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Complete active space MCSCF(CASSCF)/first-order configuration interaction (FOCI) calculations followed by relativistic configuration interaction (RCI) calculations are carried out on $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, and $^2\Sigma^+$(II) λ–s states and 1/2, 3/2, 1/2(II), 3/2(II), and 5/2 ω–ω states of PdH. Our calculations predict that the ground state is $^2\Sigma^+_{1/2}$. The spin–orbit splitting and contamination of the excited states ($^2\Pi$ and $^2\Delta$) are quite large. The two 3/2 states are quite mixed [3/2(I): 66% $^2\Delta_{3/2}$, 29% $^2\Pi_{3/2}$] in character. The spectroscopic properties (R_e, T_e, D_e, and ω_e) of all the above states are calculated and compared with available experimental results on the ground state of PdD. The Mulliken population analysis of the low-lying states of PdH shows that the $^2\Sigma^+$ state is ionic (Pd^+H^-) but the excited $^2\Pi$ and $^2\Delta$ states are a bit more ionic with the same polarity as the ground state. The 3/2 state exhibits an interesting avoided crossing.

I. INTRODUCTION

The transition metal hydrides are of considerable theoretical and experimental importance since they are useful models to gain insight into the interaction of metal with hydrogen and the nature of the metal–hydrogen bond. Theoretically, the electronic structure of heavy metal hydrides is interesting in that both correlation and spin–orbit effects are quite significant for these systems. Among the catalysts[1] for heterogeneous reactions platinum, palladium, and nickel are quite important since these systems form a relatively strong metal–hydrogen bond.

Relativistic effects such as mass–velocity correction, Darwin correction, and spin–orbit correction are quite important for molecules containing very heavy atoms.[2–7] In recent years,[2,8–17] relativistic configuration interaction (RCI) calculations have been shown to yield correct description of the electronic states of molecules containing very heavy atoms in an intermediate coupling scheme in which spin–orbit interaction and correlations are introduced simultaneously in a variational procedure.

Basch, Cohen, and Topiol[18] have made *ab initio* SCF calculations on the low-lying electronic states of PdH. Bagus and Björkman[19] have carried out nonrelativistic SCF followed by CI calculations on electronic states of NiH and PdH. More recently, Langhoff *et al.*[20] have carried out SCF/CI calculations which employ the Hay–Wadt relativistic effective potentials without spin–orbit interaction on the second-row transition metal hydrides. Thus, theoretical calculations carried out to-date on PdH do not include spin–orbit interaction. Further, as noted by these authors, correlation effects are quite significant for these compounds. Consequently, a theoretical treatment which includes correlation

effects to a higher degree such as complete active space MCSCF (CASSCF) followed by CI treatment may be some value for these compounds. The heavier diatomic analog of PdH, namely PtH, has been studied by Basch and Topial[21] and more recently by Wang and Pitzer.[22] Wang and Pitzer[22] have shown that spin–orbit splittings and contaminations are quite significant for PtH. Thus, it would be interesting to study the spin–orbit effects on the spectroscopic properties of PdH.

There are a few experimental investigations on PdH and PdD.[23–25] Lagerqvist *et al.*[23] have studied the absorption spectra of PdH and PdD in a King furnace. These authors concluded that the structure of the hydride spectrum is rather complicated while they could analyze the spectrum of PdD at 4049 Å. Knight and Weltner[24] investigated the ESR spectrum of PdH and PdD molecule in the $^2\Sigma^+$ ground state in Ar and Kr matrices. Malmberg *et al.*[25] have studied the absorption spectrum of PdH in the 4000–5000 Å region. The electronic transition they appear to have seen is tentatively assigned to $^2\Sigma^+$–$^2\Sigma^+$ transition. The R_e and ω_e values of ^{108}PdD were found from the spectra, but the properties of the excited $^2\Sigma^+$ could not be calculated due to perturbations in these bands.[25] At present, while the ground state of PdH is assigned to the $^2\Sigma^+$ state, the nature of the excited electronic states is not clear. The vibrational frequencies of the electronic states or their dissociation energies are not known. However, one could calculate the ω_e of the ground state based on the experimental ω_e for ^{108}Pd^{2}D.

The present theoretical investigation on PdH is undertaken with the object of shedding light on the nature and properties of electronic states of PdH, their spectroscopic properties, and the effect of spin–orbit interaction. Further there is a question about the participation of the d orbital in the metal–hydrogen bonding in transition metal hydrides in general and PdH, in particular. We carry out CASSCF/FOCI (compute active space MCSCF/first-order configuration interaction) calculations on $^2\Sigma^+$ $^2\Pi$, and $^2\Delta$ states of PdH. The spin–orbit interaction is introduced as a correction to CASSCF/FOCI properties through a relativistic configuration interaction scheme. Section II outlines our method while Sec. III contains results and discussion.

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TABLE I. λ–s and ω–ω states arising from low-lying MO configurations of PdH.

MO configurations	λ–s state(s)	ω–ω state(s)
$1\sigma^2 2\sigma\delta^4\pi^4$	$^2\Sigma^+$	1/2
$1\sigma^2 2\sigma^2\pi^3\delta^4$	$^2\Pi$	3/2, 1/2
$1\sigma^2 2\sigma^2\pi^4\delta^3$	$^2\Delta$	5/2, 3/2
$1\sigma^2 2\sigma 3\sigma\delta^3\pi^4$	$^4\Delta$	7/2, 5/2, 3/2, 1/2
	$^2\Delta(2)$	5/2(2), 3/2(2)
$1\sigma^2 2\sigma 3\sigma\delta^4\pi^3$	$^4\Pi$	5/2, 3/2, 1/2(2)
	$^2\Pi(2)$	3/2(2), 1/2(2)
$1\sigma^2 3\sigma\delta^4\pi^4$	$^2\Sigma^+$	1/2

TABLE III. Valence Gaussian basis set for the Pd atom.

s	Exponent	Contraction coefficient
s	0.4542	1.0
s	0.1720	1.0
s	0.0484	1.0
p	0.7368	0.03
p	0.0899	0.3
p	0.0262	1.0
d	2.3252	0.2724
d	1.0020	0.4425
d	0.4032	1.0
d	0.1452	1.0

II. METHOD OF INVESTIGATION

Table I shows a few low-lying MO configurations and the λ–s and ω–ω states arising from them. If one assumes that the δ and π orbitals will be nonbonding and lower in energy than the 2σ orbital then the ground state would be the $^2\Sigma^+$ state arising from the $1\sigma^2 2\sigma 1\delta^4 1\pi^4$ configuration. Table II shows the dissociation limits of the ω–ω states of PdH into atomic j–j states. In that state, our calculated separation of the excited dissociation atoms is compared with the experimental $^1S_0$–$^3D_3$ splitting for the Pd atom reported in Ref. 26. As one can see from that table, our theoretical splitting is about 26% off in comparison to the experimental atomic splitting. The ^1S–^3D splitting in the absence of spin–orbit interaction is 5713 cm^{-1}. Further extension of basis set could improve our results. The differential correlation errors are largest when comparing the atoms with molecules. We believe the errors should be smaller in comparing molecular states.

We employ two types of basis sets in conjugation with relativistic effective core potentials for the palladium atom.[27] LaJohn et al.[27] have generated Gaussian analytical relativistic effective potentials for the Pd atom. These authors have optimized a valence Gaussian basis set shown in Table III. We contract the two large p and d exponents which result in a ($3s2p3d$) Gaussian basis set for the Pd atom. The Gaussian basis set is used in our CASSCF/FOCI calculations which treat electron correlation quite accurately. A Slater-type orbital basis set was also optimized for the Pd atom (Table IV). Our relativistic CI code is interfaced with integral and SCF codes which perform calculations using the STO basis. Thus, the STO basis was needed in these calculations. The Gaussian basis set employed for the hydrogen atom is the one reported by Van Duijneveldt.[28] This was augmented by a set of p polarization functions with $\alpha_p = 0.9$. The exponents

for the hydrogen basis functions were multiplied by a scaling factor of 1.44. The hydrogen basis set was used by Balasubramanian and McLean[29] in SiH$_2$ calculations. The STO basis for the hydrogen atom is the one used by Balasubramanian and Pitzer[30] in other hydride calculations such as SnH and PbH.

The orbitals for first-order configuration interaction (FOCI) calculations were generated using the complete active space MCSCF (CASSCF) method with the Gaussian basis set described before. The CASSCF calculations were carried out in the C_s point group which contains just the YZ plane in addition to the identity element. The molecule was oriented in the YZ plane. The ten outer electrons (d^9s^1 or d^{10}) of the Pd atom and the $1s^1$ shell of the hydrogen atom were included in the active space. In the CASSCF method, active electrons are distributed in all possible ways among the strongly occupied orbitals of the separated atoms. The active space for PdH is the space spanned by the five outer d orbitals on Pd, the outer s orbital on Pd, and the H $1s$ orbital. In the C_s group, these orbitals span five a' and two a'' representations. The first-order configuration interaction calculations consisted of all configurations in the zeroth-order CASSCF (11 electrons distributed in all possible ways) plus the configurations generated by distributing ten electrons in the internal space and one electron in the orthogonal external space in all possible ways. The CASSCF configuration counts are 60 and 52 for $^2A'$ and $^2A''$ states, respectively. The corresponding counts for FOCI are 5374 and 5294. The C_s group was chosen mainly for convenience since two sets of calculations are only needed as all the electronic states can be obtained as higher roots. Multiple roots of each state were sought and then reassigned to the $C_{\infty v}$ group.

The spin–orbit interaction is introduced through the rel-

TABLE II. Dissociation limits for low-lying states of PdH.

Molecular states	Dissociated atoms (Pd + H)	Energy of the atoms (cm^{-1})	
		Theory	Expt.
1/2(I)	$^1S_0 + {}^2S_{1/2}$	0.0	0.0
7/2, 5/2, 3/2(I), 1/2(II)	$^3D_3 + {}^2S_{1/2}$	4826	6564.0

TABLE IV. Optimized Slater-type orbital exponents for the Pd atom.

	Pd	Type
s	2.1697	(5s)
	1.2039	(5s)
p	0.9	(5p)
d	4.0151	(4d)
	1.9796	(4d)

ativistic configuration interaction method described in Ref. 17. In general, λ–s states which give rise to the same ω–ω state could mix in the presence of spin–orbit interaction. The CASSCF/FOCI calculations described earlier include correlation corrections quite accurately but not spin–orbit splitting or spin–orbit contamination of electronic states of different λ–s states. As mentioned earlier, the relativistic CI code is interfaced with the integral generators which handle the STO basis. Thus, a single configuration SCF treatment was used to generate the MOs for RCI calculations. The SCF calculations were carried out for the $^2\Sigma^+$ ground state of PdH.

The relativistic calculations carried out were MRSDCI calculations in intermediate coupling. The 1/2 states included reference configurations arising from $^2\Sigma^+_{1/2}$ ($1\sigma^2 2\sigma 1\delta^4 1\pi^4$), $^2\Pi_{1/2}$ ($1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$). The 3/2 states included $^2\Delta_{3/2}$ ($1\sigma^2 2\sigma^2 1\delta^3 1\pi^4$) reference configurations and $^2\Pi_{3/2}$ ($1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$) reference configurations while the 5/2 state included $^2\Delta_{5/2}$ ($1\sigma^2 2\sigma^2 1\delta^3 1\pi^4$) reference configurations. Extensive single and double excitations were allowed from these reference configurations. Another set of CI calculations with the same references as in 1/2, 3/2, and 5/2 states were carried out but omitting the spin–orbit integrals. These sets of calculations yield $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ λ–s states without the inclusion of spin–orbit effects. The differences in energies and spectroscopic properties obtained with and without spin–orbit contributions with identical configuration space would then yield the corrections to these properties due to spin–orbit interaction. These corrections (to R_e, T_e, ω_e, D_e, and the actual energies) were then introduced to CASSCF/CI results obtained earlier which do not take into account the effect of spin–orbit interaction. This way we take into account both correlation and spin–orbit effects quite accurately. The CASSCF/FOCI calculations were carried out with one of the authors' (K.B.) modification of the ALCHMEY II codes[31] as described in Ref. 32. The RCI calculations were carried out with K.B.'s modified version of the RCI codes developed earlier as described in Ref. 17.

III. RESULTS AND DISCUSSION

Table V shows the calculated spectroscopic properties of PdH with and without spin–orbit interaction. Figure 1 shows the potential energy curves of low-lying states of PdH as a function of internuclear distance.

As one can see from Table V, the ground state of PdH is

TABLE V. Spectroscopic properties of low-lying states of PdH.

State	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
1/2(I)	0.0	1.53	1948	2.21
5/2	3 497	1.59	1817	2.38
3/2(I)	4 599	1.65	1711	2.24
1/2(II)	9 343	1.67	1655	1.65
3/2(II)	9 362	1.63	1721	1.65
$^2\Sigma^+$(II)	21 904	1.62	1567	$\cdots$
$^2\Sigma^+$	202	1.52	1985	2.19
$^2\Pi$	8 409	1.68	1613	1.88
$^2\Delta$	4 814	1.59	1816	2.32

the $^2\Sigma^+_{1/2}$ state. The spin–orbit splitting of the ground state (202 cm^{-1}) is somewhat small in comparison to the spin–orbit effects for the excited states. The calculated R_e (1.53 Å) is almost identical to the experimental R_e value of 1.534 Å reported by Malmberg et al.[25] as well as Knight and Weltner.[24] We calculated the ω_e value of the $X\,^2\Sigma^+$ ground state of ^{106}Pd^{1}H from the ω_e of the ^{108}Pd^{2}D reported by Malmberg et al.[25] (1446 cm^{-1}) to be 2036 cm^{-1}. This value is in reasonable agreement with our calculated ω_e value of 1948 cm^{-1} for the 1/2 ground state.

There are no experimental values for the spectroscopic properties of the excited states. There are a number of bound low-lying excited states for PdH reported in Table V which are yet to be observed. The R_e values of the excited states are somewhat larger (0.07–0.16 Å) than that of the ground state. Note that the R_e value of the 5/2 state is virtually identical to that of the $^2\Delta$ state while the R_e value of the 3/2 is somewhat larger. This arises from the fact that both the 3/2 and 3/2(II) states are contaminated quite heavily by spin–orbit interaction. At near equilibrium geometries, the 3/2 state is a mixture of $^2\Delta_{3/2}$ and $^2\Pi_{3/2}$. Since $^2\Pi$ λ–s state has a longer bond than the $^2\Delta$ state, the bond length of the 3/2(I) state is larger than the $^2\Delta$ but is between the $^2\Delta$–$^2\Pi$ bond lengths as determined by the spin–orbit contamination. Since the 3/2(II) is also a mixture of $^2\Pi_{3/2}$ and $^2\Delta_{3/2}$, its bond length falls shorter than the $^2\Pi$ R_e value. The ω_e values of the 3/2 and 3/2(II) states are also influenced to a considerable extent by spin–orbit contamination and an avoided crossing of $^2\Delta_{3/2}$ and $^2\Pi_{3/2}$ at around 3.25 bohr.

Malmberg et al.[25] have studied the absorption spectrum of PdD in the 4000–5000 Å region. As a result of strong perturbation, these authors could not perform any analysis of the spectra of PdH. The absorption bands these authors observe were of $^2\Sigma$–$^2\Sigma$ character. While they have not reported the properties of the excited state in this transition, the first group of band heads (I) appears in the region of 22 264 cm^{-1}. As one can see from Table VI, the second root of $^2\Sigma^+$ arising from the $1\sigma^2 3\sigma^1 1\pi^4 1\delta^4$ falls in this region although this state is composed of this and other configurations. As mentioned before, the properties of this excited
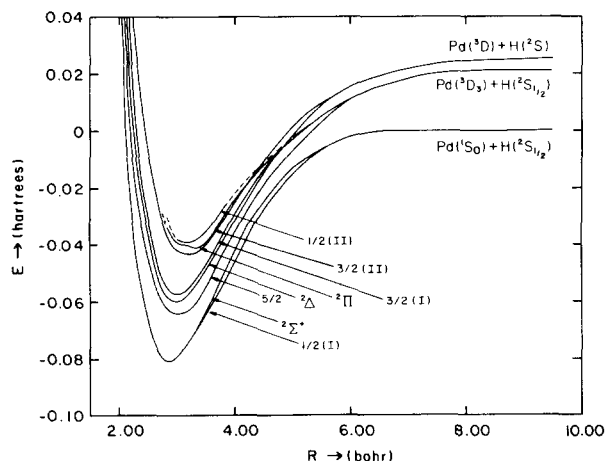

FIG. 1. Potential energy curves of low-lying electronic states of PdH with and without spin–orbit interaction.

TABLE VI. Contributions of various configurations to the electronic states of PdH. Numbers in parentheses are percentages.

State	R (bohr)	Contributions
1/2 (I)	3.00	$1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (92)
1/2 (I)	4.00	$1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (64), $1\sigma 2\sigma^2 1\pi^4 1\delta^4$ (9), $1\sigma 2\sigma 3\sigma 1\pi^4$ (5), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (5; $^2\Pi$)
1/2 (I)	5.00	$1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (90), $1\sigma 2\sigma^2 1\pi^4 1\delta^4$ (2), $1\sigma 2\sigma 3\sigma 1\pi^4 1\delta^4$ (1)
1/2 (I)	6.00	$1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (96)
3/2(I)	3.00	$1\sigma^2 2\sigma^2 1\delta^3 1\pi^4$ (66; $^2\Delta$), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (29; $^2\Pi$)
3/2 (I)	4.00	$1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (56; $^2\Pi$), $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (13; $^2\Delta$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (5; $^4\Delta$), $1\sigma^2 2\sigma 3\sigma 1\delta^4 1\pi^3$ (18, $^4\Pi$)
3/2 (I)	5.00	$1\sigma^2 2\sigma 3\sigma 1\delta^4 \pi^3$ (42; $^4\Pi$), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (38; $^2\Pi$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (8; $^4\Delta$), $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (6; $^2\Delta$)
3/2 (I)	6.00	$1\sigma^2 2\sigma 3\sigma 1\delta^4 1\pi^3$ (55; $^4\Pi$), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (19; $^2\Pi$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (9; $^4\Delta$), $1\sigma^2 2\sigma 4\sigma 1\delta^4 1\pi^3$ (4; $^4\Pi$), $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (2; $^2\Delta$), $1\sigma^2 2\sigma 5\sigma 1\delta^4 1\pi^3$ (2; $^4\Pi$)
5/2	3.00	$1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (94; $^2\Delta$)
5/2	4.00	$1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (66; $^2\Delta$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (26; $^4\Delta$)
5/2	5.00	$1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (50; $^4\Delta$), $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (42; $^2\Delta$)
5/2	6.00	$1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (64; $^4\Delta$), $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (20; $^2\Delta$), $1\sigma^2 2\sigma 4\sigma 1\pi^4 1\delta^3$ (6; $^4\Delta$), $1\sigma^2 2\sigma 5\sigma 1\pi^4 1\delta^3$ (2; $^2\Delta$)
1/2 (II)	3.00	$1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (93; $^2\Pi$), $1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (1)
1/2 (II)	3.50	$1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (88; $^2\Pi$), $1\sigma^2 2\sigma 1\delta^4 \pi^4$ (6)
1/2 (II)	4.00	$1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (58; $^2\Pi$), $1\sigma^2 2\sigma 1\delta^4 1\pi^4$ (14), $1\sigma^2 2\sigma 3\sigma 1\pi^3 1\delta^4$ (15; $^4\Pi$)
3/2 (II)	4.00	$1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (53; $^2\Delta$), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (14; $^2\Pi$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (21; $^4\Delta$), $1\sigma^2 2\sigma 3\sigma 1\delta^4 1\pi^3$ (3; $^4\Pi$)
3/2 (II)	5.00	$1\sigma^2 2\sigma^2 1\pi^4 1\delta^3$ (36; $^2\Delta$), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^3$ (44; $^4\Delta$), $1\sigma^2 2\sigma^2 1\pi^3 1\delta^4$ (6; $^2\Pi$), $1\sigma^2 2\sigma 3\sigma 1\pi^3 1\delta^4$ (8; $^4\Pi$)
3/2 (II)	6.00	$1\sigma^2 2\sigma 3\sigma 1\delta^4 1\pi^3$ (60), $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ (20), $1\sigma^2 2\sigma 4\sigma 1\delta^4 1\pi^3$ (4), $1\sigma^2 2\sigma 1\pi^4 1\delta^4$ (2), $1\sigma^2 2\sigma 3\sigma 1\pi^4 1\delta^4$ (4), $1\sigma^2 2\sigma 5\sigma 1\pi^3 1\delta^4$ (2)

electronic state could not be calculated from experimental results due to strong perturbations of the upper vibrational levels. The calculated R_e and ω_e values of this state in Table V should thus be useful in further analysis of the experimental results or future comparisons with experimental values yet to be reported.

The dissociation energy of the 1/2 ground state is calculated to be 2.21 eV. Since the 1/2 state dissociates into $Pd(^1S_0) + H(^2S)$ the spin–orbit splitting of the atomic states is zero while the molecular $^2\Sigma^+$ splitting is about 200 cm^{-1}. Thus, the molecule is stabilized by 0.02 eV as a result of spin–orbit interaction. A crude experimental D_e was calculated by Malmberg et al.[25] from the ω_e and harmonicities of PdD using the formula

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}.$$

The value obtained this way was 3.3 eV which is too high. The experimental D_e of the heavier PtH is 3.44 eV.[33] The PtH molecule is expected to have a larger dissociation energy since its ground state is $^3D_3(d^9 s^1)$ which forms a more stable bond than the $^1S_0(d^{10})$ state which is the ground state of the Pd atom. Thus, the D_e of PdH should be somewhat smaller than PtH. Our calculated D_e's with CASSCF/FOCI level of theory are about 80%–90% of the experimental values. Thus, we believe that the D_e value of 3.3 eV is somewhat high and the D_e of PdH should be about 2.45–2.75 eV. The calculated dissociation energies of the excited states in Table V could be off by as much as 25% since correlation errors in atoms $^1S_0$–$^3D_3$ splitting (long distance splitting) is off by

28% in comparison to experimental value.

The calculated results in Table V in the absence of spin–orbit interaction are in reasonable agreement with the results obtained by Langhoff et al.[20] The CASSCF/FOCI results are somewhat better than the SDCI results of Langhoff et al.[20] but are closer to their MCPF results. For example, the SDCI and MCPF D_e's reported in Ref. 20 are 1.92 and 2.22 eV, respectively. The r_e and ω_e values are not influenced to a great extent by higher order correlation corrections. The main difference between the results in Table V and that of Ref. 20 arises from the neglect of spin–orbit interaction in Ref. 20. This in particular is substantial for the $^2\Delta$ and $^2\Pi$ excited states as one can see from Table V.

We next compare the electronic states of PdH with PtH. Wang and Pitzer[19] have carried out ab initio relativistic CI calculations on PtH. They found that the ground state of PtH is $^2\Delta_{5/2}$ with $^2\Sigma_{1/2}^+$ only 1008 cm^{-1} above the ground state. The 3/2 state is 2742 cm^{-1} above the 5/2 state while the 3/2(II) state is 19 350 cm^{-1} above the 3/2(I) state. The $^2\Pi_{1/2}$ state is about 11 810 cm^{-1} above the $^2\Sigma_{1/2}^+$ state. Thus, the $^2\Delta_{5/2}$–$^2\Sigma_{1/2}$ splitting for PtH is much smaller than the corresponding splitting for PdH. Similarly, the 3/2 state is much lower for PtH. In general, the trend is higher Ω states are lower for PtH since the Pt($^3D_3$) state is about 6140 cm^{-1} below the Pt($^1S_0$) state while for Pd this is approximately reversed. The M–H bond lengths are not too different for PtH and PdH. For example, the experimental R_e for the $^2\Sigma_{1/2}^+$ state of PtH is 1.54 Å and is close to the 1.53 Å value for PdH. Thus, the bonding is similar. However, the ω_e values for PtH are larger than PdH since PtH bonding is strong-

TABLE VII. Mulliken population analysis for PdH.

	Net					Gross					Overlap
	Pd	H	Pd(s)	Pd(p)	Pd(d)	Pd	H	Pd(s)	Pd(p)	Pd(d)	
$^2\Sigma^+$	9.567	0.919	0.379	0.010	9.187	9.824	1.176	0.531	0.002	9.295	0.514
$^2\Delta$	9.426	0.942	0.589	0.008	8.715	9.742	1.258	0.892	0.005	8.845	0.632
$^2\Pi$	9.450	0.968	0.508	0.016	8.887	9.741	1.259	0.773	0.047	8.921	0.583

er than PdH. The spin–orbit contamination effects are surprisingly large for the 3/2 states of PdH.

The nature of the electronic states of PdH and the nature of bonding are considered next. Table VI shows the percentage contributions of various λ–s states to the ω–ω states of PdH. As one can see from that table, the spin–orbit contaminations for $^2\Sigma^+_{1/2}$, $^2\Delta_{5/2}$, and $^2\Pi_{1/2}$ are somewhat small. However, the 3/2 state is heavily contaminated with $^2\Delta_{3/2}$ and $^2\Pi_{3/2}$. In fact at 3.25 bohr which is not very far from the equilibrium geometry, the 3/2 state is an equal mixture of $^2\Delta_{3/2}$ and $^2\Pi_{3/2}$. At distances shorter than 3.25 bohr, the $^2\Delta_{3/2}$ dominates but is mixed heavily with $^2\Pi_{3/2}$ in the 3/2(I) state. At distances larger than 3.25 bohr, the $^2\Pi_{3/2}$ dominates in the 3/2(I) state. The 3/2(II) state exhibits an opposite behavior as this is typical of avoided crossings. This results in the slightly distorted curve for the 3/2(II) state (Fig. 1) in this region. Thus, spin–orbit effects influence the R_e, ω_e, and T_e values of the 3/2(I) and 3/2(II) states to a considerable extent.

The $^2\Sigma^+$ λ–s state arises from $1\sigma^2 2\sigma 1\delta^4 1\pi^4$ configuration. The $^2\Pi$ and $^2\Delta$ states arise from $1\sigma^2 2\sigma^2 1\delta^4 1\pi^3$ and $1\sigma^2 2\sigma^2 1\delta^3 1\pi^4$ configuration, respectively. Table VII shows the net, gross, and overlap Mulliken populations of these states. As one can see from that table, the total gross Mulliken population of Pd in all electronic states is smaller than 10 while the hydrogen population is increased to about 1.2. This reflects that the Pd–H bond has ionic character ($Pd^+ H^-$). The ionicities of the $^2\Delta$ and $^2\Pi$ states are a bit larger than that of the $^2\Sigma^+$ state. The FOCI dipole moments of the $^2\Sigma^+$, $^2\Delta$, and $^2\Pi$ states in the absence of spin–orbit interaction are 2.357, 3.137, and 3.520 D, respectively. The effect of spin–orbit interaction on the dipole moment of the $^2\Sigma^+$ state is expected to be relatively small in comparison to the transition moments. The gross d populations of the $^2\Delta$ and $^2\Pi$ states are smaller than that of the $^2\Sigma^+$ state. This is accompanied by a decrease in the s population on the Pd atom for the $^2\Sigma^+$ state. The Mulliken population of the occupied σ space (1σ, 2σ orbitals) of the PdH $^2\Sigma^+$ state shows that there are $1.187\,d$, $0.531\,s$ electrons on Pd and 1.176 electrons on hydrogen in the $^2\Sigma^+$ state. Thus, the d orbital participates in the σ bond of PdH.

IV. CONCLUSION

In this investigation, we carried out CASSCF/FOCI calculations followed by relativistic CI (RCI) calculations which include spin–orbit corrections for the low-lying electronic states of PdH. Our calculations reveal the existence of 1/2(I), 3/2, 5/2, 3/2(II), 1/2(II), and $^2\Sigma^+_{1/2}$(II) states.

Experimental results are available only on the R_e and ω_e value of the PdD molecule. Experimental spectroscopic constants for all the excited states of PdH are yet to be calculated. The dissociation energy of PdH is predicted to be 2.6 ± 0.2 eV. The 3/2 excited state of PdH exhibits an avoided crossing at 3.25 bohr.

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