The chemical bonds in CuH, Cu_2, NiH, and Ni_2 studied with multiconfigurational second order perturbation theory

Rosendo Pou-Amérigo, Manuela Merchán, and Ignacio Nebot-Gil
Departament de Química Física, Universitat de València, Dr. Moliner 50, Burjassot, E-46100 València, Spain

Per-Åke Malmqvist and Björn O. Roos
Department of Theoretical Chemistry, Chemical Centre, P.O. Box 124, S-221 00 Lund, Sweden

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The performance of multiconfigurational second order perturbation theory has been analyzed for the description of the bonding in CuH, Cu_2, NiH, and Ni_2. Large basis sets based on atomic natural orbitals (ANOS) were employed. The effects of enlarging the active space and including the core-valence correlation contributions have also been analyzed. Spectroscopic constants have been computed for the corresponding ground state. The Ni_2 molecule has been found to have a 0_g^+ ground state with a computed dissociation energy of 2.10 eV, exp. 2.09 eV, and a bond distance of 2.23 Å. The dipole moments of NiH and CuH are computed to be 2.34 (exp. 2.4±0.1) and 2.66 D, respectively.

I. INTRODUCTION

The complete active space self-consistent field (CAS SCF) method[1] has become a valuable tool to include static electron correlation due to strong configuration mixing (near degeneracy) as occurs, e.g., in bond breaking processes. However, even if a qualitatively correct energy surface can be obtained at this level of theory, dynamic correlation effects have to be added in order to obtain an accurate quantitative description of the chemical bond. The multireference configuration interaction (MRCI) method has traditionally been used for this purpose. However, this approach has severe bottlenecks with respect to the number of electrons that can be correlated and the number of configurations that can be used as a reference for the CI expansion. It has recently been shown in a number of applications that multiconfigurational second order perturbation theory can be used as a viable alternative to MRCI. Such a method has recently been developed with a CASSCF wave function used as a reference function (CASPT2).[2]

The CASPT2 approach has been applied successfully to a number of different problem areas in quantum chemistry. The electronic spectra of several organic molecules have been computed at a quantitative level.[3] Vibrational frequencies and a number of properties for ozone and other molecules have been calculated.[4] Using basis sets of moderate size, the agreement between the CASPT2 and full CI results have in different types of calibration tests been found to be satisfactory.[2,5] Similar conclusions have been reached[2,5–7] when comparing CASPT2 to the MRCI method using more extended basis sets. These tests have included a study of the geometry and binding energies of a large number of molecules (the "G1 test"),[6] and the energy barrier and exothermicity of the reaction $F+H_2 \rightarrow HF+H$.[5] Relative energies are reproduced with errors of the order of a few kcal/mol. Excitation energies in the nickel atom[7] and in transition metal ions[8] have also been studied recently yielding accurate values. The performance of the CASPT2 theory has, however, not yet been tested for the description of bonding in molecules involving transition metal atoms. Transition metal chemistry is an interesting application area for the new approach, since the electronic structures are here often complex involving many open shells and strong mixing of different electronic configurations. The large number of electrons which often have to be correlated makes it difficult to use conventional MRCI methods. The fact that CASPT2 is size consistent is an important aspect for systems with many electrons.

The CuH and Cu_2 molecules represent the simplest transition metal hydride and dimer. They are well characterized experimentally,[9–16] which allows comparison of the calculated results with reliable experimental data. Moreover, numerous theoretical studies are available.[17–27] On the other hand, the NiH molecule is a more challenging case since the low-lying atomic states of nickel are involved in the bond.[18,28–30] A balanced treatment of them in the molecular wave function is necessary in order to obtain accurate spectroscopic constants and molecular properties for nickel compounds. In addition, the Ni_2 molecule exhibits a complex electronic structure with several low-lying states in a small range of energy,[10] which makes the determination of its ground state a challenge by itself.[31–35]

In the present work, the ability of the CASPT2 method to describe the bonding in these systems is analyzed. A comparison to recently reported results using other methods of treating electron correlation effects is also included. In Sec. II details of the calculation are considered. Results for the CuH, Cu_2, NiH, and Ni_2 molecules are presented and discussed in Sec. III. Our conclusions are summarized in the last section.

II. DETAILS OF THE CALCULATION

The computational model used in the present study consists of two steps: a CASSCF calculation followed by a CASPT2 calculation. The CASPT2 method[2] computes the second order energy by expanding the first order wave function in the subspace of the full CI space that interacts with the CASSCF reference function. The zeroth-order Hamiltonian is defined as a Fock-type one-electron operator and is

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constructed in such a way that a Møller–Plesset (MP) perturbation treatment is obtained in the closed-shell determinant case. The Fock matrix can include coupling elements between active and inactive, and between active and secondary orbitals. It is computationally simpler to ignore such coupling, but the result does not then have full orbital invariance. Results using both approaches are reported here, and are called PT2F (full Fock matrix) and PT2D (diagonal Fock matrix) below.

The basis sets employed for copper and nickel atoms are derived from $(21s15p10d6f4g)$ primitive basis sets. Atomic natural orbital (ANO) type contractions were performed by using a procedure based on averaged density matrices[36] resulting in the basis set $[6s5p4d3f2g]$. The states included in the averaging were: for copper the $^2S(3d^{10}4s^1)$ and $^2D(3d^9 4s^2)$ atomic states, the $^1S(3d^{10})$ ground state of the Cu^+ cation, and the ground state of the atom placed in a homogeneous electric field of 0.005 a.u.; and for nickel the $^3F(3d^8 4s^2)$, $^3D(3d^9 4s^1)$, and $^1S(3d^{10})$ atomic states, the $^2D(3d^9)$ ground state of the Ni^+ cation, and the ground state of the atom placed in a homogeneous electric field of 0.01 a.u. In an attempt to also include the $3s$ and $3p$ correlation effects, the basis was enlarged by uncontracting four s, p, and d functions in the appropriate region. The resulting basis set $[10s9p8d3f2g]$ will be denoted hereafter as the $3s3p$ basis set. For the hydrogen atom, the ANO-type contraction used is $[3s2p1d]$ obtained from the $(8s4p3d)$ primitive set.[36]

Relativistic effects due to the mass velocity and one-electron Darwin contact term were estimated from first order perturbation calculations of the energy correction.[37] Results including the relativistic corrections will be denoted +RC in the tables.

Unless otherwise stated, the solutions to the radial Schrödinger equation are obtained through numerical integration. Spectroscopic constants are computed by a least squares fit to the computed energy levels. In the first exploratory calculations (Tables I, III, V and VIII) the molecular parameters were obtained by fitting three points around the minimum of the potential curve to a second order polynomial in $1/r$. Between 14 and 16 points were used to construct the potential for the final calculation of the spectroscopic constants (Tables II, IV, and VI).

The calculations have been performed on the IBM 9021/500-2VF computer and IBM RS/6000 workstations at the University of Valencia and the University of Lund using the MOLCAS-2 quantum chemistry software,[38] which includes the CASPT2 program as one module.

III. RESULTS AND DISCUSSION

A. The ground state of CuH

A first set of calculations was performed using the minimum active space required for a correct description of the dissociation process to ground state atoms. It comprises the bonding σ and antibonding σ^* molecular orbitals with two active electrons. Hereafter, this active space will be denoted (σ,σ^*). The remaining molecular orbitals (MOs) are inactive in the CASSCF wave function. At the CASPT2 level, the d electrons are correlated, but the core is kept frozen. The optimized bond length and dissociation energy for the $X\ ^1\Sigma^+$ state of CuH are collected in Table I.

TABLE I. Calculated equilibrium geometry (r_e), dissociation energy (D_e) and dipole moment (μ) for the ground state of CuH at different levels of theory. A $[6s5p4d3f2g/3s2p1d]$ basis set was employed.

Method	r_e (Å)	D_e (eV)	μ (D)[a]
1. Active space (σ,σ^*)[b]			
CASSCF	1.597	1.92	3.54
PT2D	1.455	2.66	2.51
PT2F	1.466	2.68	2.73
CASSCF+RC[c]	1.565	1.98	3.36
PT2D+RC[c]	1.428	2.76	2.33
PT2F+RC[c]	1.441	2.78	2.55
2. Active space (σ,σ^*,d,d')			
CASSCF+RC[c]	1.537	2.14	3.17
PT2F+RC[c]	1.458	2.67	2.73
PT2F(3s3p)+RC[d]	1.457	2.70	2.66
Previous work			
CPF[e]	1.494	2.73	2.75
CPF+RC[e]	1.468	2.87	...
MCPF[e]	1.509	2.63	2.95
QCISD(T)[f]	1.483	...	...
CCSD+T[f]	1.485	...	...
MRD-CI+RC[g]	...	...	3.23
MRD-CI+Q+RC[g]	1.466	...	...
MRSDCI+RC[g]	...	...	3.14
ACPF+RC[g]	...	...	2.66
Expt.	1.463[h]	2.75[i]	...

[a]Computed at the experimental equilibrium distance 1.463 Å.
[b]The d electrons are correlated at the second-order level.
[c]RC—including relativistic corrections (see the text).
[d]The $3s$ and $3p$ electrons are correlated at the second-order level. The $3s3p$ basis set was employed.
[e]Reference 18. Dipole moment at $r=1.509$ Å.
[f]Reference 19.
[g]Reference 21. Dipole moment at $r=1.535$ Å.
[h]Reference 13.
[i]Recommended value from Ref. 9.

The valence CASSCF procedure is known to overestimate the effect of configurations with antibonding orbitals occupied, yielding, therefore, a too long bond distance and a too small bond energy. Inclusion of dynamic electron correlation by means of the perturbational treatment improves, as expected, the results. The computationally less demanding diagonal Fock matrix treatment (PT2D) gives results close to those obtained with the more accurate full Fock matrix calculation (PT2F). Adding relativistic corrections decreases r_e by an additional 0.027 (0.025 Å) and increases D_e by 0.10 (0.10) eV at the PT2D (PT2F) level.

A valuable feature of the CASPT2 method is the possibility to analyze the result in terms of different types of correlation effects. A partitioning of the CASPT2 correlation energy can be used to identify the main differential correlation contributions to the dissociation energy D_e. The results obtained with the full Fock matrix and the diagonal Fock matrix at the experimental bond distance are nearly identical. The differential correlation contribution ΔD_e associated with the σ and σ^* MOs, which is taken into account by the perturbation treatment, is 0.36 eV. Adding the CASSCF+RC

bond energy 1.93 eV gives a total $\sigma-\sigma$ contribution of 2.29 eV to D_e. This is then the main driving force of the bond making process and represents about 80% of the dissociation energy. The $d-\sigma$ and $d-d$ correlation contributions are required, however, for a quantitatively accurate description of the bonding. The largest contribution arises from the $d-\sigma$ correlation $\Delta D_e=1.09$ eV. The $d-d$ term shows a larger weight at long than at short bond distances, resulting in a negative contribution to the dissociation energy $\Delta D_e=-0.60$ eV. This decrease in the $d-d$ correlation energy is due to the contribution of the d^9s^2 electronic configuration to the wave function at shorter bond distances.

It is well known that a correct description of the bonding in transition metal hydrides requires a balanced mixture of the $3d^n4s^2$ and $3d^{n+1}4s^1$ atomic states in the molecular wave function.[18] An accurate description of the relative energies of these different electronic states is needed in order to correctly measure their relative contribution in the bond making process. A new set of calculations was carried out by extending the active space to include two $3d$ shells and 12 active electrons. Thus, the CASSCF wave function enables mixing of configurations with different number of d electrons. It has previously been illustrated[7] that the introduction of a second $3d$ shell has a major impact on the quality of the wave function and the computed excitation energies. The enlarged active space will be denoted as (σ,σ^*,d,d'). The results obtained at CASSCF+RC and PT2F+RC levels with this active space are also presented in Table I.

The importance of including the second $3d$ shell already at the CASSCF+RC level of theory is clear—the bond distance decreases 0.028 Å and the bond energy increases 0.16 eV. At the PT2F+RC level, the enlargement of the active space improves the molecular parameters by +0.017 Å (r_e) and −0.11 eV (D_e) with respect to the values obtained with the (σ,σ^*) space. An analysis of the CASSCF wave function reveals that the d^9s^2 configuration contributes to the wave function for bond distances around the equilibrium value. It is also reflected on the population of copper d orbitals at this geometry, which becomes 9.90 instead of 10. Consequently, the (σ,σ^*,d,d') active space seems to be the most consistent choice for CuH. Moreover, in calculations of energy differences, it is preferable that the weight of the reference CASSCF wave function in the total first-order wave function is about the same in both calculations. This requirement is better fulfilled for the larger active space, which shows weights of 0.959 and 0.965 at short and long distances, respectively. With the (σ,σ^*) active space, these weights are 0.903 and 0.914, respectively.

It was recently shown for the nickel atom that it was necessary to include core correlation effects in order to obtain an accurate description of the electronic spectrum.[7] Also, an extended study of transition metal atoms and ions has confirmed the importance of $3p-3p$ and $3p-3d$ correlation effects for the electronic spectrum.[8] It may then be expected that also properties of chemical bonds with transition metal atoms or ions are affected, since the creation of an atomic "valence state" is involved in the bond making process.

The results for CuH obtained at the PT2F+RC level also correlating the $3s$ and $3p$ electrons, using the $3s3p$ basis set and the (σ,σ^*,d,d') active space, are included in Table I. The contribution of the core–valence and core–core correlation energy to D_e is +0.03 eV and their effect on r_e is small (−0.001 Å). The final results ($D_e=2.70$ eV and $r_e=1.457$ Å) are in agreement with experiment. Table I also includes previous theoretical findings reported in this system. The CASPT2 results are of the same quality as those obtained by employing other methods for including the dynamic correlation effects, such as coupled-pair functional (CPF), configuration interaction (CI), or coupled-cluster (CC) techniques.

The dipole moment of CuH was computed at different levels of theory using a finite-field perturbation approach. The results obtained at the experimental bond distance have been included in Table I. The (σ,σ^*) active space provides, as expected, too large values at the CASSCF level, since it does not allow the mixture between the $3d^{10}4s^1$ and the $3d^94s^2$ occupations. Correlating the $3d$ electrons at second order decreases μ significantly. Nevertheless, the diagonal and full Fock matrix treatments yield values which differ from each other by about 0.2 D. Enlargement of the active space by including two $3d$ shells is required in order to obtain a correct description of the mixing of the atomic states and reliable dipole moments. Using this active space decreases μ by 0.19 D at the CASSCF+RC level and increases μ by 0.18 D at the PT2F+RC level. The PT2F+RC value obtained by also correlating the $3s$ and $3p$ electrons, using the $3s3p$ basis set, is 2.66 D, where the relativistic contribution is computed to be −0.18 D, which is consistent with previous theoretical estimates.[18,20,21] There is no experimental value to which this result can be compared, but the corresponding result obtained for NiH (see below) is within the error limits of the experiment (±0.1 D) and we can expect the value obtained for CuH to be of similar quality. A comparison with earlier theoretical predictions shows that the present result is close to the CPF result of Chong *et al.*[18] 2.75 D (computed at $r=1.509$ Å). The corresponding MCPF value[18] is somewhat larger 2.95 D. The MRCI+RC method seems to give too large values for the dipole moment 3.23 D (MRD-CI) and 3.14 D (MRSDCI).[21] The corresponding ACPF result is in perfect agreement with the present value 2.66 D.[21] These results indicate that it is necessary to use a size-consistent procedure when estimating the correlation effects on the dipole moment in CuH (see also the discussion below for NiH).

Table II gives the equilibrium molecular constants for ^{63}CuH obtained by solving the Schrödinger equation for the nuclear motion numerically. The results have been obtained at the PT2F($3s3p$)+RC level of theory. The agreement between the CASPT2 results and available experimental data is satisfactory. The vibration frequencies computed with other methods[18,20,21] are within the range 1941–1980 cm^{-1}. The previously reported[21] $\omega_e x_e$ and B_e values are 35.0 and 7.90 cm^{-1}, respectively. The accuracy of the results obtained here for the ground state of CuH is thus of at least the same quality as the corresponding CPF and MRCI values.

B. The ground state of Cu_2

The ground state of the Cu_2 molecule can be described as a $4s-4s$ single bond arising from the $^2S(3d^{10}4s^1)$

TABLE II. Molecular constants for the ground state of ^{63}CuH. Level of calculation PT2F($3s3p$)+RC. Active space (σ,σ^*,d,d'). Basis set [$10s9p8d3f2g/3s2p1d$].

	Calculated	Experimental[a]
r_e (Å)	1.457	1.463
D_e (eV)	2.70	2.75[b]
ω_e (cm^{-1})	1 936.1	1 940.7
$\omega_e x_e$ (cm^{-1})	38.62	37.17
B_e (cm^{-1})	8.008	7.945
α_e (cm^{-1})	0.264 5	0.255 0
γ_e (cm^{-1})	0.001 68	0.001 13

[a]Values from Ref. 13 except as noted.
[b]Recommended value from Ref. 9.

TABLE III. Calculated equilibrium geometry (r_e) and dissociation energy (D_e) for the ground state of Cu_2 at different levels of theory. Active space (σ,σ^*).[a] A [$6s5p4d3f2g$] basis set was employed.

Method	r_e (Å)	D_e (eV)
CASSCF	2.507	0.80
PT2D	2.249	1.88
PT2F	2.254	1.84
CASSCF+RC[b]	2.456	0.87
PT2D+RC[b]	2.223	1.99
PT2F+RC[b]	2.228	1.96
PT2F($3s3p$)+RC[c]	2.215	2.07
PT2F($3s3p$)+RC-BSSE[d]		1.97
Previous work		
MRSDCI+Q[e]	2.270	1.76
MRSDCI+Q+RC[e]	2.230	1.88
MP4(SDTQ)[e]	2.227	2.20
MP4(SDTQ)+RC[e]	2.190	2.31
CPF[f]	2.261	1.806
CPF+RC[g]	2.238	1.842
MCPF[h]	2.267	1.744
Expt.	2.219[i]	2.08[j]

[a]The d electrons are correlated at the second-order level.
[b]RC—including relativistic corrections (see the text).
[c]The $3s$ and $3p$ electrons are correlated at the second-order level. The $3s3p$ basis set was employed.
[d]BSSE corrected value.
[e]Reference 24.
[f]Reference 26.
[g]Reference 25.
[h]Reference 27.
[i]Reference 16.
[j]Reference 14.

ground state of the copper atom.[22] However, if only the $4s$ electrons are correlated, the calculated dissociation energy is only about 60% of the experimental value.[17,23,24] Differential correlation involving the $3d$ electrons has to be taken into account to properly describe the Cu–Cu bonding. Here, the CASSCF (σ,σ^*) wave function ($3d$ orbitals inactive) is used as the zeroth-order reference for the CASPT2 calculation. The $3d$ electrons are correlated by the second-order perturbation treatment. The equilibrium bond length and the computed bond energy for the $X\ ^1\Sigma_g^+$ state of Cu_2 are shown in Table III. A compilation of results obtained in earlier studies of this system is also included.

The electron correlation treatment given by the CASSCF (σ,σ^*) approach is not accurate enough as reflected by the r_e and D_e values, which are far from the experimental data. Further inclusion of dynamic correlation effects by means of the CASPT2 method improves considerably the spectroscopic constants; the deviations in r_e and D_e from the experimental values are now +0.035 Å and −0.24 eV, respectively. When relativistic corrections are included, the errors in the computed equilibrium geometry (+0.009 Å) and in the bond energy (−0.12 eV) lie within the expected range. The present results are actually in better agreement with experiment than those obtained with other methods. Even when corrected for the size-consistency error, the MRSDCI approach overestimates the bond distance and underestimates the bond energy, although inclusion of relativistic effects decreases the errors to about +0.01 Å and −0.20 eV.[24] Similar findings were reported using the CPF and MCPF methods.[25–27] The dissociation energy computed by the MP4(SDTQ) procedure shows, however, an opposite trend.[24] In this case, corrections due to relativistic effects increases the error in the computed D_e value.[24]

In order to get insight into the nature of the Cu–Cu bond, an analysis of the differential correlation contributions was carried out. The magnitude of the $\sigma-\sigma$ contribution included by the CASPT2 treatment ΔD_e=0.33 eV is quite similar to CuH. The $d-\sigma$ differential correlation ΔD_e=0.64 eV also gives a significant contribution. The $d-d$ term ΔD_e=0.24 eV has an opposite effect compared to the hydride, i.e., the $d-d$ correlation at the equilibrium Cu–Cu distance is larger than at infinite separation. The above trends in the different correlation contributions can be rationalized as follows: Polarization of the d orbitals at short bond distances is larger in CuH than in Cu_2 due to the partially ionic character of the bonding and the decrease in the $3d$ population. Therefore, the intra-atomic $d-d$ correlation in CuH is larger at long internuclear separations than at short bond distances and the $d-\sigma$ and $d-d$ contributions show an opposite trend. In Cu_2, the d orbitals are not so distorted with respect to the isolated copper atom, making the differential $d-\sigma$ term smaller than in CuH. On the other hand, in addition to the intra-atomic $d-d$ changes, the interatomic $d-d$ correlation effects make the total differential $d-d$ energy positive, i.e., the total $d-d$ correlation energy is larger at the equilibrium bond distance than at infinite separation.

The effect of the core ($3s,3p$) correlation on the spectroscopic constants of Cu_2 was incorporated at the PT2F+RC level by correlating these electrons at second order. The $3s3p$ basis set was used. The final results have been included in Table III. The contribution of this type of correlation to r_e (−0.013 Å) and D_e(+0.11 eV) is much more important here than in CuH. The final values are in agreement with experimental data and show small errors both for the dissociation energy (−0.01 eV) and for the bond distance (−0.004 Å).

The value of the computed dissociation energy was also corrected for the basis set superposition error. It was computed at the PT2F($3s3p$)+RC level by using a counterpoise technique with the $3s3p$ basis set. The contribution of the basis set superposition error (BSSE) to D_e was determined to

TABLE IV. Molecular constants for the ground state of $^{63}Cu_2$. Level of calculation PT2F($3s3p$)+RC. Active space (σ,σ^*). Basis set [$10s9p8d3f2g$].

	Calculated	Experimental[a]
r_e (Å)	2.215	2.219
D_e (eV)	1.97[b]	2.08[c]
ω_e (cm^{-1})	276.8	266.5
$\omega_e x_e$ (cm^{-1})	0.91	1.04
$10^3 \cdot \omega_e y_e$ (cm^{-1})	59.2	0.92
B_e (cm^{-1})	0.1092	0.1088
$10^4 \cdot \alpha_e$ (cm^{-1})	6.28	6.20
$10^6 \cdot \gamma_e$ (cm^{-1})	8.94	2.42

[a]Values from Ref. 16 except as noted.
[b]BSSE corrected value.
[c]Reference 14.

be +0.10 eV. If this value is subtracted, the final result (1.97 eV) shows a small deviation of −0.11 eV from the experimental value.

The computed molecular constants for the ground state of Cu_2 calculated at the PT2F($3s3p$)+RC level are listed in Table IV. The results are in agreement with experiment. The most accurate vibrational frequency values obtained in previous studies are those obtained with the CPF+RC[20] (ω_e=247 cm^{-1}) and SDCI(5)+Q[24] methods (ω_e=259 cm^{-1}).

TABLE V. Calculated equilibrium geometry (r_e) and dissociation energy (D_e) for the ground state of NiH employing the (σ,σ^*,d,d') active space and a [$6s5p4d3f2g/3s2p1d$] basis set.

Method	r_e (Å)	D_e (eV)
CASSCF	1.541	2.12
PT2D	1.465	2.71
PT2F	1.462	2.74
CASSCF+RC[a]	1.511	2.25
PT2D+RC[a]	1.441	2.86
PT2F+RC[a]	1.439	2.89
PT2F($3s3p$)+RC[b]	1.440	2.91
Previous work		
CASSCF[c]	1.541	···
CASSCF+RC[d]	1.518	···
MCPF[e]	1.485	2.69
MCPF+RC[d]	1.466	···
MRCI+Q[c]	1.463	···
ACPF[c]	1.464	···
CCI(29 ref.)+RC[d]	1.462	···
Expt.	1.454[f]	2.70[g]

[a]RC—including relativistic corrections (see the text).
[b]The $3s$ and $3p$ electrons are correlated at the second-order level. The $3s3p$ basis set was employed.
[c]Reference 30.
[d]Reference 29.
[e]Reference 18.
[f]Reference 40.
[g]Recommended value from Ref. 9.

C. The ground state of NiH

The ground state potential curves of the copper hydride and dimer have been extensively used as benchmarks for theoretical studies of transition metal bonding because of the simplicity of their $s-s$ single bond, with all d orbitals fully occupied. In contrast, the corresponding nickel compounds are usually referred to as especially intriguing cases. The $^3F(3d^84s^2)$ and $^3D(3d^94s^1)$ states of the nickel atom are almost degenerate with a splitting of only 0.03 eV (Ref. 39) and are characterized by quite different chemical behavior. In systems such as the $^2\Delta$ ground state of the NiH molecule, where both states take part in the bonding, an accurate description of the low-lying Ni atomic states is required. This has been recognized as a very difficult theoretical problem. Extensive CASSCF+MRCI treatments, employing large basis sets, have to be carried out in order to obtain term splittings in reasonable agreement with experiment.[29] The CASPT2 method was recently applied to this problem[7] and it was shown that the new approach was capable of reproducing the splittings among the d^8s^2, d^9s, and d^{10} electronic states with an accuracy better than 0.1 eV. It may then be expected that the approach is accurate enough to give a good characterization of the bonding in the ground state of NiH.

The selection of the active space for NiH is not trivial. Several active spaces have been reported in the literature. The different CASSCF results vary dramatically.[28–30] The smallest set of active orbitals for the $^2\Delta$ ground state, which allows a proper dissociation and also takes into account the important $3d\sigma$ correlation, comprises the singly occupied $3d_{xy}$ orbital and three σ orbitals ($3d_{z^2}$, σ, and σ^*). A fourth weakly occupied σ orbital was also added to the active space. In both cases, the molecular properties obtained were not accurate enough.[28–30] MRCI+Q and ACPF calculations with the most important CASSCF configurations in the reference space improve the spectroscopic constants, although r_e is underestimated and ω_e is too large. Multireference CI calculations[28] based on CASSCF orbitals, where the additional $3d\delta(3d_{x^2-y^2})$ and its correlating orbital were included in the active space, gave spectroscopic constants in close agreement with the experimental values. In addition, calculations with a larger CAS comprising all 11 valence electrons distributed in 12 active orbitals (σ,σ^*,d,d') have been also reported.[29,30] Further inclusion of dynamic correlation effects by means of MRCI or ACPF methods yielded results in agreement with experiment. This large active space is the most consistent choice of active orbitals as evidenced from the results obtained for CuH and in particular for the electronic spectrum of the Ni atom.[7] It has therefore been chosen for carrying out the present calculations. It is worth pointing out that in the present treatment, all the configuration functions (CFs) of the CAS are included in the zeroth-order reference for the second-order perturbation calculation. It corresponds to 84 852 CFs in the CASSCF wave function (C_{2v} symmetry). On the contrary, in the MRCI and ACPF treatments,[29,30] the number of electrons per symmetry had to be constrained thus reducing the number of CFs to 6944.

The calculated bond length and dissociation energy for the $X\,^2\Delta$ state of NiH obtained with the (σ,σ^*,d,d') active space are presented in Table V. With this CASSCF wave function, the ^3D state of nickel is predicted to be the ground state and it has been used as the asymptotic limit. For the sake of comparison, the experimental data and previous theo-

TABLE VI. Equilibrium molecular constants for the ground state of ^{58}NiH. Level of calculation PT2F($3s3p$)+RC. Active space (σ,σ^*,d,d'). Basis set [$10s9p8d3f2g/3s2p1d$].

	Calculated	Experimental[a]
r_e (Å)	1.440	1.454
D_e (eV)	2.91	2.70[b]
ω_e (cm^{-1})	2082.3	2001.3
$\omega_e x_e$ (cm^{-1})	50.18	37.09
B_e (cm^{-1})	8.204	8.051
α_e (cm^{-1})	0.2651	0.2537
$10^3\cdot\gamma_e$ (cm^{-1})	3.775	...

[a]Values from Ref. 40 except as noted.
[b]Recommended value from Ref. 9.

retical results based on the same active space are also included. It is worth noting that there has been a controversy regarding the experimental values. In fact, two different sets of molecular constants can be found in the literature: one of them is obtained directly from the spectrum,[11] whereas the other is obtained after deperturbation treatments.[40] If available, Table V shows the data reported by Gray *et al.*[40]

The optimized bond length computed at the CASSCF level is similar to that of the previous study.[30] Inclusion of dynamic correlation through CASPT2 improves r_e and D_e. Adding relativistic corrections deteriorates the computed spectroscopic constants at the PT2F+RC level, with deviations of -0.015 Å and $+0.19$ eV in r_e and D_e, respectively, with respect to the experimental values. Compared to other methods, both single-reference (MCPF) and multireference (ACPF, MRCI), the present results are quite satisfactory and confirm that CASPT2 can be a viable alternative to them. In multireference methods, a large list of reference configurations is usually needed in order to achieve accurate spectroscopic constants. It actually represents the bottleneck of the procedure and quite often the reference space has to be reduced. Instead, CASPT2 offers a more consistent treatment over the whole potential curve since no truncation is introduced. The inclusion of the ($3s,3p$) correlation has a very small effect on the spectroscopic constants. The bond distance is lengthened 0.001 Å and the dissociation energy is increased 0.02 eV.

The computed equilibrium molecular constants for the $X\,^2\Delta$ state of NiH at the PT2F($3s3p$)+RC level of calculation are shown in Table VI, where the experimental data are also included.

The vibration frequencies computed with other methods[18,29,30] are in the range 1948–1997 cm^{-1} and $\omega_e x_e$ values[28,29] are in the range 33–46 cm^{-1}. Blomberg *et al.*[28] also reported B_e and α_e values computed at the multireference CI level B_e=7.9 cm^{-1} and α_e=0.27 cm^{-1}, which are close to the results reported here.

The dipole moment of NiH has been the subject of many theoretical studies for of two reasons. First, the magnitude of the dipole moment can be expected to be a sensitive measure of the degree of mixing of the different asymptotes of the metal atom in the chemical bond.[18,30] Hence it provides an excellent test of the quality of the wave function. This analysis becomes especially useful in the case of the nickel hydride where the bonding arises from a mixture of the nearly degenerate ^3D and ^3F states of the Ni atom, whose bond formation mechanisms are rather different. Second, the experimental value was available early.[41] This made possible a comparison of the reliability of the different theoretical methods in providing wave functions, which can adequately describe this type of properties.

TABLE VII. Computed dipole moment (μ) for the ground state of NiH at different levels of theory. Basis set [$6s5p4d3f2g/3s2p1d$]. Active space (σ,σ^*,d,d').

Method	Experimental bond distance (r=1.454 Å) μ(D)	Optimized bond distance (r=1.440 Å) μ(D)
CASSCF[a]	3.12(3.15)	3.10(3.13)
PT2D	2.56	2.54
PT2F	2.67	2.65
CASSCF+RC[b]	2.90	2.87
PT2D+RC[b]	2.34	2.32
PT2F+RC[b]	2.45	2.43
PT2F($3s3p$)+RC[c]	2.34	2.32
Previous work		
SDCI	3.686[d]	3.676[e]
CPF	1.758[d]	1.806[f]
CPF+RC	1.36[g]	...
MCPF	2.540[d]	2.557[b]
MCPF+RC	2.32[g]	...
CASSCF	3.11[h]	3.31[j]
CASSCF+RC	3.00[g]	...
CASSCF+MRCI	2.900[i]	2.954[k]
CASSCF+ACPF	2.471[i]	2.522[l]
CASSCF+ACPF+RC	2.32[g]	...
CASSCF+MRCI+NO	2.39[d]	...
Expt.[m]	2.4±0.1	

[a]Expectation values within parentheses.
[b]RC—including relativistic corrections (see the text).
[c]The $3s$ and $3p$ electrons are correlated at the second-order level. The $3s3p$ basis set was employed.
[d]Reference 18. Values computed at r=1.476 Å.
[e]Reference 18. Value computed at the optimized distance at this level (r =1.483 Å).
[f]Reference 18. Value computed at the optimized distance at this level (r =1.506 Å).
[g]Reference 29. Values computed at r=1.482 Å.
[h]Reference 18. Value computed at the optimized distance at this level (r =1.485 Å).
[i]Reference 30. Values computed at r=1.429 Å.
[j]Reference 30. Value computed at the optimized distance at this level (r =1.541 Å).
[k]Reference 30. Value computed at the optimized distance at this level (r =1.471 Å).
[l]Reference 30. Value computed at the optimized distance at this level (r =1.464 Å).
[m]Reference 41.

The computed dipole moment (μ) of the nickel hydride at different levels of theory is collected in Table VII. It has been evaluated as a numerical energy derivative using fields of -0.01, 0, and $+0.01$ a.u., both at the experimental and the PT2F($3s3p$)+RC optimized geometry. For the sake of comparison, the dipole moment evaluated as an expectation value at the CASSCF level has been included. The difference between the two results gives a measure of the accuracy of the precision in the numerical estimate of the energy derivative.

The trends shown by Table VII are very similar to those seen in Table I for the CuH case. The incorrect treatment of the mixing of the atomic states at the CASSCF level is reflected in the too large value of the computed dipole moment. This large value shows the bias that this method gives to the $3d^9 4s^1$ asymptote with the formation of a Ni($4s$)–H($1s$) bond polarized towards hydrogen. It is the overemphasis of this structure in the CASSCF wave function that leads to a too large value for the dipole moment. It is clear that the perturbational procedure corrects this bias to a large extent and more properly describes the influence of the $3d^8 4s^2$ configuration in the wave function. As a result, the size of dipole moment decreases significantly. Further inclusion of relativistic corrections (−0.22 D) and the $3s3p$ correlation effects (−0.11 D) brings the computed dipole moment into agreement with experiment. Table VII also includes previous theoretical values reported for this system. The variation in the dipole moment from one method to another illustrates the difficulties associated with the calculation. The CASPT2 results are similar to those obtained with other advanced methods for including the dynamic correlation effects, such as MRCI+NO.[18] The accurate calculation of the dipole moment of NiH is one further illustration of the capacity of the CASSCF/CASPT2 method in treating systems with a complex electronic structure.

D. The ground state of Ni_2

The determination of the ground state of Ni_2 has been the subject of much controversy, both experimental and theoretical. On the one hand, the available experimental data are quite inconclusive.[10] The first gas-phase spectroscopic study of the nickel dimer provided experimental verification of a high density of electronic states.[42] The rotational analysis of one of the bands showed that it originated from a state with $\Omega=4$, which was assumed to be the ground state. Since the lowest electronic states had been predicted to have electronic configurations with two holes in the δ orbitals, the only plausible candidates for the ground state consistent with these data were $^1\Gamma_g$ and $^3\Gamma_u$. New experiments[43] on Ni_2 using argon carrier gas instead of helium point out, however, the existence of a ground state with $\Omega=0_g^+$ or 0_u^-, which would be a mixture of $^3\Sigma_g^-$ and $^1\Sigma_g^+(0_g^+)$ or $^3\Sigma_u^+$ and $^1\Sigma_u^-(0_u^-)$.

On the other hand, the theoretical calculations have not definitely determined the character of the ground state.[31–35] Indeed, about 20 low-lying excited electronic states, within the range 0.5 eV, have been predicted.[33] Very recently, Bauschlicher *et al.*[34] reported internally contracted ACPF calculations based on CASSCF wave functions (CASSCF +ICACPF) and concluded that the ground state is almost certainly $^1\Gamma_g$. It is derived from $3d^9 4s^1$ Ni atoms, with a single bond between the $4s$ orbitals, little $3d$ involvement, and the holes localized in the $3d\delta$ orbitals. Nevertheless, the six states arising from configurations with holes in the $3d\delta$ orbitals ($\delta\delta$-holes states) were predicted to have similar energies. Spain and Morse[35] have also recently reported calculations on the nickel dimer based on a ligand-field plus spin–orbit model. Their results predict, however, that the ground state is characterized by $\Omega=0_g^+$, 0_u^-, or 5_u.

In this work, we present CASSCF/CASPT2 calculations for the six low-lying $\delta\delta$-holes states of Ni_2. The active space included the open shell $3d\delta$ orbitals together with the bonding and antibonding $4s$ orbitals (eight electrons in six orbitals). The remaining $3d$ electrons were correlated at second order. Calculations have been performed with and without correlating the $3s,3p$ electrons. The computed spectroscopic constants at different levels of theory are summarized in Table VIII. The effect of spin–orbit coupling (SO) has been estimated by allowing the appropriate $\delta\delta$-hole states to mix with coupling parameters taken from the ligand-field treatment of Morse.[35] The dissociation energy is computed with respect to two nickel atoms in the $d^9 s(^3D)$ state.

At the CASSCF level, the six states are found in a very narrow energy range, 0.02 eV, with triplet states above the singlet states. Relativistic corrections increase the dissociation energies by 0.07 eV, but the relative ordering of the states is kept. At the PT2F+RC level of theory, the lowest state is predicted to be $^1\Gamma_g$, even though the $^1\Sigma_g^+$ state is located only 0.01 eV above. The energy interval between the six states is computed to be 0.04 eV. It is similar to the range obtained at the ICACPF level: 0.05 eV.[34] In order to analyze the effect of the $(3s,3p)$ correlation, a new set of calculations was performed with these electrons included in the second-order correlation treatment (using again the $3s3p$ basis set). The obtained results are also included in Table VIII. The effect of this type of correlation on the computed D_e is about the same for the six states. The distance between them is the same, 0.04 eV, and now the two lowest states $^1\Gamma_g$ and $^1\Sigma_g^+$ are virtually degenerate. Column 6 of Table VIII gives the binding energies when also the spin–orbit coupling has been included. This coupling mixes the $^1\Sigma_g^+$ state with $^3\Sigma_g^-$ and $^1\Sigma_u^-$ with $^3\Sigma_u^+$. The coupling matrix element is 2×603 $cm^{-1}=0.15$ eV.[35] In addition, the $^1\Gamma_g$ state mixes with the $^3\Phi_g$ state, which is not a $\delta\delta$-hole state, but a $\pi\delta$-hole state. Since it lies higher in energy, the spin–orbit coupling effect is expected to be small. Nevertheless, an estimate can be obtained by employing the energy difference between both states reported by Bauschlicher *et al.*[34] obtained at the ICACPF level, 0.162 eV, and the corresponding coupling matrix element 603 $cm^{-1}=0.075$ eV. The estimated values have been indicated in Table VIII within parentheses. Since the energy differences between the six $\delta\delta$-hole states computed at the PT2F($3s3p$)+RC level are very small, the different electronic states are largely affected by spin–orbit coupling. Thus, while the $^3\Gamma_u(5_u)$ state decreases with 0.15 eV, and the $^1\Sigma_g^+(0_g^+)$ and the $^1\Sigma_u^-(0_u^-)$ states decrease by 0.14 eV, $^1\Gamma_g(4_g)$ decreases only by 0.03 eV. The range of the energy interval is now larger, 0.32 eV. The ground state is predicted to be the 0_g^+ state. The 0_u^- and 5_u states are located to be 0.01 and 0.03 eV above, respectively. The computed binding energy at this level of theory, 2.20 eV, is larger than the experimental energy, 2.09 eV. Additional calculations were performed in order to compute the BSSE corrections to D_e by employing the $3s3p$ basis set. The final column of Table VIII shows the results when this contribution, 0.10 eV, is subtracted. The excellent agreement with experiment is most certainly fortuitous. Normally CASPT2 is expected to give slightly too small binding energies due to a systematic

TABLE VIII. Calculated equilibrium geometry (r_e), vibration frequency (ω_e), and dissociation energy (D_e) for the six lowest-lying electronic states of Ni_2 at different levels of calculation. (CAS eight electrons/six orbits). Basis set [$6s5p4d3f2g$].

	r_e (Å) Level of calculation			
State	CASSCF	+RC	+PT2	+$3s3p$[a]
$^3\Sigma_u^+$	2.520	2.470	2.252	2.237
$^3\Sigma_g^-$	2.517	2.467	2.242	2.228
$^1\Gamma_g$	2.520	2.471	2.244	2.230
$^3\Gamma_u$	2.520	2.470	2.252	2.237
$^1\Sigma_u^-$	2.522	2.472	2.251	2.237
$^1\Sigma_g^+$	2.521	2.471	2.245	2.231
Exp.		2.200[b], 2.155[c]		
	ω_e (cm^{-1}) Level of calculation			
State	CASSCF	+RC	+PT2	+$3s3p$[a]
$^3\Sigma_u^+$	168	182	284	297
$^3\Sigma_g^-$	167	181	280	294
$^1\Gamma_g$	167	179	282	293
$^3\Gamma_u$	168	182	283	297
$^1\Sigma_u^-$	167	181	282	297
$^1\Sigma_g^+$	167	180	282	294
Exp.		280±20[d]		
	D_e (eV) Level of calculation			

State[e]	CASSCF	+RC	+PT2	+$3s3p$[a]	+SO[f]	BSSE[g]
$^3\Sigma_u^+(0_u^-)$	0.68	0.75	1.91	2.02	1.88	1.78
$^3\Sigma_g^-(0_g^+)$	0.68	0.75	1.93	2.04	1.90	1.80
$^1\Gamma_g(4_g)$	0.70	0.77	1.95	2.06	(2.09)[h]	(1.99)[h]
$^3\Gamma_u(5_u)$	0.68	0.75	1.91	2.02	2.17	2.07
$^1\Sigma_u^-(0_u^-)$	0.70	0.77	1.93	2.05	2.19	2.09
$^1\Sigma_g^+(0_g^+)$	0.70	0.77	1.94	2.06	2.20	2.10
Expt.			2.09[i]			

[a]The $3s3p$ basis set was employed.
[b]The r_0 value for the $\Omega=4$ state (Ref. 42).
[c]The r_0 value for the $\Omega=0$ state (Ref. 43).
[d]Reference 12.
[e]The Ω component of the substate reported in the column +SO is indicated within parentheses.
[f]Including the effect of spin–orbit coupling.
[g]BSSE corrected values.
[h]Estimated values based on the ICACPF splitting (see the text).
[i]Reference 43.

error in the method, which favors systems with unpaired electrons. The systematic error of CASPT2 is, however, not expected to largely affect the relative energies, since the $3d\delta$ electrons are only weakly coupled.

Table VIII also shows the computed r_e and ω_e values at the different levels of calculation. Too large bond distances and too small vibration frequencies are obtained at the CASSCF level. Relativistic corrections and the perturbation treatment significantly improve these values. The experimental determination of the dissociation energy and the bond distance has been carried out for both the $\Omega=4$ and the $\Omega=0$ states.[42,43] Whereas the dissociation energy is almost the same ($D_0=2.068$ and 2.067 eV, respectively), the bond distance shows surprising shortening ($r_0=2.200$ and 2.155 Å, respectively). The calculated bond distance at the PT2F($3s3p$)+RC level for the six $\delta\delta$-hole states lie in a very narrow range (2.228–2.237 Å). It is not likely that improved calculations would change these values very much. The differences in the electronic structure between the $\Omega=4$ and $\Omega=0$ states are small, which makes it unlikely that the bond distances would be very different. Also, the experimental distance for Ni_2 is considerably shorter than that found for Cu_2 ($r_e=2.219$ Å) (Ref. 16) and NiCu ($r_0=2.235$ Å),[44] while the results presented above predict a slightly longer distance for nickel ($r_e=2.231$ Å) than for the copper dimer ($r_e=2.215$ Å). The computed value for Cu_2 is only 0.004 Å shorter than the experimental value.

With respect to the vibration frequency, the six states show very similar values at the best level of calculation. These results lie within the error bars of the experimental measurement (280±20 cm^{-1}).[12] In addition, this experimental value is in line with those reported for NiCu (273±1 cm^{-1}) (Ref. 15) and Cu_2 (266.5 cm^{-1}).[16] This similarity is also reflected in the computed values for Ni_2 and Cu_2, 294

and 276.8 cm^{-1}, respectively. It is therefore difficult to understand the large difference in measured values for the equilibrium distances in the two molecules, since all other parameters are very similar.

IV. CONCLUSIONS

The four molecules CuH, NiH, Cu_2, and N_2 have been studied theoretically using the newly developed CASSCF/CASPT2 approach. For the three first molecules, the method is capable of predicting the electronic structure and spectroscopic constant with an accuracy that is at least as good as that of large scale MRCI calculations. The calculated bond energies (D_e) are within 0.1 eV of the experimental estimates for all molecules except NiH, where the deviation is 0.2 eV. The dipole moment of NiH has been computed to be 2.34 D, which is within the error bars of the experiment. The ground state of Ni_2 has been predicted to be 0_g^+ in agreement with the most recent experimental evidence, but at variance with earlier theoretical predictions. The bond distance in Ni_2 has been predicted to be close to that of Cu_2 and NiCu and considerably longer than a recent experimental estimate. The results confirm the ability of the CASPT2 method to compute reliable spectroscopic constants and dipole moments for systems involving first-row transition metal atoms as well as it does for molecules built from first- and second-row atoms.[6] A comparison of the present results to those computed with other methods such as MRCI, CPF, MCPF, or ACPF suggests that the CASSCF/CASPT2 approach can be a viable alternative to them, especially for larger systems, where it is hardly possible to perform such calculations, or where it is not possible to select a proper reference space. The presumption has been confirmed in recent studies of the structure and bond energies of $Ni(CO)_x$ ($x=1,4$), $Fe(CO)_5$, $Cr(CO)_6$, $Ni(C_2H_4)$, and ferrocene.[45]

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