic states of CoH₂ are linear. The same trend holds for PtH₂ and PdH₂. The CoH₂ electronic states are all less stable than Co (4F) + H₂ while for ScH₂ and YH₂ the bent doublet states are more stable than the separated species. For

TABLE VI. Geometries and energies of low-lying states of ScH₂ and YH₂.

State	ScH ₂			YH ₂		
	r_e (Å)	θ_e (deg)	E (eV)	r_e (Å)	θ_e (deg)	E (eV)
2A_1	1.81	133.4	0.0	1.94	123	0
$^2\Sigma^+$	1.84	180	0.04	2.01	180	0.36
$^2\Pi_g$	1.91	180	0.20	2.08	180	1.16
$^2\Delta_g$	1.91	180	0.66	2.08	180	1.71
2B_1				2.02	132	1.04
2A_2				2.02	126	1.56

TABLE VII. Comparison of the low-lying electronic states of PtH₂ and PdH₂.

State	PtH ₂			PdH ₂		
	r_e (Å)	θ_e	E (eV)	r_e (Å)	θ_e	E (eV)
1A_1	1.52	85.1	0.0	1.67	30	0.0
1A_1				1.50	62	0.25
$^1\Sigma^+$	1.68	180	2.33	1.62	180	2.10
$^3\Delta_g$	1.70	180	2.01	1.65	180	2.93
$^3\Pi_g$	1.71	180	3.0	1.68	180	3.55
$^1\Pi_g$	1.71	180	3.02	1.69	180	3.70
$^1\Delta_g$	1.69	180	4.98	1.79	180	4.63

PtH₂ also we find that the bent 1A_1 state is more stable than both Pt (3D) + H₂ and Pt (1S) + H₂.

The bent 1A_1 minimum of PtH₂ is considerably more stable than the corresponding bent minimum of PdH₂ with respect to M + H₂ (Table VII). This is primarily because the ground state of Pd arises from the $4d^{10}$ configuration while for Pt the ground state is $5d^96s^1$ (3D_3). The 1S state arising from d^{10} is not likely to form a strong bond with H₂ unless excitation to the s shell is favorable. The $5d$ - $6s$ excitation energy for Pt is considerably smaller than the $4d$ - $5s$ excitation energy of the palladium atom. These are the reasons for the difference in the properties of PtH₂ and PdH₂. The first minimum for PdH₂ corresponds to a weak-complex of Pd(d^{10}) H₂ while the second bent minimum arises from relativistic stabilization of the $4d$ - $5s$ excitation. In fact, nonrelativistic calculations on PdH₂ such as the one made by Blomberg et al [57] do not yield the second bent minimum. However, the relativistic GVB/CI calculations of Low and Goddard [58, 59] on the 1A_1 state of PdH₂ yield this minimum. For both PtH₂ and PdH₂, the 1S state of the metal atom inserts spontaneously into the H₂ bond while the 3D state has to surmount a large barrier for the insertion into the hydrogen bond. The relativistic spin-orbit effects are considerably larger for PtH₂ in comparison to PdH₂. For example the $^3\Pi_g$ spin-orbit splittings for PtH₂ and PdH₂ are 0.74 and 0.18 eV, respectively.

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