Electronic structure of transition-metal hydrides: NiH and PdH

Paul S. Bagus and Cecilia Björkman*

IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193

(Received 9 September 1980)

Ab initio self-consistent field (SCF), and configuration interaction (CI), calculations have been performed for the diatomic transition metal hydrides NiH and PdH to study the behavior of the d electrons and their effect on chemical bonding. SCF calculations have been carried out for the three low-lying states, $^2\Delta$, $^2\Pi$, and $^2\Sigma^+$, which can be formed with the metal atom in the (d^9s^1) configuration. The ground state of NiH is $^2\Delta$ with the $^2\Pi$ and $^2\Sigma^+$ states only about 0.1 eV above. In the case of PdH the $^2\Sigma^+$ state is the lowest with the $^2\Delta$ about 0.6 eV above. This difference can be attributed to the participation of the $4d$ electrons in the PdH bond. The $3d$ electrons in NiH seem to be more localized and "atomic d-like." In both cases the potential energy curves are too broad and the equilibrium bond lengths are longer than those found from spectral data. For both molecules, the CI results are considerably improved over those from the SCF calculations. However, there are still significant differences between the computed (CI) and observed values for the ground-state equilibrium bond length and force constant. Two effects are considered in order to understand these errors. For NiH, the limited CI is unable to properly account for the differential correlation energy of the $3d^9 4s^1$ and $3d^8 4s^2$ terms of the free Ni atom and this probably leads to the errors in the calculation. For PdH, differential atomic correlation energies are likely to be much less important, but relativistic effects are likely to be important. We have also investigated some excited states and the calculated vertical term energies are compared with experimental results.

I. INTRODUCTION

The present investigation deals with the two transition-metal hydrides NiH and PdH. The purpose has been to study and compare properties of transition-metal compounds from the first and second series. Special emphasis has been put on the study of the d electrons and their role in bonding for the two hydrides. Potential energy curves for ground and excited states have been calculated, the wave functions analyzed, and some properties computed.

There is very little experimental information available for the two hydrides; absorption spectra have been measured for both,[1-4] and for PdH the ESR spectrum has been analyzed.[5] To our knowledge, no theoretical investigation of PdH has been reported previously. Several theoretical studies have been concerned with NiH, mainly in connection with studies of hydrogen chemisorption on transition metals. Effective core potential Hartree-Fock (HF),[6] unrestricted HF and generalized valence bond (GVB),[7] and linear combination of atomic orbital local density (LCAO-$X\alpha$) (Ref. 8) methods have been used in these studies. In the present investigation, we have undertaken *ab initio* self-consistent-field (SCF), configuration-interaction (CI), and multiconfiguration SCF (MCSCF) calculations. These calculations have provided the most accurate theoretical results to date for NiH. Not only have we used more accurate models for the wave function, including more correlation than in previous work, but we have also used quite large Slater-type basis sets to represent the molecular orbitals (MO's).

It is useful to consider some qualitative aspects which influence the bonding properties of these molecules. Ni and Pd belong to the same group in the periodic system, but the electronic structure of the free atoms is rather different.[9] The lowest term of Ni is $^3F_4(d^8s^2)$ with the $^3D_3(d^9s^1)$ term only 204 cm^{-1} above. The ^3F and ^3D multiplets are thus almost degenerate; for the weighted average of the multiplets, the ^3D is 240 cm^{-1} lower than the ^3F. The $^1S(d^{10})$ term is much higher at about 15 000 cm^{-1}. For Pd, on the other hand, the lowest term is the $^1S(d^{10})$. The $^3D(d^9s^1)$ and $^3F(d^8s^2)$ multiplets are 7666 and 27 236 cm^{-1}, respectively, above the ground state. For these atoms, the d shell is much more contracted than the valence s shell. The $\langle r \rangle$ for HF atomic orbitals for the $d^9s^1(^3D)$ states of Ni and Pd are

$$\text{Ni} \quad \langle r \rangle_{3d} = 1.050, \quad \langle r \rangle_{4s} = 3.379,$$

$$\text{Pd} \quad \langle r \rangle_{4d} = 1.446, \quad \langle r \rangle_{5s} = 3.675.$$

[The values for the $d^8s^2(^3F)$ states are very similar.] These values clearly show the much greater spatial extent of the s shell. On the basis of the sizes of the orbitals, we would expect the $(n+1)s$ electrons (probably with substantial p hybridization) to be more involved in the metal to H bonding than the nd electrons.

Neither the d^{10} nor the d^8s^2 atomic configurations are particularly suitable starting points for the formation of a covalent bond with H. All shells are filled in the d^{10} configuration and it will be rather inert unless there is substantial hybridization of the d with the valence s and p shells. Hybridization of this sort is unlikely because of the different spatial extents of the shells. The open

d shell of the d^8s^2 configuration is shielded by the diffuse filled $(n+1)s$ shell and is, thus, likely to be prevented from having substantial participation in the bonding. For the bonding of H with the valence s^2 shell, it is appropriate to have sp hybridization of the form $(s+p)^1(s-p)^1$. The energy required for this hybridization is roughly the excitation energy to $d^ns^1p^1$ ($n=8$ for Ni and Pd), and it is compensated by the formation of a bond. This is, in fact, the bonding mechanism for the ground $X^7\Sigma^+$ state of MnH. For Mn, the $3d^54s^14p^1$ configuration is rather low lying,[9] while for both Ni and Pd, the $d^8s^1p^1$ configurations are quite high above the ground state.[9] Furthermore, if the bond were formed in this way, the ground-state multiplicity would be quartet; d^8 (triplet) plus $(s-p)^1$ (doublet). However, analysis of optical spectra for NiH (Refs. 1–3) and PdH[4] show that the ground state is a doublet. Thus we can eliminate d^8s^2 as the atomic configuration which leads to bonding in these cases.

The lowest state that can lead to the formation of a stable bond with H arises from the d^9s^1 configuration. For Ni, $3d^94s^1(^3D)$ is the lowest multiplet, and for Pd, $4d^95s^1(^3D)$ is less than 1 eV above the ground $4d^{10}(^1S)$ state. The singly occupied valence s electron is available to form a single two-electron bond with H $1s$. Thus, to a first approximation, we expect the metal-H bond to be formed by the outermost s electron in the metal and the hydrogen $1s$.

In order to look at the possible contributions to the bonding of the metal nd and $(n+1)s$ electrons in another way, we have calculated overlap integrals between SCF atomic orbitals (AO's) of the metal atoms and H. (The free metal AO's were obtained for the $d^9s^1(^3D)$ term using Slater basis sets given by Clementi and Roetti.[10]) The metal atom to H distances used, R(Ni-H) = 2.88 and R (Pd-H) = 3.1 bohrs, were close to the calculated SCF equilibrium bond lengths r_e and slightly larger than the experimental r_e.[3,4] The values of $\langle nd\sigma|\mathrm{H}(1s)\rangle$ and $\langle (n+1)s|\mathrm{H}(1s)\rangle$ are given in Table I. Two conclusions can be drawn from the size of the overlaps: The outer s electron on the metal atom is indeed likely to be primarily responsible for the bonding to the hydrogen atom. However, the overlaps between the hydrogen s and the metal d orbitals are not negligible, and it is thus possible that the d electrons participate to some extent in the bonding. The ratio of $\langle$metal $s|\mathrm{H}(1s)\rangle$ to $\langle$metal $d\sigma|\mathrm{H}(1s)\rangle$ is considerably larger for Ni (~3.5) than for Pd (~2.4). We therefore expect the $4d$ electrons of Pd to play a more important role than the $3d$ electrons of Ni.

For this picture of the bonding, NiH and PdH have an open, essentially atomic, d shell with

TABLE I. Overlap integrals calculated for atomic SCF orbitals. NiH distance = 2.88 bohr; PdH distance = 3.10 bohr.

$\langle \mathrm{Ni}(3d\sigma)\,\vert\,\mathrm{H}(1s)\rangle$	0.147
$\langle \mathrm{Ni}(4s)\,\vert\,\mathrm{H}(1s)\rangle$	0.496
$\langle \mathrm{Pd}(4d\sigma)\,\vert\,\mathrm{H}(1s)\rangle$	0.192
$\langle \mathrm{Pd}(5s)\,\vert\,\mathrm{H}(1s)\rangle$	0.458

one hole. In the axial symmetry of the molecule, the atomic d level splits into δ, π, and σ levels. There are, thus, three possible symmetries for the "d hole" leading to $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ states of the molecule. If the d electrons are not strongly involved in the bonding, these states will be close together. We find that this is, in fact, the case, especially for NiH.

In the following, we shall be primarily concerned with the energetic order and other properties of these three states. We shall also be concerned with the characterization of excited states which have the same symmetry as the ground state. In Sec. II, the choice of basis sets and methods of computation are discussed. In Sec. III, the results of the computations are reported and discussed. Finally, the conclusions of this work are summarized in the last section.

II. COMPUTATIONAL DETAILS

Large Slater-type basis sets were used in the calculations. Two different sets were used for Ni. The first was Clementi and Roetti's $(11s, 6p, 5d)$ set,[10] optimized for the $^3D(3d^94s^1)$ state, augmented with three $4p$ and two $4f$ functions. The purpose of the $4p$ basis functions was to serve as polarization functions for the $4s$ orbital. Values for the exponents of the added $4p$'s were chosen to be the same as those of the three most diffuse $4s$ functions. The $4f$ functions were intended to be polarization functions for the $3d$'s and the exponents were chosen so that the radial maxima of the f and outermost d functions coincided. Only basis functions in the σ, π, and δ representation of $C_{\infty v}$ were used. Counting the doubly degenerate π and δ functions once, the total number of basis functions centered on Ni was 50: 27σ, 16π, and 7δ. In some calculations a second, smaller, basis set was used. This was based on the $(8s, 5p, 4d)$ set of Bagus et al.,[11] optimized for $^3F(3d^84s^2)$, and augmented with two $4p$ functions chosen in the manner described above. The second basis set was used in the SCF calculations to test basis set convergence and was also used for the larger MCSCF calculations. Unless otherwise specified, the larger set was used in the calculations reported.

For Pd, Clementi and Roetti's $(11s, 7p, 5d)$ set,[10] optimized for the $^3D(4d^95s^1)$ state, was used. This set was augmented with three $5p$ and two $4f$ functions where exponents were chosen in the same way as for Ni. This gave a total number of 52 functions centered on Pd: 28σ, 17π, and 7δ. In order to determine the ability of these sets to accurately represent SCF wave functions for different atomic states, atomic calculations were performed for the $^3F(d^8s^2)$ and $^3D(d^9s^1)$ terms of Ni and Pd and for the $^1S(d^{10})$ state of Pd. The computed total energies are compared in Table II with numerical HF (NHF) results.[12] For both Ni and Pd the deviation of the SCF energies from the NHF results is the same for the ^3F and ^3D states. For the ^1S state of Pd, the deviation is only slightly larger.

For H, Preston's $(5s, 2p)$ basis set, reported in Ref. 13, was used. In a study of MnH,[13] several H basis sets were used and this one was found to give the lowest total energy. Moreover, the results for MnH were found to be relatively insensitive for any choice of a reasonably flexible H basis set. SCF, MCSCF, and CI calculations were performed for internuclear distances in the range 2.58 to 3.18 bohr (NiH), and 2.70 to 3.30 bohr (PdH). (A description of these methods may be found in Refs. 14 and 15.) An MCSCF program developed by Hinze[16] was used; all other molecular computations were carried out using the ALCHEMY programs developed by Bagus, Liu, McLean, and Yoshimine.

SCF and two-configuration MCSCF (TCSCF) calculations were carried out for all three low-lying states $^2\Delta$, $^2\Pi$, and $^2\Sigma^+$. MCSCF calculations employing additional configurations were also performed for the ground state of NiH. Details concerning these calculations will be given in connection with the discussion of the results in Sec. III B.

CI calculations were performed for the ground and for the lowest excited states of the ground-state symmetry. Our treatment of correlation has been limited in that we have correlated only

TABLE II. Comparison of atomic SCF results with numerical Hartree-Fock (NHF) results for Ni and Pd. Energies are in hartrees.

Ni	SCF	NHF	Δ(NHF–SCF)
$^3F(d^8s^2)$	−1506.869	−1506.871	−0.002
$^3D(d^9s^1)$	−1506.823	−1506.825	−0.002
Pd			
$^1S(d^{10})$	−4937.903	−4937.922	−0.019
$^3D(d^9s^1)$	−4937.882	−4937.894	−0.012
$^3F(d^8s^2)$	−4937.771	−4937.784	−0.013

those electrons believed to be directly involved in the metal-H bonding. The configurations used in the CI were formed by making excitations from the SCF ground-state configuration. For NiH, 2- and 4-electron CI calculations were performed. In the 2-electron CI, all single and double excitations (SD) from the predominantly Ni $4sp + $ H s bonding 7σ MO (see Sec. III A) were included; we denote this as 2-el CI/SD. In the 4-electron CI, all SD excitations from both the 7σ and the predominantly Ni $3d/6\sigma$ (see Sec. III A) were included (4-el CI/SD). For PdH, full 3-electron CI calculations including all SD and triple (SDT) excitations from the 9σ and 10σ MO's (3-el CI/SDT) which, in the SCF configuration, are doubly and singly occupied, respectively (see Sec. III A). These are the MO's which are responsible for the bonding and involve the $4d$, $5s$, $5p$, and H$1s$ atomic orbitals.

The orbitals from which the excitations are made are referred to as the internal space; those into which they are made as the external space. The external space was chosen as a subset of the Slater basis set orthonormalized to the occupied SCF MO's.[17] This was done in order to span the space important for correlation with a relatively small number of orbitals. Two external spaces were constructed; the first consisted only of s- and p-type functions and the second included d functions as well.

For NiH, the sp external space contained 13σ and 5π orbitals. These orbitals, together with the occupied 7σ MO spanned the space of the four $4s$ and three $4p$ basis functions on Ni and of the five s- and two p-type functions on H. The spd external space contained, in addition, 4σ, 4π, and 4δ functions which, together with the occupied $3d$-like MO's spanned the full space of the five $3d$ basis functions on Ni. For PdH, the sp external space contained 12σ and 5π functions; the spd space contained in addition 2σ, 2π, and 2δ functions. These external spaces, together with the occupied orbitals, spanned the space of the $5s$, $5p$, and $4d$ basis functions on Pd and of the s and p functions on H. CI calculations using the sp space are denoted CIA, and those using the spd space are denoted as CIB. For NiH, the 2-el CIA/SD contained 246 CSF's; the 4-el CIA/SD and 4-el CIB/SD contained 1032 and 2304 CSF's, respectively. For PdH, the 3-el CIA/SDT and 3-el CIB/SDT contained 1260 and 2306 CSF's.

The choice of the internal space reflects the limited nature of the CI. A more extensive treatment should include at least the "passive" metal $d\pi$ and $d\delta$ electrons and possibly also the $3s$ and $3p$ electrons. Such a treatment is required to properly describe the behavior of the metal-d electrons and to correctly locate atomic states with different

d occupations. Of course, such CI's will be much larger than those performed in this work. As we shall see in Sec. III, our limited CI does give a substantial improvement over the SCF description. In the Appendix, we tabulate total energies for all the calculations described above.

III. RESULTS AND DISCUSSION

The discussion of the results is divided into several subsections. In Sec. III A, we present the results of the SCF calculations and analyze these results to obtain an overall description of the bonding and electronic structure of the ground and low-lying states. In Sec. III B, we discuss the MCSCF calculations and results. The CI results for the ground states are presented in III C and for the excited states in III D.

A. SCF results and electronic structure

As discussed in the introduction, we are concerned with states that can be described to first order as involving a metal $sp + H1s$ bond and a d shell with one hole. For NiH, the three states which can be formed within this model are

$$^2\Delta \quad 6\sigma^2 7\sigma^2 3\pi^4 1\delta^3, \tag{1a}$$

$$^2\Pi \quad 6\sigma^2 7\sigma^2 3\pi^3 1\delta^4, \tag{1b}$$

$$^2\Sigma^+ \quad 6\sigma^1 7\sigma^2 3\pi^4 1\delta^4. \tag{1c}$$

The 6σ, 3π, and 1δ MO's are expected to be more or less localized Ni$3d$, and 7σ the bonding MO. The configuration of Eq. (1c), where the open shell 6σ MO is shown as having a lower orbital energy than the filled 7σ should not be surprising. The aufbau principle is often not followed, neither for free transition metal atoms (where $d^n s^2$ or $d^{n+1}s^1$ are commonly the ground-state configurations), nor for transition metal hydrides.[13] For PdH, the equivalent configurations are

$$^2\Delta \quad 9\sigma^2 10\sigma^2 5\pi^4 2\delta^3, \tag{2a}$$

$$^2\Pi \quad 9\sigma^2 10\sigma^2 5\pi^3 2\delta^4, \tag{2b}$$

$$^2\Sigma^+ \quad 9\sigma^2 10\sigma^1 5\pi^4 2\delta^4. \tag{2c}$$

In Eq. (2c), we anticipate the result that the 9σ and 10σ MO's have substantial bonding and antibonding character, respectively, and that the aufbau principle is, in fact, followed. The core orbitals not shown in Eqs. (1) and (2) are expected to be localized metal-atom core levels.

The SCF potential energy curves are shown in Figs. 1 and 2 for NiH and PdH. (The calculated total SCF energies are given in the Appendix in Tables VIII–XI.) For NiH, the ground state is found to be $^2\Delta$. This is in agreement with the analyses of the optical spectra of NiH.[1-3] The
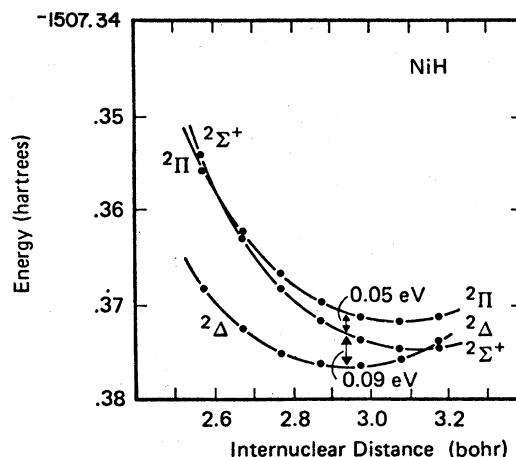

FIG. 1. SCF potential energy curves for NiH.

excited states $^2\Sigma^+$ and $^2\Pi$ are very close in energy. The vertical excitation energies are 0.09 and 0.14 eV, respectively. [With the smaller Bagus et al.[12] basis set, the order of the states is the same, but the $^2\Sigma^+$ and $^2\Pi$ states are even closer together; the total (vertical) energy range $^2\Delta$ to $^2\Pi$ is 0.19 eV.]

The equilibrium bond length r_e, and quadratic vibrational force constant k_e, found for the $^2\Delta$ curve are given in Table III. The computed r_e is
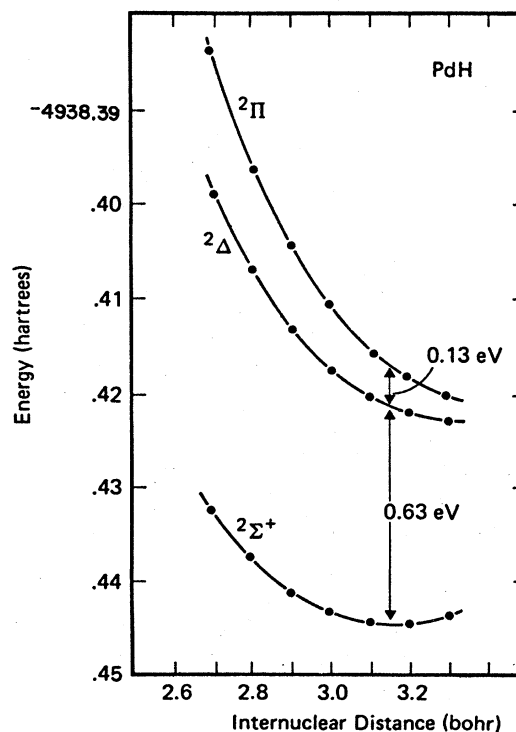

FIG. 2. SCF potential energy curves for PdH.

TABLE III. Equilibrium bond lengths r_e, and force constants k_e, for various calculations on the ground state. The notation for the CI calculations is explained in Secs. II and III C.

	r_e (bohr)	k_e (mdyn/Å)
NiH($^2\Delta$)		
SCF	2.94	1.5
SCF[a]	2.92	1.5
TCSCF	2.96	1.2
11-configuration		
MCSCF[a]	3.01	1.6
2-el CIA/SD	3.10	0.8
4-el CIA/SD	2.82	1.6
4-el CIB/SD	2.83	1.6
Experiment[b]	2.78	~2.2
PdH($^2\Sigma^+$)		
SCF	3.15	1.3
TCSCF	3.19	1.1
3-el CIA/SDT	3.11	1.6
3-el CIB/SDT	3.11	1.7
Experiment[c]	2.90	~2.4

[a] With the Bagus et al. Ni basis set (see Ref. 11).
[b] See Ref. 3.
[c] See Ref. 4

seen to be too long—2.94 compared to 2.78 bohr found from spectral data.[3] The value of k_e is too small; i.e., the curves are too broad. This is contrary to what one would expect. Usually SCF curves which do not lead to the proper dissociation (and that is the case here) are too steep and have minima at bond lengths that are too small.[14]

For PdH, the order of the states and their relative energies are different. The $^2\Sigma^+$ state is the lowest state with the $^2\Delta$ and $^2\Pi$ states well above, 0.65 and 0.76 eV, respectively (vertical excitation energies). The reason for this lowering of the $^2\Sigma^+$ state will be discussed below in connection with a Mulliken population analysis. The $^2\Sigma^+$ symmetry of the ground state has also been established from spectral data.[4] Accurate values for r_e and k_e are known from the spectra, and in this case too, the computed bond length is too long and the potential energy curve too broad; see Table III. Further support for a $^2\Sigma^+$ ground state is found from an ESR investigation,[5] which also predicts an excited $^2\Pi$ state with strong coupling to the ground state.

We present, now, some properties which characterize the PdH and NiH wave functions. These properties include orbital energies ϵ, orbital values of $\langle z \rangle$ (z is the internuclear axis), dipole moments μ, and Mulliken gross population analyses.[18] In Table IV(a), we present results for the $^2\Sigma^+$ state of PdH and NiH and in Table IV (b) for the $^2\Delta$ state. The results are presented for internuclear dis-

tances r(Pd–H) = 3.1 and r(Ni–H) = 2.88 bohr, near the calculated SCF r_e for the ground state. The results for the $^2\Pi$ state (not given) are very similar to those for $^2\Delta$. The orbital properties are given only for the highest occupied σ MO's. All the other MO's, including the highest $d\pi$ and $d\delta$, are essentially localized metal-atom orbitals for all states.

The doubly occupied 9σ MO of the $^2\Sigma^+$ PdH ground state has substantial Pd $4d$, some Pd $5s$, and a large amount of H $1s$ character. It is best described as a bonding combination of Pd $4d$ and $5s$ and H $1s$. The singly occupied 10σ orbital is mainly populated with Pd $4d$ electrons, but has some Pd $5s$ and some H $1s$ character. Rather than being a localized $4d\sigma$, the 10σ MO has antibonding character. This bonding and antibonding character is consistent with the ordering of the orbital energies $\epsilon(9\sigma^2) < \epsilon(10\sigma^1)$. The total amount of $4d$ character in this state is 9.2 electrons. For the $^2\Pi$ and $^2\Delta$ states, the number of $4d$ electrons must be less than or equal to nine since the $5\pi(4d\pi)$ or $2\delta(4d\delta)$ hole is a localized $4d$ hole. The actual number of $4d$ electrons for the $^2\Delta$ state is 8.9. The $^2\Sigma^+$ ground state for PdH is consistent with the fact that the ground state of the free Pd atom is $4d^{10}5s^0$. Thus the ground-state symmetry of the molecule may have its origin, in part, in the atomic character of the metal atom.

Our results are in qualitative agreement with the conclusions from the ESR measurements by Knight and Weltner.[5] Their analysis of the hyperfine coupling and g tensors indicates that the odd electron in the ground state of PdH is predominantly $4d\sigma$, but with considerable $5s$ character (an estimated 30%). However, they consider the bond to be essentially ionic, which is not quite in accordance with our findings. The character of the NiH $^2\Sigma^+$ state is quite different from that found for PdH. The singly occupied 6σ orbital is an almost pure Ni $3d\sigma$ and the doubly occupied 7σ orbital is a bonding combination of Ni $4s$ and H $1s$ with almost no Ni $3d$ character. The localized d character is further supported by the very small $\langle z \rangle_{6\sigma}$. The $\langle z \rangle_{7\sigma}$ is large and reflects the H $1s$ and bonding character of the 7σ MO. As noted earlier, $\epsilon(6\sigma^1) < \epsilon(7\sigma^2)$, which is a behavior characteristic of localized open-shell orbitals where a large Coulomb repulsion would be expected if another electron were added to the shell. The total $3d$ population is 9.0 electrons. All in all, the bonding in this state is quite close to the situation which we discussed in Sec. I.

The $^2\Delta$ states of PdH and NiH are similar to each other. The lower σ MO (9σ for PdH and 6σ for NiH) has predominantly metal-d character with a small 15–20% admixture of H $1s$. The upper

TABLE IV. (a) SCF properties of the $^2\Sigma^+$ state at $r = 3.1$ bohr for PdH and $r = 2.88$ bohr for NiH. The orbital energies ϵ, the $\langle z \rangle$, and the dipole moment μ, are all given in atomic units. The $\langle z \rangle$ is taken with respect to the Ni nucleus as origin. The Mulliken gross populations are divided in s, p, d, and f character and normalized to the shell occupation. (b) SCF properties of the $^2\Delta$ state. Bond distances and definitions are as given in Table IV (a).

(a)

Orbital	ϵ		Pd	H	Orbital	ϵ		Ni	H	$\langle z \rangle$
9σ	−0.4124	s	0.20	1.16	6σ	−0.5075	s	0.03	0.01	0.011
		p	0.08	0.01			p	0.00	0.00	
		d	0.55				d	0.95		
		f	0.01				f	0.00		
		tot	0.84	1.16			tot	0.99	0.01	
10σ	−0.3844	s	0.15	0.13	7σ	−0.3629	s	0.42	1.37	2.395
		p	0.04	0.00			p	0.12	0.01	
		d	0.68				d	0.08		
		f	0.00				f	0.00		
		tot	0.87	0.13			tot	0.62	1.38	
Total		s	8.35	1.29	Total		s	6.46	1.38	$\mu = -1.760$
		p	18.11	0.02			p	12.12	0.01	
		d	19.22				d	9.02		
		f	0.01				f	0.00		
		tot	45.69	1.31			tot	27.60	1.40	

(b)

Orbital	ϵ		Pd	H	Orbital	ϵ		Ni	H	$\langle z \rangle$
9σ	−0.5138	s	0.00	0.29	6σ	−0.4616	s	0.00	0.39	0.740
		p	0.01	0.00			p	0.03	0.00	
		d	1.69				d	1.58		
		f	0.00				f	0.00		
		tot	1.70	0.30			tot	1.61	0.39	
10σ	−0.3054	s	0.70	0.94	7σ	−0.3220	s	0.69	0.87	1.572
		p	0.14	0.00			p	0.10	0.00	
		d	0.23				d	0.33		
		f	0.01				f	0.00		
		tot	1.06	0.94			tot	1.13	0.87	
Total		s	8.69	1.23	Total		s	6.70	1.25	$\mu = -1.618$
		p	18.15	0.01			p	12.13	0.01	
		d	18.90				d	8.90		
		f	0.01				f	0.00		
		tot	45.75	1.25			tot	27.73	1.27	

σ MO is predominantly metal sp plus H$1s$ with small, ~15%, metal-d character. (The population analysis description is supported by the values of $\langle z \rangle$ for NiH.) This does fit with our qualitative picture of the metal-H bonding. (We should caution that, for the $^2\Delta$ and $^2\Pi$, it is difficult to rigorously identify a "bonding" orbital. Since the two σ orbitals are both doubly occupied, it is possible to transform them among each other and leave the total wave function unchanged. The canonical Hartree-Fock MO's are one particular—more or less arbitrary—choice of transformation. This problem does not arise for the $^2\Sigma^+$ states since the transformation between a closed and an

open shell does not leave the wave function invariant.) The total d character in both cases is 8.9 electrons, suggesting that while the dominant metal-atom configuration is $d^9(sp)^1$, there is some involvement of $d^8(sp)^2$.

In the introduction, we indicated that we expected the $3d$ electrons in NiH to be more localized and participate less in the metal-hydrogen bond than the $4d$ electrons in PdH: cf. the atomic overlaps in Table I where the Ni$3d$–H$1s$ overlap is smaller than the Pd$4d$–H$1s$ overlap. This expectation appears to be borne out for the $^2\Sigma^+$ states, but not for the $^2\Delta$ (or $^2\Pi$) states. All states of both molecules have a partly ionic structure which is ap-

proximately q(metal) $= + 0.3$ and q(H) $= -0.3$ electrons. The dipole moments for NiH, $\mu \approx 1.7$ a.u., support this polarity. The order of the $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ states of a d hole in the presence of a negative point charge[23] is $^2\Sigma^+$ lowest, followed by $^2\Pi$ and $^2\Delta$ highest. Clearly, this order is not followed for either PdH ($^2\Sigma^+, ^2\Delta, ^2\Pi$) or NiH ($^2\Delta, ^2\Pi, ^2\Sigma^+$). The order of these states is thus not determined by the (weak) crystal-field splitting.

Another way to characterize the electronic structure is to consider the transition matrix elements between the various states. The matrix elements were calculated for the transitions $^2\Pi - ^2\Delta$ and $^2\Pi - ^2\Sigma^+$ for both molecules. (The $^2\Delta - ^2\Sigma^+$ transition is of course symmetry forbidden.) To a first approximation, these transitions are d-d transitions and are parity forbidden. Thus we expect weak transitions. The transition matrix elements M given in Table V are taken between total SCF wave functions for the two states; for example,

$$M (^2\Delta - ^2\Pi) = \langle \Psi (^2\Delta, m = +2) | x + iy | \Psi (^2\Pi, m = +1) \rangle. \quad (3)$$

The one-electron matrix element which makes the largest contribution to M is identified in the table. For NiH, the values of M are small, supporting the localized nature of the $3d$ electrons. The value of $M(^2\Delta - ^2\Pi)$ is also small for PdH, however, $M(^2\Pi - ^2\Sigma^+)$ is an order of magnitude larger. This confirms that the singly occupied 10σ MO in the $^2\Sigma^+$ state is not merely a $4d\sigma$ orbital and is in agreement with the population analysis which showed significant molecular character for the 9σ and 10σ MO's. By contrast, the 7σ orbital of NiH in the $^2\Sigma^+$ state is almost pure d from the population analysis and the transition matrix element for the $^2\Pi - ^2\Sigma^+$ is very small.

From the SCF results, the computed dissociation energies D_e are 1.46 eV for NiH and 1.71 eV for PdH. These values have been determined by subtracting the SCF energy of the molecule from the sum of the SCF energies of the separated

atoms. For the metal atom the energy of the $^3D(d^9s^1)$ state was used. Experimentally, the $^3F(d^8s^2)$ and $^3D(d^9s^1)$ terms are almost degenerate for Ni, but in the Hartree-Fock limit the energy difference is 1.25 eV with the ^3F state as the lowest. Thus, there is a larger correlation error for the ^3D state. Since the metal atom in the hydride has approximately a (d^9s^1) configuration, the proper atomic state to use in computing the dissociation energy is the ^3D state. In the case of Pd, the Hartree-Fock method gives the separation of the atomic states $^1S(d^{10})$ and $^3D(d^9s^1)$, $^3F(d^8s^2)$ with much better accuracy, and it may be more appropriate to use the Pd(^1S) atomic SCF energy to compute D_e. If this is done, $D_e = 1.02$ eV. Experimental estimates for D_0 are 3.0 eV for NiH[3] and 3.3 eV for PdH[4]. It is, of course, expected that calculated SCF D_e will be too small[11] by about 1 eV for each new two-electron bond formed in the molecule. The results for the dissociation energies are collected in Table VI.

Our conclusion that the ground state of NiH is $^2\Delta$ and that the bonding primarily involves the Ni $4s$ and $4p$ electrons is in agreement with previous theoretical work cited in Refs. 6–8. Melius et al.[6] have performed HF calculations on NiH where the Ar core of Ni is replaced with an effective (or pseudo) potential and only 11 electrons are explicitly treated. The basis set used in their calculations is a contracted Gaussian set of double-zeta quality.[19] They report only orbital energies and Mulliken populations at the experimental r_e. Their results are similar to ours in Table IV(b); the differences are due, in part, to our use of a much more extended basis set. Dunlap et al.[8] report a potential curve of the $^2\Delta$ state obtained using a LCAO-$X\alpha$ formalism. They find $r_e = 3.75$ bohr, $D_e = 2.2$ eV, and do not report a value for k_e. Their r_e is much, ~1 bohr, larger than both our SCF value and experiment and is very poor indeed. Kunz et al.[7] have used a perfect-pairing GVB method to obtain wave functions for the three low-lying states $^2\Delta$, $^2\Pi$, and $^2\Sigma^+$. Since the GVB approach they use is identical to our two-configuration MCSCF approach, we defer further discussion

TABLE V. Electronic transition matrix elements among the low-lying states of NiH and PdH. The matrix elements $M = \langle \Psi_I | x \pm iy | \Psi_J \rangle$ are taken between total SCF wave functions for the states. The dominant orbital contribution to M is listed. (M is given in bohrs.)

	Transition	M	Dominant one-electron contribution
NiH	$^2\Delta - ^2\Pi$	0.010	$\langle 3\pi \| x \pm iy \| 1\delta \rangle$
	$^2\Pi - ^2\Sigma^+$	0.009	$\langle 7\sigma \| x \pm iy \| 3\pi \rangle$
PdH	$^2\Delta - ^2\Pi$	0.019	$\langle 5\pi \| x \pm iy \| 2\delta \rangle$
	$^2\Pi - ^2\Sigma^+$	0.138	$\langle 10\sigma \| x \pm iy \| 5\pi \rangle$

TABLE VI. Computed and experimental dissociation energies (in eV).

	SCF	TCSCF	Expt. estimate [c]
NiH [a]	1.46	1.96	3.1
PdH [a]	1.71	2.08	3.3
PdH [b]	1.02	1.39	3.3

[a] Relative to ^3D (d^9s^1) state of the metal atom.
[b] Relative to ^1S (d^{10}) state of the metal atom.
[c] D_0, see Ref. 3 for NiH and Ref. 4 for PdH.

468   PAUL S. BAGUS AND CECILIA BJÖRKMAN   23

until the next section where we present our MCSCF results.

B. MCSCF calculations

A frequently used approach to improve SCF wave functions is to use MCSCF functions where one or a few configurations are added and variational equations solved for both MO's and the CI coefficients.[14] Often, the additional configurations are chosen so that the molecule will dissociate to either neutral separated atoms or to the correct ground states of the atoms.[14,20]

In order to see if such an approach would improve our rather poor SCF results for r_e and k_e, we performed two-configuration MCSCF, TCSCF, calculations for all three low-lying states of NiH and PdH. The TCSCF wave functions will give dissociation to neutral atoms with configurations metal d^9s^1 and $H\,1s^1$. For NiH, the second configuration needed is the one in which the $7\sigma^2$ MO in Eq. (1) is excited to $8\sigma^2$. For $^2\Delta$, for example, $\psi(\text{TCSCF})$ is given by

$$\psi(\text{TCSCF}) = A\{6\sigma^2 7\sigma^2 3\pi^4 1\delta^3\} + B\{6\sigma^2 8\sigma^2 3\pi^4 1\delta^3\}. \quad (4)$$

At large Ni to H separation, 7σ and 8σ go to

$$7\sigma = \frac{1}{\sqrt{2}}[\text{Ni}(4s) + \text{H}(1s)],$$

$$8\sigma = \frac{1}{\sqrt{2}}[\text{Ni}(4s) - \text{H}(1s)], \quad (5)$$

and $A = -B = 1/\sqrt{2}$. For PdH, the second configuration involves the excitation $9\sigma^2$ to $11\sigma^2$. The wave functions and MO's at large Pd–H separation are analogous to those for NiH. The total TCSCF energies are tabulated in the Appendix in Tables VIII–XI.

The results of the TCSCF and the one-configuration SCF calculations are fairly similar. The order of the states is the same; the TCSCF bond lengths are slightly longer and the potential energy curves are broader (i.e., smaller k_e). These results for the ground state are given in Table III; the dissociation energies D_e are given in Table VI. As for the SCF case, the D_e are computed using atomic SCF energies for the dissociation limit. The TCSCF values are larger than the SCF since the second configuration in Eq. (4) adds correlation energy only at internuclear distances at which the atoms interact.

We encountered a significant problem with the TCSCF calculations for NiH. For internuclear distances r smaller than ~2.75 bohr, the TCSCF orbitals changed character; the 7σ MO became primarily a $3d\sigma$ orbital and the 6σ MO became primarily a $4sp\sigma + H\,1s$ bonding orbital. In effect, for $r < 2.75$ bohr, the TCSCF wave function included

correlation for the $3d\sigma$; for $r > 2.75$ bohr, the bonding MO was correlated. This switch lead to a discontinuity in the potential curve and TCSCF results for small r are not given in Tables VIII and X. As in the case of NiH, the TCSCF results for the ground state of PdH give worse results than the SCF calculations for r_e and k_e. However, in this case there was no problem with discontinuities in the curve.

For the $^2\Delta$ ground state of NiH, we also performed a more extended MCSCF calculation where we included an additional 9σ orbital intended to correlate the $6\sigma(3d\sigma)$ SCF MO. This was done in the hope of achieving a balanced treatment of the $d\sigma$ and valence electrons. The calculation included the following 11 CSF's which are double excitations from the SCF configuration, Eq. (1a):

$$6\sigma^2\ 7\sigma^2, \quad 6\sigma^2\ 9\sigma^2,$$
$$6\sigma^2\ 8\sigma^2, \quad 7\sigma^2\ 9\sigma^2,$$
$$7\sigma^2\ 8\sigma^2, \quad 6\sigma^2\ 7\sigma9\sigma(^3\Sigma^+),$$
$$6\sigma^2\ 7\sigma8\sigma(^3\Sigma^+), \quad 6\sigma7\sigma^2\ 9\sigma(^3\Sigma^+),$$
$$6\sigma7\sigma^2\ 8\sigma(^3\Sigma^+), \quad 6\sigma7\sigma9\sigma^2(^1\Sigma^+),$$
$$6\sigma7\sigma8\sigma^2(^1\Sigma^+),$$

The symmetry designation in parentheses gives the intermediate coupling between the electrons in the singly occupied orbitals. The calculation was performed using the smaller Bagus et al.[11] basis set. The r_e and k_e are given in Table III.

This 11-configuration MCSCF gives an r_e that is even worse than the SCF or TCSCF results. The force constant is slightly better, but still rather far from experiment. The potential energy curve is continuous. However, an analysis of the natural orbitals shows that, at short bond distance, mainly the $3d\sigma$ electrons are correlated. The Ni $3d$ population is decreasing and is in fact close to eight. Thus, although the curve is continuous, it does not give a consistent description of the Ni–H bond for all internuclear separations. Clearly, these limited MCSCF calculations do not give, except for the D_e values, an improvement over the SCF results. In fact, they give a slightly worse representation of the potential curve near equilibrium.

The perfect pairing GVB method used in Ref. 7 to describe the low-lying states of NiH is identical to our TCSCF approach. The basis set used in Ref. 7 is a contracted Gaussian set of double-zeta quality with polarization functions and is considerably smaller than the extended Slater-type set which we use. (The total energies reported in Ref. 7a are ~1.6 hartrees=~44 eV higher than ours.) Potential curves for the $^2\Sigma^+$ state are shown and energies for the $^2\Pi$ and $^2\Delta$ states are reported at one point. The order of the states is the same as that which we find and the separation appears to be

similar. From the curve shown in Ref. 7a, we estimate r_e for $^2\Sigma^+$ to be 3.4 bohrs. (Dunlap et $al.$[8] quote r_e from Ref. 7a, as 3.5 bohrs.) This is rather larger than our TCSCF r_e=3.0 bohrs for $^2\Delta$ and is, of course, in poor agreement with experiment. No value for the force constant is given in Ref. 7. From the data given, the GVB D_e of Ref. 7 for $^2\Delta$ is about 1.9 eV and close to our value in Table VI. All in all, the GVB results of Ref. 7 confirm our conclusion that the TCSCF method does not give a particularly good representation of the NiH potential curve. The fact that our TCSCF value for r_e is rather better than their result is probably due to the fact that we have used a much more flexible basis set.

C. Configuration-interaction results for the ground state

For the ground states, NiH ($^2\Delta$) and PdH ($^2\Sigma^+$), correlation effects were investigated with CI calculations. In these calculations, we correlated only those electrons likely to participate directly in the metal-H bonding. The details of the CI calculations have been given in Sec. II; the calculated energies are given in Tables VIII and IX of the appendix.

We consider first the results for NiH. If the 7σ orbital was primarily responsible for the bonding, a rather good representation of the potential curve around r_e should be given by a two-electron CI, including all single and double excitations from $7\sigma^2$. The virtual space for our two-electron CI included only s and p orbitals (see Sec. II) since the 7σ SCF MO has only a limited amount of d character. As can be seen from Table III, the two-electron CI results, denoted 2-el CIA/SD, are rather poor: The bond length is much too long and the force constant much too small. Although the 7σ SCF MO is primarily a bonding combination of Ni $4s$ and H $1s$, it contains some $3d$ character as well. The 6σ orbital is predominantly Ni $3d\sigma$ with some H $1s$ character. This mixing of s and d indicates that excitations out of both 6σ and 7σ orbitals should be included in the CI expansion. In the 4-electron CI, all single and double excitations from the four electrons in $6\sigma^2$ $7\sigma^2$ were included. Two virtual orbital spaces were used. The first, denoted 4-el CIA/SD, contained only s and p-type orbitals; the second, denoted 4-el CIB/SD, contained s, p, and d-type orbitals. The potential curves obtained with either virtual space are quite different from the two-electron CI results. The curves are steeper and the bond length is much smaller (see Table III). In fact, the 4-el CIA and CIB results are very close to each other. The bond length is only 2% larger than the experimentally derived value, although

the force constant is still considerably smaller than experiment. These are the best results that have been obtained for NiH by us or anyone else.[7,8]

For the $^2\Sigma^+$ ground state of PdH, Eq. (2c), we performed full 3-electron CI calculations for $9\sigma^2$ $10\sigma^1$. In 3-el CIA/SDT, the virtual orbital space contained only s- and p-type orbitals; in 3-el CIB/SDT, the virtual space included, in addition, d-type orbitals. As for NiH, the results obtained using these two different virtual spaces were very similar. The bond length is smaller and closer to experiment than in any other calculation, although it is still 7% too large. The force constant is somewhat larger than the SCF and MCSCF values, but it is still considerably lower than experiment.

These CI calculations have significant limitations which we will mention briefly here and discuss in more detail in Sec. IV. For NiH, we have not included sufficient correlation to correct the atomic SCF error of 1.25 eV for the separation of the Ni $3d^8$ $4s^2$(^3F) and $3d^9$ $4s^1$(^3D) terms. For PdH, the separation of the atomic terms for $4d^{10}$, $4d^9 5s^1$, and $4d^8 5s^2$ is given reasonably well by an SCF calculation. However, we neglect relativistic effects which are known to be important for the spatial extent[21] of the Pd valence electrons, particularly the $5s$ electron.

D. CI results: Excited states

The lowest excited states of the same symmetry as the ground state were investigated at the experimental internuclear distance (NiH: 2.78 bohr, PdH: 2.90 bohr). In Table VII, the term values of the four lowest states are given for the CI calculations described in Sec. II and III C.

Absorption spectra of PdH and PdD have been observed in the region 3100-6400 Å,[4] but no analysis was made for PdH because of strong perturbations in the spectrum. The PdD spectrum, however, was less perturbed and a rotational and (in part) vibrational analysis could be undertaken. It was established that the bands were of $^2\Sigma$-$^2\Sigma$ character and a tentative assignment was made for the 0-0 band of the transition from the ground state to the lowest excited state. The energy corresponding to this transition is close to our result for the lowest excited state.

For NiH, more experimental evidence about the lowest excited $^2\Delta$ states is available.[1-3] From the analysis of the red spectrum of NiH, five bands were found.[1,2] They were interpreted as $^2\Delta_{5/2}$-$^2\Delta_{5/2}$ subbands of two $^2\Delta$-$^2\Delta$ transitions from the lowest state $X^2\Delta_{5/2}$, to the $A^2\Delta_{5/2}$ and $B^2\Delta_{5/2}$ states which are only separated by 457 cm^{-1}. A later investigation[3] established both $^2\Delta_{5/2}$-$^2\Delta_{5/2}$ and $^2\Delta_{3/2}$-$^2\Delta_{3/2}$ subbands in the violet spectrum

TABLE VII. Vertical term values (in cm^{-1}) for excited states of $^2\Delta$ symmetry for NiH at $r = 2.78$ bohr and $^2\Sigma^+$ symmetry for PdH at $r = 2.90$ bohr. The notation for the CI calculations is explained in Secs. II and III C.

		NiH		
State	2-el CIA/SD	4-el CIA/SD	4-el CIB/SD	Experiment[a]
C	54 520	47 200	48 400	23 760
B	31 340	30 050	30 900	15 977
A	26 300	20 230	19 600	15 520
X	0	0	0	0

	PdH		
State	3-el CIA/SDT	3-el CIB/SDT	Experiment[b]
C	47 332	47 834	
B	32 877	29 540	
A	23 619	23 627	~22 300
X	0	0	0

[a] $^2\Delta_{5/2} - {}^2\Delta_{5/2}$ transitions (see Refs. 2 and 3).
[b] $^2\Sigma^+ - {}^2\Sigma^+$ 0-0 transition (see Ref. 4).

corresponding to transitions to a $C^2\Delta$ level. These three $\Delta_{5/2}$ levels are at 15 520, 15 977, and 23 760 cm^{-1}. Our 4-el CIB/SD results (see Table VII) place the $A^2\Delta$ vertical term value rather larger than the experimentally assigned value for $A^2\Delta_{5/2}$, but not terribly in error, ~0.5 eV, considering the limited nature of the CI. Our result for $B^2\Delta$, 30 900, is larger than the experimental assignment for $B^2\Delta_{5/2}$ by ~2 eV. In fact, it seems more reasonable to associate our $B^2\Delta$ term with the state assigned to $C^2\Delta_{5/2}$. Our CI is, of course, rather limited. Of particular importance for the excitation spectrum, it does not include excitations from $3d\pi(4\pi)$. However, our results do provide evidence that there may be a misinterpretation of the red spectrum of NiH. This impression seems to be shared by the investigators of the violet bands who "consider it to be extremely necessary to reanalyze the red band system.[3]" They do not, however, give explicit reasons for this consideration except that they find it unsatisfactory that no $^2\Delta_{3/2} - {}^2\Delta_{3/2}$ subbands have been found in this region.

IV. CONCLUSIONS

The ground states of the transition metal hydrides NiH and PdH are $^2\Delta$ and $^2\Sigma^+$, respectively. The $3d$ electrons in NiH seem to be more localized and atomic d-like than the $4d$ electrons in PdH. The gross description of the metal-atom d character for both systems is d^9. However, for PdH, there is substantial participation of $4d$ electrons in the bonding $9\sigma^2$, and antibonding $10\sigma^1$, valence MO's of the $^2\Sigma^+$ ground state. The Mulliken gross atomic d population for NiH($^2\Delta$) is 8.9. The role of the $4d$ in the PdH($^2\Sigma^+$) bonding leads to a larger amount, 9.2 electrons, of $4d$ character.

In all calculations, SCF, MCSCF, and CI, of the ground-state potential curves, the computed bond lengths are too long and the curves too broad (force constants too small). Considering the large basis sets used, the SCF results are surprisingly far off the experimental values.[14] The MCSCF calculations give results that are generally worse than those from the SCF calculations. The best results are obtained in the limited CI calculations

TABLE VIII. Total energies for NiH($^2\Delta$). The quantity $E + 1507.0$ is tabulated.

r(bohr)	SCF	SCF[a]	TCSCF	11-configuration MCSCF[a]	2-el CIA/SD	4-el CIA/SD	4-el CIB/SD
2.58	−0.367 879	−0.364 828		−0.401 623	−0.387 244	−0.422 912	−0.435 129
2.68	−0.372 257	−0.368 806		−0.405 657	−0.391 526	−0.425 478	−0.437 805
2.78	−0.374 878	−0.371 063	−0.393 181	−0.408 659	−0.394 386	−0.426 403	−0.438 842
2.88	−0.376 078	−0.371 946	−0.394 366	−0.410 470	−0.396 177	−0.426 049	−0.438 608
2.98	−0.376 132	−0.371 735	−0.394 619	−0.411 179	−0.397 154	−0.424 703	−0.437 386
3.08	−0.375 262	−0.370 652	−0.394 091	−0.410 867	−0.397 504	−0.422 624	−0.435 426
3.18	−0.373 645	−0.368 875	−0.392 927	−0.409 675	−0.397 325	−0.419 977	−0.432 891

[a] With the Bagus et al. Ni basis set (see Ref. 11).

TABLE IX. Total energies for PdH($^2\Sigma^+$); E(tabulated)$= E$(total) $+ 4938.0$.

r(bohr)	SCF	TCSCF	3-el CIA/SDT	3-el CIB/SDT
2.70	−0.432 280	−0.446 731	−0.471 159	−0.473 736
2.80	−0.437 586	−0.451 523	−0.476 560	−0.478 949
2.90	−0.441 157	−0.454 787	−0.480 103	−0.482 277
3.00	−0.443 326	−0.456 858	−0.482 133	−0.484 102
3.10	−0.444 342	−0.457 959	−0.482 932	−0.484 724
3.20	−0.444 395	−0.458 239	−0.482 732	−0.484 383
3.30	−0.443 641	−0.457 822	−0.481 730	−0.483 275
3.40		−0.456 819		

where the electrons in the metal-hydrogen bond and the d electrons of the same symmetry (σ) are correlated.

A serious limitation in all of our calculations for NiH is related to the fact that the SCF results for the Ni atom fail to properly describe the seperation of the $3d^8 4s^2$ and $3d^9 4s^1$ configurations. While these levels are nearly degenerate,[9] the SCF energy for ^3F is lower by 1.25 eV than that for ^3D (cf. Table II). This SCF error is due to electron correlation effects which involve at least ten electrons ($3d$ and $4s$ shells) and are likely to involve all 18 electrons in the $n=3$ and 4 shells.[22] In our calculations we do not have enough configurations to treat this problem properly since we have only correlated those electrons directly involved in the NiH bonding. Taking this limitation, the errors found are not surprising. In fact, it is quite encouraging that our simple CI model leads to reasonable values for r_e and k_e which are significantly improved over the SCF and MCSCF results.

The SCF model gives a better treatment of the relative energies of the d states for Pd than for Ni. From experiment[9] the energy of the $^3D(4d^9 5s^1)$ and $^3F(4d^8 5s^2)$ levels are 0.95 and 3.38 eV, respectively, higher than the lowest level $^1S(4d^{10})$. Hartree-Fock calculations give results that are reasonably close as shown in Table II. Thus, our CI is not likely to have the same inherent errors as for NiH. However, for Pd relativistic effects are

much more important than for Ni. Desclaux[21] has shown for Rh and Ag (the atoms to the left and right of Pd in the periodic table), that the relativistic $\langle r \rangle_{5s}$ is 5% smaller than the nonrelativistic value. This relativistic contraction must hold for Pd as well. It is reasonable to expect that the r_e for PdH would be reduced by about this amount in a relativistic calculation. Our best nonrelativistic value for r_e, obtained from the 3-electron CI calculation, is 7% too large. Clearly, relativistic effects account for a large fraction of this error and may be expected to contribute significantly to the error in the force constant as well.

Our results clearly show that d electrons play an important role in determining the electronic structure and bonding for the two hydrides. This is obvious in the case of PdH where the $4d$ electrons mix strongly with the bonding $5s$ electrons. In NiH the $3d$ electrons, although they seem more localized, are certainly not unimportant for the bonding. This is demonstrated in the CI calculations where the correlation of the d electrons is essential in order to get meaningful results. Thus neither Ni nor Pd can be treated as a one electron system.

Finally, we recall that our calculated excited state spectrum of $^2\Delta$ symmetry for NiH does not agree well with experimental findings. We feel that there may be a misinterpretation of the measured absorption spectrum.

TABLE X. Total energies, E(tabulated)$= E$(total) $+ 1507.0$, for the $^2\Sigma^+$ and $^2\Pi$ states of NiH.

| r(bohr) | $^2\Sigma^+$ state | | | $^2\Pi$ state | | |
	SCF	SCF[a]	TCSCF	SCF	SCF[a]	TCSCF
2.58	−0.354 790	−0.347 902		−0.355 920	−0.351 420	
2.68	−0.362 560	−0.355 518		−0.362 455	−0.357 664	
2.78	−0.368 027	−0.360 873	−0.384 030	−0.366 941	−0.361 903	−0.383 927
2.88	−0.371 606	−0.364 380	−0.387 950	−0.369 748	−0.364 510	−0.386 986
2.98	−0.373 638	−0.366 381	−0.390 382	−0.371 179	−0.365 790	−0.388 759
3.08	−0.374 407	−0.367 153		−0.371 486	−0.365 991	−0.389 486
3.18	−0.374 144	−0.366 924		−0.370 872	−0.365 314	

[a]With the Bagus *et al.* Ni basis set (see Ref. 11).

TABLE XI. Total energies for the $^2\Delta$ and $^2\Pi$ states of PdH; E(tabulated) $= E$(total) $+ 4938.0$.

	$^2\Delta$ state		$^2\Pi$ state	
r(bohr)	SCF	TCSCF	SCF	TCSCF
2.70	−0.398 200	−0.415 115	−0.384 758	
2.80	−0.406 707	−0.423 725	−0.395 656	−0.412 041
2.90	−0.412 981	−0.430 178	−0.404 214	−0.420 692
3.00	−0.417 410	−0.434 860	−0.410 547	−0.427 274
3.10	−0.420 312		−0.415 101	
3.20	−0.421 952		−0.418 166	
3.30	−0.422 551		−0.419 992	

ACKNOWLEDGMENT

APPENDIX

In this appendix we present four tables which give the total energies, calculated by the various methods discussed in the text, for the three low-lying states $^2\Delta$, $^2\Pi$, and $^2\Sigma^+$. The energies are in hartrees and the notation for the CI calculations is defined in Secs. II and III C. The ground-state results for NiH($^2\Delta$) and PdH($^2\Sigma^+$) are in Tables VIII and IX, respectively. The excited-state results are in Tables X for NiH, and XI for PdH.

*Present address: Department of Chemical Physics, The Technical University of Denmark, DTH 301, DK-2800 Lyngby, Denmark.

[1] A. G. Gaydon and R. W. B. Pearse, Nature (London) 134, 287 (1934); Proc. R. Soc. London Ser. A 148, 312 (1935).

[2] A. Heimer, Z. Phys. 105, 56 (1937).

[3] N. Åslund, H. Neuhaus, A. Lagerqvist, and E. Andersén, Ark. Fys. 28, 271 (1965).

[4] C. Malmberg, R. Scullman, and P. Nylén, Ark. Fys. 39, 495 (1969).

[5] L. B. Knight, Jr. and W. Weltner, Jr., J. Mol. Spectrosc. 40, 317 (1971).

[6] C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baillie, and M. A. Ratner, Surf. Sci. 59, 279 (1976).

[7] (a) M. P. Guse, R. J. Blint, and A. B. Kunz, Int. J. Quant. Chem. 11, 725 (1977); (b) A. B. Kunz, M. P. Guse, and R. J. Blint, ibid. 105, 283 (1976).

[8] B. I. Dunlap, J. W. D. Conolly, and J. R. Sabin, Int. J. Quant. Chem. S11, 81 (1977).

[9] C. E. Moore, NSRDS-NBS Circular No. 35, Vols. I–III, Washington, D.C. (unpublished).

[10] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[11] P. S. Bagus, T. L. Gilbert, and C. C. J. Roothaan, Argonne National Laboratory Technical Report, 1972 (unpublished); J. Chem. Phys. 56, 5195 (1972).

[12] C. Froese Fischer, Some Hartree-Fock Results for the Atoms Helium to Radon (Department of Mathematics, University of British Columbia, Vancouver, Canada, 1968); Comput. Phys. Commun. 4, 107 (1972).

[13] P. S. Bagus and H. F. Schaefer, J. Chem. Phys. 58, 1844 (1973).

[14] H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Mass., 1972).

[15] P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, in Wave Mechanics: The First Fifty Years, edited by W. C. Price, S. C. Chissick, and T. Ravensdale (Butterworths, London, 1973).

[16] J. Hinze, J. Chem. Phys. 59, 6424 (1973).

[17] P. S. Bagus, C. M. Moser, P. Goethals, and G. Verhaegen, J. Chem. Phys. 58, 1886 (1973).

[18] R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955); 23, 1841 (1955).

[19] C. F. Melius (private communication).

[20] See, for example, A. C. Wahl and G. Das, Adv. Quantum Chem. 5, 261 (1970).

[21] J. P. Desclaux, At. Data Nucl. Data Tables 12, 311 (1973).

[22] P. S. Bagus and C. W. Bauschlicher (unpublished results).

[23] D. M. Gruen, Prog. Inorg. Chem. 14, 119 (1971). See also, J. S. Griffith, The Theory of Transition-Metal Ions (Cambridge University Press, London, 1971); and G. Herzberg, Electronic Spectra of Polyatomic Molecules (Van Nostrand, New York, 1966).