

Extensive relativistic calculations on the palladium hydride molecule

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The lower states of the PdH molecule have been studied with different relativistic methods. At the spin-free level, relativistic effects are shown to be crucial for a proper description of the molecule. PdH is shown to be a single-configuration molecule, but the configuration interaction (CI) results are highly sensitive to the choice of orbital basis. Spin-orbit interaction has been included through spin-orbit CI theory based on the second order Douglas-Kroll operator and through fully relativistic CI calculations based on the Dirac-Coulomb Hamiltonian. The results are in good agreement, but requires a proper choice of orbital basis in the spin-orbit CI calculation to ensure a balanced description of all $\Lambda\Sigma$ states coupled by spin-orbit interaction. © 1997 American Institute of Physics. [S0021-9606(97)00735-6]

I. INTRODUCTION

The study of transition-metal chemistry and especially its role in catalytic processes has been one of the more active areas in modern chemistry.¹ The understanding of this chemistry has for a long period been a challenge to theoretical chemistry. The development of fast computers and effective algorithms has made calculations on the first period elements an almost routine procedure, whereas the need to account for relativistic effects in the second and third periods² has hampered the same development for these elements.

Over the last decade, however, much effort has been invested in the development of efficient and accurate algorithms that also include the relativistic effects.³ The relativistic effective core potential (RECP) methods have been available for quite a long time⁴ and have with some success been applied to a broad spectrum of problems. Lately, however, all-electron methods, based on the Dirac equation, have appeared, and have enabled theorists to approach this chemistry with greater success. The four-component Dirac-Coulomb method has matured over the last few years and can now be applied to small and medium size molecules.⁵ This method is, however, still relatively resource-demanding and for larger systems more effective approximate methods have been developed. Among these, the second-order Douglas-Kroll method,⁶ as implemented by Hess *et al.*,⁷ has received much attention and has successfully been applied to a series of molecules.⁸

Palladium and palladium compounds are important in catalytic processes in the petroleum industry, for instance in the formation of methanol from carbon monoxide.⁹ These type of processes are, however, poorly understood and the

technology involves to some extent trial and error. In spite of this, there have been relatively few calculations on palladium compounds.¹⁰

Essential to the understanding of the palladium chemistry is an understanding of small Pd-hydrides, and especially PdH. The ground state of the palladium atom is a $^1S(d^{10})$ configuration with a $^3D(d^9s^1)$ state 7666 cm^{-1} above. The latter state binds with hydrogen through an $s-s$ σ -bond, leaving the d -occupation with a hole. Within the $\Lambda\Sigma$ coupling scheme, this results in the $^2\Sigma$, $^2\Delta$, and $^2\Pi$ states. The $\omega\omega$ -coupling scheme, on the other hand, predicts two 1/2 states, two 3/2 states and one 5/2 state. This simple bonding picture may be modified by the participation of d -orbitals in the Pd-H bond.

Previous calculations on this open-shell molecule include nonrelativistic configuration interaction (CI) and averaged coupled pair functional (ACPF) calculations,^{11,12} RECP,¹³ and two-component calculations based on the Breit-Pauli operator.¹⁴ We have in the present work studied the energy splitting and bond distance within the $\Lambda\Sigma$ coupling scheme using two different spin-free Hamiltonians: (a) nonrelativistic (NR) and (b) using a second-order one-component Douglas-Kroll (DK) operator. Calculations including spin-orbit interaction have been carried out using (a) a two-component Douglas-Kroll operator and (b) the full Dirac-Coulomb (DC) operator. All calculations are carried out using the multireference singly and doubly excited CI (MRSDCI) method.

II. COMPUTATIONAL DETAILS

A. One-component calculations

One-component calculations were carried out both non-relativistically and with the spin-free second order Douglas-Kroll operator,

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$$H = \sum_i [E_i + V_{\text{eff}}^{\text{sf}}(i)] + \sum_{i < j} \frac{1}{r_{ij}}, \quad (1)$$

where the kinetic energy part E_i and effective potential $V_{\text{eff}}^{\text{sf}}(i)$ are defined in Ref. 7. CAS reference calculations were carried out followed by a MRSDCI based on this reference calculation. The calculations were carried out in C_{2v} symmetry using a modified version of the MOLECULE SWEDEN program.¹⁵ We use the notation $(n_{A1}, n_{A2}, n_{B1}, n_{B2})$ for active spaces, where for instance n_{A1} is the number of active orbitals of A_1 symmetry. For Π and Δ states proper, axial symmetry was ensured by averaging over contributing irreps.

B. Two-component calculations

The two-component calculations are carried out by including the second order Douglas–Kroll spin–orbit operator,

$$H^{\text{so}} = \sum_i B_i \mathbf{L}_i - \mathbf{s}_i B_i + \sum_{i < j} B_i A_j \mathbf{L}_{ij} \cdot \mathbf{s}_j B_i A_j + \sum_{i < j} 2B_j A_i \mathbf{L}_{ij} \cdot \mathbf{s}_j B_i A_j, \quad (2)$$

where

$$A_i = [(E_i + mc^2)/2E_i]^{1/2}$$

and

$$B_i = cA_i/(E_i + mc^2),$$

with

$$\mathbf{L}_i = \sum_{\mu} \frac{Z_{\mu}}{|\mathbf{r}_i - \mathbf{r}_{\mu}|^3} \cdot (\mathbf{r}_i \times \mathbf{p}_i) \quad (3)$$

and

$$\mathbf{L}_{12} = r_{12}^{-3} (\mathbf{r}_{12} \times \mathbf{p}_1). \quad (4)$$

In order to simplify the calculations, the kinematic factors in the two-electron spin–orbit operator are averaged.

The first term of H^{SO} represents the spin–orbit interaction in the field of the fixed nuclei (indices μ), and the two final terms represent spin-own orbit and spin-other orbit interaction, respectively. The first two terms of H^{SO} are derived from the Dirac–Coulomb Hamiltonian, whereas the spin-other orbit term stems from the Breit (or Gaunt) term.⁷ Previous studies indicate that this term has a minor effect on molecular spectra.¹⁶ The spin–orbit operator is included as a variational perturbation applying the spin-free Douglas–Kroll CI wave functions as the zero order wave functions.

The perturbation calculations were carried out using the RASCI program LUCIA,¹⁷ extended to include the spin–orbit operator.¹⁸ For compatibility reasons, the CAS calculations of the $\Lambda\Sigma$ -reference states were done with the program SIRIUS.¹⁹ Integrals were generated by a version of the program HERMIT²⁰ extended to include scalar and spin–orbit integrals over the second order Douglas–Kroll operator.

TABLE I. Summary of radial expectations values (in Å) and orbital energies (in hartrees) of valence orbitals for various electronic configurations of the palladium atom. For each configuration the second row gives nonrelativistic numbers obtained by scaling the speed of light with a factor 1000. All numbers have been obtained by average level (AL) calculations using the atomic structure program GRASP.

	$4d_{3/2}$		$4d_{5/2}$		$5s_{1/2}$	
	$\langle r \rangle$	ϵ	$\langle r \rangle$	ϵ	$\langle r \rangle$	ϵ
d^{10}	0.809	−0.341	0.828	−0.320
	0.811	−0.336	0.811	−0.336
d^9s^1	0.766	−0.480	0.779	−0.460	1.865	−0.233
	0.765	−0.491	0.765	−0.491	1.970	−0.217
d^8s^2	0.733	−0.625	0.743	−0.605	1.715	−0.268
	0.730	−0.649	0.730	−0.649	1.787	−0.254

C. Four-component calculations

The four-component calculations are based on the Dirac–Coulomb operator,

$$H = \sum_{i=1}^n h_{\text{ext}}^D(i) + \sum_{i < j} \frac{1}{r_{ij}}, \quad (5)$$

where h_{ext}^D is the usual Dirac operator for one electron in an external field. The calculations were carried out in C_{4v} double group symmetry using the MOLFDIR program.²¹ In this symmetry the spinors $\Omega = 1/2$ and $\Omega = 7/2$ transform as the fermion irrep E_1 and $\Omega = 3/2$ and $\Omega = 5/2$ as the fermion irrep E_2 . On Dirac–Fock level of calculation the two lowest states ($\Omega = 1/2, 5/2$) may be described by one determinant with a hole in the highest spinor in E_1 and E_2 , respectively. RASCI calculations on the two lower states were carried out using the corresponding DF orbitals. The upper $\Omega = 1/2$ state and the two $\Omega = 3/2$ states were calculated using configurational averages over the two $\Omega = 1/2$ and $\Omega = 3/2$ states, respectively. Accordingly, four separate CI-calculations were performed for each PdH distance. The calculations in the E_1 symmetry were carried out with eight occupied valence spinors in RAS1, the four open spinors in RAS2 and 92 virtual spinors in RAS3. In the case of E_2 the numbers were 6, 6, and 92. Virtual orbitals with orbital energies higher than 4.8 a.u. are excluded, giving approximately 230 000 determinants in each symmetry.

D. Basis sets

Table I presents radial expectation values and orbital energies for the $4d$ and $5s$ orbitals for the configurations d^{10} , d^9s^1 , and d^8s^2 of the palladium atom at the relativistic and nonrelativistic levels. Radial expectation values are seen to vary by about 0.1 Å between configurations, which means the basis set for palladium must be endowed with great flexibility in the valence region in order to facilitate an adequate description of bonding in palladium hydride. One may also note that the spin–orbit splitting of the $4d$ orbital is approximately 0.54 eV and varies negligibly between configurations.

The calculations presented in this paper all originate from a nonrelativistically optimized $17s13p9d3f$ Gaussian

TABLE II. Basis set for the Dirac–Coulomb calculations.

	Large components		Small components	
	Primitive	Contracted	Primitive	Contracted
Pd basis	17s14p9d3f	7s9p7d2f	14s26p17d9f3g	6s12p11d7f2g
H basis	6s1p	3s1p	1s6p1d	1s3p1d

basis set for palladium. At the one-component level, a general contraction scheme $[5s + 2,3p + 3,2d + 3,1f + 1]$ was employed. Contraction coefficients were generated by an atomic calculation on the 3D (d^9s^1) state using the appropriate spin-free Hamiltonian. Contraction coefficients for a $5p$ orbital were obtained from a calculation on the 3P (d^9p^1) state. The hydrogen basis was taken from Duijneveldts²² $5s$ basis contracted to $3s$ functions and augmented with one p -function with exponent 0.8.

In the four-component calculations, the palladium basis set was supplemented with a tight p -exponent to improve the description of the $2p_{1/2}$ orbital. A small component primitive basis set was generated using the kinetic-balance relation. Contraction coefficients for the large and small components were generated analogously to the one-component case using the relativistic atomic program GRASP²³ in its basis set extension.²⁴ The spin–orbit components were contracted separately. The relativistic contraction scheme thereby gives a less efficient reduction in the number of basis functions. For hydrogen, a primitive $6s1p$ gaussian basis set was relativistically contracted to $3s1p$. The basis sets used in the four-component calculations are summarized in Table II.

III. SPIN-FREE RESULTS

The bonding in PdH is a σ -bond primarily constructed from the $5s$ -orbitals on Pd and the $1s$ on H. There is, however, a strong interaction with the $4d_{2z^2-(x^2+y^2)}$ and the $5p$ orbital, reducing electron repulsion through a σ lone-pair formation. We have performed a number of CAS+CI calculations on the lower three $\Lambda\Sigma$ -states of the PdH molecule. Results from MRSDCI calculations with 11 electrons in 7 active orbitals (bonding σ , σ^* and all $4d$ orbitals) are presented in Table III. We refer to these calculations as CAS(4111)+CI(4111). A Mulliken population analysis at the CAS level is given in Table IV.

It is clear from the results in Table III that the introduction of relativistic effects leads to a significant modification

TABLE III. Bond distances and transition energies from CAS(4111) + CI(4111) calculations using spin free methods. Bond distances R_e in a.u. and excitation energies T_e in eV.

State	NR		DK ^a	
	R_e	T_e	R_e	T_e
$^2\Sigma$	3.00	0.00	2.96	0.00
$^2\Delta$	3.18	0.97	3.03	0.74
$^2\Pi$	3.33	1.09	3.18	0.98

^aDK, second order spin-free Douglas–Kroll operator.

TABLE IV. Population analysis for CAS(4,1,1,1) results obtained with the Douglas–Kroll operator. Numbers in parentheses give selected populations from corresponding nonrelativistic calculation.

State	Platinum				Hydrogen		Overlap
	s	p	d	f	s	p	
$^2\Sigma$	0.606(0.49)	0.102	9.192(9.27)	0.060	1.022	0.019	0.628
$^2\Delta$	0.948(0.81)	0.130	8.781(8.88)	0.058	1.067	0.016	0.675
$^2\Pi$	0.823(0.72)	0.149	8.840(8.88)	0.059	1.116	0.013	0.661

of the molecular spectrum. The excitation energies are changed by approximately 0.23 and 0.11 eV for $^2\Delta$ and $^2\Pi$, respectively. There is furthermore a bond contraction of 0.15 a.u. for the $^2\Delta$ and $^2\Pi$ states. The energy lowering of the various $\Lambda\Sigma$ -states correlate with the s -populations given in Table IV and may therefore be understood in terms of the relativistic stabilization of s orbitals.

The spin-free operator predicts $^2\Sigma$ as the ground state for palladium hydride with an energy gap of approximately 1 eV to the other two $\Lambda\Sigma$ -states. The population analysis in Table IV reveals that there is a significantly higher d -orbital population in the $^2\Sigma$ state than in the $^2\Delta$ and $^2\Pi$ states. In the former case the hole may be in the σ lone-pair dominated by s - and p -orbitals. This possibility is prohibited in the $^2\Delta$ and $^2\Pi$ states resulting in a fairly low d -population. This explains the energy gap as the Pd atom favors the d^{10} state.

In Table V we present CAS+CI results for PdH using various combinations of active spaces. From the first series of calculations it is seen that excitation energies and bond lengths change appreciably as the active spaces are increased. In the second series, however, the CAS(5111)—orbitals are employed in CI(3111) and CI(4111) calculations. The changes in molecular properties are then negligible compared to the CI(5111) result, indicating that PdH is a single-configuration system, as is further corroborated by the fact that the reference determinant in the CI(3111) calculation has a weight of more than 90%. The CI calculations are therefore obviously very sensitive to the orbital sets used. Accordingly, increasing the active space at the CAS level, orbitals that are better suited for the CI calculation are obtained. Table V shows that the energy difference between the $^2\Delta$ and $^2\Pi$ states is almost independent of the orbital set used, and the total energies for these states hardly change as the active space is increased at the CAS level. In contrast, the $^2\Sigma$ state is lowered with 0.12 eV when the orbital set from the CAS(5111) is applied compared to using CAS(3111) orbital set. It is well known that high d -orbital occupation requires extensive correlation, and accordingly the correlation energy will be more important for the $^2\Sigma$ state than for the two other states. Consequently, orbitals generated without the possibility of reasonable dynamic correlation may be too diffuse, which is the case for the CAS(3111) orbital set.

We may investigate this effect using Mulliken population analysis. The population analysis should be interpreted with care, since the orbitals may be rotated among each other and the populations are basis dependent. The open shell σ -orbital of the $^2\Sigma$ state is, however, fixed and clearly shows

TABLE V. Summary of spin-free results including scalar relativistic effects. Excitation energies (in eV) with respect to the ${}^2\Sigma$ ground state. Bond lengths (in a.u.) are given in parenthesis. DAV refers to the Davidson correction. Δ - Π gives the energy gap between the ${}^2\Delta$ and the ${}^2\Pi$ states.

Method	${}^2\Sigma$	${}^2\Delta$	${}^2\Pi$	Δ - Π
First series (this work)				
CAS(3111)+ CI(3111)	0.00 (2.89)	0.74 (3.04)	0.98 (3.16)	0.24
CAS(4111)+ CI(4111)	0.00 (2.96)	0.74 (3.03)	0.98 (3.18)	0.24
CAS(5111)+ CI(5111)	0.00 (2.91)	0.86 (3.06)	1.11 (3.19)	0.25
CAS(5111)+ CI(5111)+DAV	0.00 (2.89)	0.92 (3.05)	1.17 (3.17)	0.25
Second series (this work)				
CAS(5111)+ CI(4111)	0.00 (2.91)	0.87 (3.07)	1.11 (3.19)	0.24
CAS(5111)+ CI(3111)	0.00 (2.90)	0.86 (3.05)	1.10 (3.17)	0.24
Previous work				
CAS-ACPF ^a	0.00 (2.90)	0.91 (3.06)	1.15 (3.18)	0.24

^aReference 12.

the effect of the increase in the active space at the CAS level (Table VI). At the CAS(4111) level, the inclusion of antibonding σ -orbital reduces the d -population of palladium, but shifts too much density from the Pd(s)-orbital to the H(s)-orbital. This explains the increase in bond length for the ${}^2\Sigma$ state at the CAS(4111) level. The imbalance is remedied at the CAS(5111) level with the introduction of an additional bonding σ -orbital.

The results by Jenderek and Marian¹² are obtained with largely the same procedure as our results, that is, a MRSDCI wave function based on the spin-free DK operator. Their ${}^2\Sigma$ CAS reference state is generated from three electrons in four active orbitals (bonding σ , $4d_\sigma$ and two σ^*), whereas the ${}^2\Delta$ and ${}^2\Pi$ are generated from five electrons in six active orbitals by extending the ${}^2\Sigma$ active space with one $4d_\delta$ and one $4d_\pi$ orbital, respectively. These active spaces are comparable to our (5111) space but differ in that an ACPF procedure was used at the CI level and in that no symmetry averaging was performed for the ${}^2\Delta$ and ${}^2\Pi$ states. It is difficult to assess the effect of the lack of symmetry averaging in the calculations of Jenderek and Marian. The ACPF size-extensivity correction to SDCI energies can be approximated by the Pople correction²⁵

TABLE VI. Population analysis of the open shell σ -orbital of the ${}^2\Sigma$ state from three different CAS calculations. Occ. refers to occupation.

	CAS(3111)	CAS(4111)	CAS(5111)
Occ.	1.0000	1.0065	1.0058
Pd(<i>s</i>)	0.2293	0.0909	0.3236
Pd(<i>p</i>)	0.0259	0.0191	0.0180
Pd(<i>d</i>)	0.6324	0.5419	0.5413
He(<i>s</i>)	0.1111	0.2640	0.1155

TABLE VII. Vertical excitation energies (in eV) for $\Lambda\Sigma$ states using various combinations of active spaces and orbital basis.

Method	${}^2\Sigma$	${}^2\Delta$	${}^2\Pi$
Calculations at $r = 3.00$ a.u.			
CAS(5111)+CI(5111) (separate references)	0.00	0.89	1.17
CAS(5111)+CI(5111) (${}^2\Sigma$ -reference)	0.00	0.93	1.22
CAS(5111)+CI(5111) (${}^2\Pi$ -reference)	0.00	-1.04	-0.85
CAS(5111)+CI(5111) (${}^2\Delta$ -reference)	0.00	-1.29	-0.94
CAS(3111)+CI(3111) (separate references)	0.00	0.76	1.02
CAS(3111)+CI(3111) (${}^2\Sigma$ -reference)	0.00	0.93	1.13

$$\frac{(1-g)(1-C_0^2)}{C_0^2+g(1-C_0^2)} E_c, \quad (6)$$

where $g = 2/N$, N is the number of correlated electrons, C_0^2 is the reference weight, and E_c the correlation energy. Note that the Pople correction reduces to the Davidson correction²⁶ as $g \rightarrow 0$. Since 11 electrons are being correlated at the (5111) level and the reference weight is more than 90%, one would expect the results of Jenderek and Marian to be very similar to our CAS(5111)+CI(5111) results with the Davidson correction included. This is indeed found to be a correct assumption.

IV. CALCULATIONS INCLUDING SPIN-ORBIT

The two-component calculations including spin-orbit are carried out with two different active spaces. We have carried out calculations with the large active space, CAS(5111)+CI(5111), to obtain orbitals on the CAS level that are better suited for the CI calculations. In order to compare the two-component with the four-component results, we also carried out calculations applying the active space CAS(3111). This active room corresponds to the one determinant description used in the four-component calculations. In both these two sets of calculations, the second order Douglas-Kroll spin-orbit operator was included as a variational perturbation. Only one set of reference orbitals are used in this procedure in order to preserve the orthonormality of the orbitals. We chose the ${}^2\Sigma$ orbitals as reference since it gives the overall best representation of the $\Lambda\Sigma$ states at the CI level, as revealed in Table VII. The discrepancy in the excitation energies between using the separate and the ${}^2\Sigma$ orbital sets for ${}^2\Delta$ and ${}^2\Pi$ is from 0.05 to 0.17 eV. The variational perturbation calculation was compared with a full spin-orbit CI using the full CI-matrix at the (5111)-level. The differences were found to be negligible, indicating that the coupling between electron correlation and spin-orbit effects is negligible for this molecule. We furthermore compared the use of the Douglas-Kroll spin-orbit operator with the performance of the corresponding Breit-Pauli operator. No major deviations were found, but since the computational cost of employing the Douglas-Kroll operator instead of the Breit-Pauli operator are relatively small, the Douglas-Kroll operator was chosen.

TABLE VIII. Summary of results for the five lower $\omega\omega$ -states of PdH. Excitation energies (in eV) are with respect to the $1/2(1)$ ground state. Bond lengths (in a.u.) are given in parentheses.

State	This work			Previous work	
	DK(5111)	DK(3111)	DC	CM ^a	BF ^b
1/2(1)	0.00 (2.91)	0.00(2.90)	0.00 (2.89)	0.00	0.00 (2.89)
5/2	0.79 (3.05)	0.83(3.05)	0.67 (3.03)	0.72	0.43 (3.00)
3/2(1)	0.97 (3.08)	0.96(3.14)	0.85 (3.08)	0.89	0.57 (3.12)
3/2(2)	1.30 (3.08)	1.30(3.12)	1.20 (3.08)	1.23	1.16 (3.08)
1/2(2)	1.33 (3.10)	1.27(3.18)	1.28 (3.18)	1.24	1.16 (3.16)

^aReference 14.

^bReference 13.

The results obtained at the two-component level are compared with the results obtained using a fully relativistic CI based on the Dirac–Coulomb Hamiltonian. All results are in Table VIII.

The excitation energy from the lowest $1/2$ state to the $5/2$ state calculated with the DC procedure (0.67 eV) is 0.12 eV lower than the value obtained in the DK(5111) calculation (0.79 eV). The difference between the DK and the DC results for the excitation energies to all the other states from the $5/2$ state is, however, within 0.07 eV. One should take into account, however, that the DC calculation corresponds to the DK(3111) results. Accordingly, the DK(5111) calculations have a better description of the correlation energy that favors the lowest $1/2$ state and should generally give larger excitation energies, which is also the case. The DK(3111) results (0.83 eV) seem, however, to contradict the conclusion above since the excitation energy from the ground state to the $5/2$ state is even higher than for the DK(5111) case. This apparent contradiction is explained by the fact that the DK calculations are carried out using a orbital basis determined from a calculations on the $^2\Sigma$ state resulting in to high energies for all states except the lower $1/2$ state. For the DK(3111) calculations this effect is considerable, leading to an upward shift of approximately 0.17 eV and 0.11 eV for the $^2\Delta$ and $^2\Pi$, respectively. Adding these values bring the DK(3111) results in reasonable agreement with the DC results.

In Table VIII we have included some results from previous work for comparison with our results. The results presented in Ref. 13 are based on CAS+MRSDCI and RECP and are quite different from all the other results.

The excitation energies calculated in Ref. 14 are generally smaller than the energies obtained by our DK method, bringing them closer into agreement with the DC result. The major difference between the two DK calculations is the use of an ACPF functional at the CI level in Ref. 14. From Table X it is seen that the $1/2$ state has a distinctly higher d population than the other Ω states. One would expect the size extensivity corrections obtained with the ACPF method to scale with the d populations of the various states. It is therefore a little surprising that the excitation energies obtained in Ref. 14 are smaller than ours.

From our calculated excitation energies, it is clear that the grouping 1:2:2 of the five lower states of PdH is dis-

TABLE IX. Expansion coefficients for the $\Lambda\Sigma$ states in the different $\omega\omega$ -states for the two-component calculations at bond length 3.10 a.u.

State	$\Lambda\Sigma$ -		$\Lambda\Sigma$ -	
	coefficient	$\Lambda\Sigma$ -state	coefficient	$\Lambda\Sigma$ -state
1/2(2)	0.992	$M_L=1, M_S=-0.5$	0.122	$M_L=0, M_S=0.5$
3/2(2)	0.730	$M_L=1, M_S=0.5$	-0.684	$M_L=2, M_S=-0.5$
3/2(1)	0.730	$M_L=2, M_S=-0.5$	0.684	$M_L=1, M_S=0.5$
1/2(1)	0.992	$M_L=0, M_S=0.5$	-0.122	$M_L=1, M_S=-0.5$

tinctly different from the 3:2 grouping found in PtH (Ref. 5). This difference can be explained by the weaker spin–orbit splitting in the palladium atom as compared to platinum. Based on the variational perturbation calculation, the $\omega\omega$ states may be expanded in the $\Lambda\Sigma$ states, as in Table IX. From these numbers one may conclude that the $1/2$ states are almost pure $^2\Sigma-$ and $^2\Pi$ states whereas the $3/2$ states are constructed from a strong mixing of $^2\Pi$ and $^2\Delta$. This may be understood from the nonrelativistic results where the $^2\Pi$ and $^2\Delta$ states were very close and much higher than the $^2\Sigma$, allowing for a strong coupling of the $3/2$ states, whereas the energy separation prohibits interaction between the two $1/2$ states.

The population analysis for the DC calculations is presented in Table X. The numbers reveal a similar pattern as for the $\Lambda\Sigma$ calculations. The s -occupation in the lowest $1/2$ state is only 0.45 electrons, indicating that the bonding has a strong d - and p -contribution. The overall population confirms that the dominant atomic configuration is the $(d^9s^1)^3D$ state. The lowest $1/2$ state has, however, a substantial contribution from the $(d^{10})^1S$ and all the other states a similar contribution from the atomic $(d^8s^2)^3F$ state.

Table X furthermore gives the valence populations in terms of the nonrelativistic σ , π , and δ orbitals. These results very clearly show why the $\Lambda\Sigma$ -coupling scheme is unsatisfactory for the PdH molecule. The $1/2(1)$, $5/2$, and the $1/2(2)$ states may be characterized as almost pure $1\sigma^22\sigma^11\pi^4\delta^4$, $1\sigma^22\sigma^21\pi^4\delta^3$, and $1\sigma^22\sigma^21\pi^3\delta^4$ configurations. The $3/2$ states, however, are a mixture of the $1\sigma^22\sigma^21\pi^4\delta^3$, and $1\sigma^22\sigma^21\pi^3\delta^4$ states. The coupling is so strong that the states cannot be characterized within a nonrelativistic scheme.

V. CONCLUSION

The PdH molecule has been studied with different relativistic methods. From the results it appears that the inclusion of relativistic effects is crucial for a reasonable description of Pd-systems. For the PdH molecule, the bond contraction is substantial and the spectrum is quite different when relativistic methods are invoked. The spin–orbit interaction is significant, although not as pronounced as for the homologous PtH molecule. The spin–orbit interaction leads to a considerable mixing of the Π and Δ states.

There is no multiconfigurational mixing in the description of this molecule. The dynamic correlation is, however, large and much larger for the Σ state than for the Π and Δ states. The two-component calculations are hampered by the

TABLE X. Valence population analysis of four-component calculations on PdH.

ω	Occ.	Palladium			Hydrogen				
		<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	σ	π	δ
$\Omega = 1/2(1)$		0.45	0.15	9.26	1.05	0.02	2.97	4.02	3.99
1/2	5.0	0.45	0.16	3.31	1.05	0.01	2.97	2.03	0.00
3/2	4.0	0.00	-0.01	3.97	0.00	0.05	0.00	1.99	2.00
5/2	2.0	0.00	0.00	1.98	0.00	0.00	0.00	0.00	1.99
$\Omega = 5/2$		0.85	0.18	8.79	1.09	0.01	3.94	4.04	3.00
1/2	6.0	0.85	0.18	3.83	1.09	0.01	3.94	2.05	0.00
3/2	4.0	0.00	0.00	3.97	0.00	0.00	0.00	1.99	2.00
5/2	2.0	0.00	0.00	0.99	0.00	0.00	0.00	0.00	1.00
$\Omega = 3/2(1)$		0.81	0.19	8.82	1.11	0.02	3.94	3.60	3.45
1/2	6.0	0.81	0.19	3.85	1.11	0.01	3.94	2.05	0.00
3/2	3.0	0.00	0.00	2.99	0.00	0.00	0.00	1.54	1.46
5/2	2.0	0.00	0.00	1.98	0.00	0.00	0.00	0.00	1.99
$\Omega = 3/2(2)$		0.80	0.19	8.82	1.11	0.02	3.94	3.50	3.54
1/2	6.0	0.80	0.19	3.85	1.11	0.01	3.94	2.05	0.00
3/2	3.0	0.00	0.00	2.99	0.00	0.00	0.00	1.45	1.56
5/2	2.0	0.00	0.00	1.98	0.00	0.00	0.00	0.00	3.99
$\Omega = 1/2(2)$		0.67	0.21	8.88	1.16	0.01	3.92	3.08	3.99
1/2	5.0	0.67	0.21	2.93	1.16	0.01	3.92	1.09	0.00
3/2	4.0	0.00	0.00	3.97	0.00	0.00	0.00	1.99	2.00
5/2	2.0	0.00	0.00	1.98	0.00	0.00	0.00	0.00	1.99

necessity of using the same orbital sets for all the states. Our results demonstrate the sensitivity of the results at the CI level to the choice of orbital basis when the two-component method is used. Due to a large number of *d*-electrons, the orbitals calculated at the CAS-level tend to be too diffuse for the CI-description. It is therefore necessary to include more dynamic correlation at the CAS level in order to obtain suitable basis for the CI calculation.

The four-component and two-component calculations are in reasonable agreement.

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¹J. Sauer, *Chem Rev.* **89**, 199 (1989).

²P. Pyykk, *Adv. Quantum Chem.* **11**, 353 (1978); in *Lecture Notes in Chemistry* (Springer, Berlin, 1993); P. Pyykk, in *The Effects of Relativity in Atoms, Molecules and Solid State (Proc. Meet.)*, edited by S. Wilson, I. P. Grant, and B. L. Gyorffy (Plenum, New York, 1991), pp. 1-13; P. Pyykk, *Chem. Rev.* **88**, 563 (1988).

³J. Almlf and O. Gropen, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1996), Vol. 8.

⁴O. Gropen, in *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1988), Vol. 2, pp. 109-135.

⁵L. Visscher, T. Saue, W. C. Nieuwoort, K. Fgri, and O. Gropen, *J. Chem. Phys.* **99**, 6704 (1993).

⁶M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).

⁷B. A. Hess, *Phys. Rev. A* **32**, 756 (1985); **32**, 3742 (1986); R. Samzow, B. A. Hess, and G. Jansen, *J. Chem. Phys.* **96**, 1227 (1992).

⁸C. M. Marian, *J. Chem. Phys.* **93**, 1176 (1990); **94**, 5574 (1991); G. Jansen and B. Hess, *Z. Phys. D.* **13**, 363 (1989).

⁹M. A. Vannice, *Catal. Rev.* **14**, 153 (1976).

¹⁰J. Carroll, K. L. Hauge, J. C. Weisshaar, M. R. S. Blomberg, P. E. M. Siegbahn, and M. Svensson, *J. Phys. Chem.* **99**, 38 (1995).

¹¹H. Bash, D. Cohen, and S. Topiol, *Isr. J. Chem.* **19**, 233 (1980); P. S. Bagus and C. Bjrkman, *Phys. Rev.* **23**, 461 (1981).

¹²J. Jenderek and C. M. Marian, *Theor. Chim. Acta* **88**, 13 (1994).

¹³K. Balasubramanian, P. Y. Feng, and M. Z. Liao, *J. Chem. Phys.* **87**, 3981 (1987).

¹⁴C. M. Marian, in *New Challenges in Computational Quantum Chemistry*, edited by P. C. Aerst, P. S. Bagus, and R. Broer (Department of Chemical Physics and Material Science Centre, University of Groningen, 1994).

¹⁵J. Almlf, MOLECULE, a Gaussian integral program; P. E. M. Siegbahn, C. W. Bauschlicher, Jr., B. O. Roos, A. Heiberg, P. R. Taylor, and J. Almlf, SWEDEN, a vectorized MC SCF and CI program.

¹⁶K. M. S. Saxena and G. Malli, *Can. J. Phys.* **48**, 1088 (1968); **47**, 2805 (1968); *Int. J. Quantum Chem.* **S5**, 619 (1971); U. Wahlgren, M. Sjvvoll, H. Fagerli, B. Schimmelpfennig, and O. Gropen, *Theor. Chem. Acc.* (to be published).

¹⁷J. Olsen, B. O. Roos, P. Jrgensen, and H. J. Aa. Jensen, *J. Chem. Phys.* **89**, 2185 (1988).

¹⁸M. Sjvvoll, J. Olsen, and O. Gropen, *Theor. Chem. Acc.* (to be published).

¹⁹SIRIUS, a program for the calculation of MCSCF wave functions written by H. J. Jensen, H. Ågren, and J. Olsen.

²⁰HERMIT, a molecular integral program written by T. Helgaker, P. R. Taylor, K. Ruud, O. Vahtras, and H. Koch.

²¹L. Visscher, O. Visser, H. Aerts, H. Merenga, and W. C. Nieuwoort, *Comput. Phys. Commun.* **81**, 81 (1994).

²²F. B. van Duijneveldt, IBM Research Report No. RJ 945, 1971.

²³K. G. Dyall, I. P. Grant, C. T. Johnson, E. P. Plummer, and F. A. Parpia, *Comput. Phys. Commun.* **50**, 375 (1989).

²⁴K. G. Dyall, K. Fgri, P. Taylor, and H. Patridge, *J. Chem. Phys.* **95**, 2583 (1991).

²⁵J. A. Pople, R. Seeger, and R. Krishnan, *Int. J. Quantum Chem. Quantum Chem. Symp.* **11**, 149 (1977).

²⁶S. R. Langhof and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).