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Homonuclear Dimers of First and Second Transition Metal Series

ABSTRACT. *In the present work we have reviewed the experimental and the theoretical knowledge of first and second series transition metal diatomics. In addition, new calculational results have been included for the molecules Ni_2, Fe_2, and Rh_2. Presently, the combined experimental and theoretical knowledge indicates that ab initio calculations provide valuable insight into the nature of the chemical bonds of such molecules, and even reasonable spectroscopic data, if carried far enough. The »d electron rich« transition metal dimers exhibit »bands« of low-lying electronic states. The chemical bonds in the molecules Cu_2, Ni_2, Co_2, and Fe_2, are mainly due to the delocalized $4s\sigma_g$ molecular orbitals. The 3d electrons localize around the nuclei and interact through Heisenberg exchange couplings, giving rise to the small energy splittings between the low-lying electronic states. In the corresponding dimers of the second transition metal series, Ag_2, Pd_2, Rh_2, and Ru_2 the principal bonding orbitals are the delocalized $5s\sigma_g$ molecular orbitals. For Ag_2 and Pd_2 the 4d electrons are essentially localized, while they get increasingly delocalized from Rh_2 to Ru_2. The d electrons in the »d electron deficient« transition metal dimers are appreciably delocalized and their combined contributions to the chemical bonds are comparable to the contributions due to the outermost $s\sigma_g$ molecular orbitals.*

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Introduction

Conceptually, modern chemistry builds on the quantum theory that appeared in the 1920s. The quantum theory was devised to explain a variety of phenomena for which the classical physics did not offer any satisfactory explanations. These phenomena include the black-body radiation, the photoelectric effect, and the line spectra of the atoms. The black-body radiation was explained by Planck in 1901 by introduction of energy quantization and of the Planck constant h. The photoelectric effect led in 1905 Einstein to suggest quantization of light, and in 1913 Bohr proposed quantization of angular momentum in his atomic model,

which accounted for the spectrum of the hydrogen atom in terms of an energy-level diagram.

Based on the prior developments in physics Schrödinger in 1926 suggested a general wave equation for describing the motion of atomic and subatomic particles and soon after, this equation was applied to chemical problems. Thus, already in 1927 Bohr communicated a paper by Burrau, who had utilized the new equation to elucidate the ground state of the H_2^+ molecular ion. However, better known is the work by Heitler and London 1927, in which they discuss the chemical bond in the H_2 molecule. Heitler and London invent a mathematical formulation of the covalent bond, and attribute the energy of the electron pair bond to the resonance energy arising from the exchange of the two electrons. The method introduced by Heitler and London has later become known as the valence bond method.

The molecular orbital method which is widely used in quantum chemistry nowadays was introduced by Hund 1928 and also by Mulliken 1928. This method is an extension of the Bohr theory of electronic configurations from atoms to molecules. Each electron is assigned to a molecular orbital that is the quantum mechanical analogue of the electron orbit in an atom.

It is recognized that the foundation of modern quantum chemistry was laid at an early stage and already in 1929 Dirac made his famous remark: »The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known«. However, he did add »the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed«.

The approximate methods developed since the early days of quantum mechanics have made use of the fact that the Schrödinger equation is equivalent to a variational principle. Hylleraas 1930 carried out very accurate calculations for the He atom using this principle. His methods, however, were not suited for generalization to many electron systems. Thus, the methods applied in quantum chemistry to-day have their origin in the self-consistent-field work by Hartree 1928. After Slater 1929 introduced the determinantal wave functions, Slater 1930 and Fock 1930 independently invented what is now commonly known as the Hartree-Fock method.

Although the development of the quantum theory in principle opened up the possibilities of quantitative studies of atoms and molecules, it was

only with the technological development of the electronic computers that such studies also became practically feasible. Calculations of electronic states of atoms and molecules with more than one or two electrons are strongly dependent on the existence of electronic computers. In 1951 and 1960 Roothaan introduced the formulations of the Hartree-Fock equations which are especially suited for electronic computations, and even though much progress has been achieved since, Roothaan's equations are still the natural starting point for quantum chemistry calculations.

Nowadays, quantum chemical calculations can be performed by routine even on rather large molecules composed of atoms from the first and the second row in the periodic system, such as organic molecules, but compounds containing transition metal atoms still constitute great challenges.

During recent years several research groups have been devoting great efforts to experimental or theoretical investigations striving to understand and elucidate the chemistry and physics of small clusters composed of transition metal atoms. The current interest in the transition metal clusters is influenced by their relevance to surface science and heterogeneous catalysis. Thus, finely dispersed transition metals supported on high surface materials such as porous silica act as catalysts for the hydrogenation of carbon monoxide, and presently it appears likely that this process or similar ones will be of great importance for securing the energy supply in future. Therefore, it is essential to aquire profound insight into the mechanism of such reactions at the atomic and molecular levels.

Both experimental and theoretical investigations of transition metal clusters are very difficult to carry out and strongly dependent on each other for appropriate interpretations.

The present paper has been devoted to the smallest possible units consisting of transition metal atoms, namely the diatomic molecules. In particular, we have concentrated on the theoretical investigations of the molecules where the author has been most actively involved, that is, the homonuclear transition metal dimers composed of atoms with more than half filled d shells belonging to the first and the second transition metal series. These elements also include some of the most commonly used in catalyses.

The paper is structured as follows: The next section contains a brief account of available experimental data concerning first and second row transition metal dimers. Thereafter a few computational details are pre-

sented followed by a detailed discussion of the results for the individual molecules. The conclusions of the work are found in the last section.

Experimental investigations of transition metal dimers

The first experimental data obtained for any transition metal dimers date back to 1954 and 1955, when the electronic spectra of the molecules Cu_2 and Ag_2 were measured by Kleman and Lindkvist and also by Ruamps 1954. A little later Dowart and Honig 1956, 1957 and Schissel 1957 determined the dissociation energies of Cu_2, Ag_2, and Au_2 from measurements of the dimer to monomer ratios in high temperature mass spectrometric studies.

During the 1960s all the homonuclear dimers of the first transition metal series have been studied using the high temperature equilibrium mass spectrometric method. This has been reviewed by Gingerich 1980, and the dissociation energies obtained including later corrections and also results of new measurements are displayed in Table I.

The high temperature mass spectrometric method has also been utilized for studying the homonuclear dimers composed of atoms with non closed d shells of the second transition metal series. The first of these investigations was performed by Verhaegen et al. 1964, and dealt with the Y_2 molecule. The dimers of the most refractory metals have been studied mainly by Gingerich and his collaborators as is seen from Table I.

In the mass spectrometric investigations the dimer to monomer ratios are measured, but in order to derive the dissociation energies from the measured data, it is necessary to evaluate the partition functions for both the monomers and the dimers. This gives rise to inaccuracies in the published dissociation energies, because the spectroscopic constants, such as equilibrium distances, vibrational frequencies, and low-lying electronic states needed for the evaluation of the partition functions are only currently becoming available for the transition metal dimers composed of atoms with partly filled d shells. Recently we have performed new mass spectrometric measurements for the molecules Fe_2, Shim and Gingerich 1982, and Pd_2, Shim and Gingerich 1984. The utilization of the calculated low-lying electronic states in the evaluation of the partition function for Fe_2 resulted in a dissociation energy 0.78 ± 0.17 eV as compared to the value of 1.04 ± 0.22 eV derived by Lin and Kant 1969b.

As reviewed by Huber and Herzberg 1979, well-resolved UV-visible gas phase spectra have been measured many years ago for the molecules

Table I. Experimental spectroscopic constants of the first and second row transition metal dimers.

Molecule	Matrix isolation studies			Gas phase spectroscopic studies				High temperature mass spectrometric studies	Nearest neighbour internuclear distance in bulk metal (a.u.)[1]
	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	r_e(a.u.)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	r_e(a.u.)	D_0(eV)	D_0°(eV)	
Sc$_2$	238.91[2]	0.93[2]						1.65±0.22[3]	6.15
Ti$_2$	407.9[4]	1.08[4]						1.41±0.22[5]	5.50
V$_2$	537.5[4]	4.2[4]		535[6]	3.34[6]	1.85[6]		2.47±0.22[5]	4.95
Cr$_2$	427.5[7]	15.75[7]		470[10]		3.17[9,10]		1.56±0.22[11]	4.71
						3.184[8,34]			
				472.7[35]	10.2[35]				
				493.3[35]	20.5[35]				
Mn$_2$	124.7[2]	0.24[2]						0.43±0.30[12]	4.27
Fe$_2$	300.26[2,13]	1.4[13]	3.53±0.25[14]					0.78±0.17[16]	4.69
			3.82±0.04[15]						
Co$_2$	290[7]							0.95±0.26[17,33]	4.72
Ni$_2$	380.9[18]	1.08[18]				4.157±.013[19]	2.068±.01[19]	2.00±0.22[20,21]	4.71
Cu$_2$				264.55[22]	1.025[22]	4.1947[22]		2.04±0.13[12]	4.82
Y$_2$								1.62±0.22[23]	6.72
Zr$_2$									5.97
Nb$_2$								5.21±0.10[24]	5.40
Tc$_2$									5.11
Mo$_2$	475.7[25]			477.1[34]	1.51[34]	3.645[34]	4.12±0.65[34]	4.18±0.22[27]	5.14
						3.666±0.017[26]			
Ru$_2$									5.06
Rh$_2$								2.92±0.22[28]	5.08
								2.80±0.13[29]	
Pd$_2$								1.03±0.17[30]	5.20
Ag$_2$	194[31]			192.4[22]	0.643[22]	4.690[32]		1.65±0.07[12]	5.46

1) From J. Donohue, »The Structure of the Elements«, (Krieger, Malabar, Florida 1982). – 2) Moskovits, DiLella, and Limm 1984 (Ar). – 3) Drowart 1967. – 4) Cossé, Fouassier, Mejean, Tranquille, Dilella, and Moskovits 1980 (Ar). – 5) Kant and Lin 1969. – 6. Langridge-Smith, Morse, Hansen, Smalley, and Merer 1984. – 7) Ford, Huber, Klotzbücher, Kündig, Moskovits, and Ozin 1977 (Ar). – 8) Efremov, Samoilova, and Gurvich 1974. – 9) Michalopoulos, Geusic, Hansen, Powers, and Smalley 1982. – 10) Bondybey and English 1983. – 11) Kant and Strauss 1966. – 12) Kant, Lin, and Strauss 1968. – 13) Moskovits and DiLella 1980 (Ar) – 14) Montano and Shenoy 1980 (EXAFS in Ar) – 15) Purdum, Montano, Shenoy, and Morrison 1982 (EXAFS in Ne). – 16) Shim and Gingerich 1982. – 17) Kant and Strauss 1964. – 18) Ahmed and Nixon 1979. – 19) Morse, Hansen, Langridge-Smith, Zheng, Geusic, Michalopoulos, and Smalley 1984. – 20) Kant 1964. – 21) Noell, Newton, Hay, Martin, and Bobrowicz 1980. – 22) Huber and Herzberg 1979. – 23) Verhaegen, Smoes, and Drowart 1964. – 24) Gupta and Gingerich 1979. – 25) Pellin, Foosnaes, and Gruen 1981. – 26) Hopkins, Langridge-Smith, Morse, and Smalley 1983. – 27) Gupta, Atkins, and Gingerich 1978. – 28) Gingerich and Cocke 1972; Cocke and Gingerich 1974. – 29) Piacente, Balducci, and Bardi 1974. – 30) Shim and Gingerich 1984. – 31) Schulze, Becker, Minkwitz, and Manzel 1978. – 32) Srdanov and Pešić 1981. – 33) Shim and Gingerich 1983b. – 34) Efremov, Samoilova, Kozhukhovsky, and Gurvich 1978. – 35) Riley, Parks, Pobo, and Wexler 1983.

Cu_2 and Ag_2. The spectra of Cu_2 have resulted in accurate determination of both the equilibrium distance and the vibrational frequency of the electronic ground state. Similar spectroscopic data are also known for the Ag_2 molecule, but in this case the equilibrium distance has been derived recently from data of Srdanov and Pešić 1981.

Due to experimental difficulties the knowledge of the spectroscopic data for the open shell transition metal dimers have been scarce until recently. The first spectroscopic investigations of such molecules have been carried out using the matrix isolation technique introduced by Whittle, Dows and Pimentel 1954 and by Becker and Pimentel 1956. In this method, the metal vapor is cocondensed with an inert gas at very low temperatures $\sim$10K. Of course, use of the matrix isolation technique results in loss of the rotational fine structures, and therefore this method is not suitable for determining the equilibrium distances of the molecules. In addition, it is often difficult or impossible to identify with certainty the carriers of the electronic transitions observed. Compared to gas phase spectra, frequency shifts of the absorptions occur and also possibly splittings due to local site symmetries. Thus, not even the spectra arising from atomic species can unambiguously be assigned to the gas phase spectra.

The first matrix isolation study of the spectroscopic transitions of an open shell transition metal dimer, where an assignment of the spectrum of the diatomic molecule was attempted, has been carried out by Green and Gruen 1972 for the Nb_2 molecule. Klotzbücher and Ozin 1977 and 1980a have also investigated the Nb_2 molecule in inert gas matrices, but they did not observe any absorption in the spectral region where Green and Gruen found the features they attribute to Nb_2.

The difficulties encountered in matrix isolation studies of transition metal atoms and molecules are clearly recognized in the work done on Ni and Ni_2. The first investigation of Ni_2 in an inert gas matrix (Ar) was performed by de Vore et al. 1975. They have reported a single absorption system with an average vibrational spacing of 192 cm^{-1} and with 0-0 band at 21 786 cm^{-1}. Moskovits and Hulse 1977, however, observed two discrete band systems with origins at 18 920 cm^{-1} and 26 500 cm^{-1}, respectively, and also a continuous band peaking at 24 000 cm^{-1}. Furthermore, they pointed out that the matrix shifts of the atomic Ni absorptions are large and not at all uniform ranging from 1270 cm^{-1} to 3450 cm^{-1}. Recently Cellucci and Nixon 1984 have performed laser-induced fluorescence studies of Ni atoms isolated in different inert gas matrices. In their work they find evidence for a $^3F_4(3d)^8(4s)^2$ ground term of Ni in

a Ne matrix while the ground term of Ni isolated in an Ar or Kr matrix probably is $^3D_3(3d)^9(4s)^1$. Furthermore, they only find very small matrix shifts.

Matrix isolation studies are presently known for all first row and a few second row homonuclear transition metal dimers. In Table I we have summarized the ground state spectroscopic data as derived in the matrix isolation investigations.

The matrix isolation technique has also formed the basis for other kinds of experimental investigations of the transition metal dimers such as Mössbauer and ESR studies. Mössbauer studies of the Fe_2 molecule have in particular been carried out by Montano and collaborators as described by Montano et al. 1976 and by Montano 1980. ESR spectra of the Sc_2 molecule obtained by Knight et al. 1983 have established the ground state of Sc_2 as a $^5\Sigma$ state. ESR studies by Van Zee et al. 1981, by Rivoal et al. 1982, and by Baumann et al. 1983 have revealed that the Mn_2 molecule has a $^1\Sigma_g^+$ ground state arising from antiferromagnetic coupling of the atoms. This is in agreement with the early theoretical work by Nesbet 1964.

Gas phase spectroscopic investigations of transition metal dimers are still rather scarce. Due to the refractory nature of the transition metals, special techniques such as laser vaporization or hot ovens are required to produce the metal vapors. Thereafter the clusters can be created in a cold gas bath and finally effused into a vacuum, where the spectra are measured, Powers et al. 1983.

The first gas phase studies of open shell transition metal dimers have been carried out by Efremov et al. They obtained absorption and emission spectra of the molecules Cr_2, 1974 and Mo_2, 1978 in flash photolysis of the molecules $Cr(CO)_6$ and $Mo(CO)_6$, respectively. From the spectra of the Cr_2 molecule they derived an equilibrium distance of only 3.184 a.u. This distance seemed so incredibly short that they suggested other carriers of the observed spectral bands, such as CrO_2 or CrC_2. However, the recent spectroscopic investigations by Michalopoulos et al. 1982, by Bondybey et al. 1983, and by Riley et al. 1983 all confirm the short bond distance in the Cr_2 molecule.

From Table I it is noted that besides the molecules Cr_2 and Mo_2 also V_2 and Ni_2 have been studied in the gas phase. In the work by Morse et al. 1984 of the Ni_2 molecule no spectroscopic transitions were observed over the entire range 570-350 nm, which covers all known matrix absorption systems of Ni_2. They attribute this to predissociation of the excited state. From 600 to 900 nm they found an exceptionally high

density of spectroscopic transitions for a diatomic molecule, and they consider this as a proof of the theoretical predictions by Upton et al. 1978, by Shim et al. 1979, and by Noell et al. 1980 of the many low-lying electronic states.

Computational details

The electronic structures of the molecules Fe_2, Co_2, Ni_2, Cu_2, Ru_2, Rh_2, Pd_2, Ag_2, and Nb_2 have been investigated by the author using all electron ab initio Hartree-Fock (HF) and configuration interaction (CI) calculations. The computations have been carried out in the Hartree-Fock-Roothaan formalism, Roothaan 1951 and 1960, folllowed by configuration interaction treatments. The integrals have been calculated using the program MOLECULE★. For the HF calculations we have utilized the ALCHEMY program system★★, and finally the CI calculations have been performed using ALCHEMY in conjunction with the program ENERGY★★★ for generating the symbolic energy expressions.

The basis sets used consisted of Gaussian type functions. For the first row transition metal atoms we have utilized modified versions of the basis sets optimized for the atomic ground terms by Wachters 1970. Relative to Wachters' our basis sets have been extended by addition of two p functions and also a diffuse d function. The exponents of the two most diffuse s functions have been altered to contract the radial charge densities resulting in improved description of the valence regions in the molecules. For the first row transition metal dimers the primitive bases (14s, 11p, 6d) have been contracted to (8s, 6p, 3d). The coefficients of the contracted functions have been derived in HF calculations on the ground terms of the respective atoms. In the contracted bases the 3d orbitals are represented by triple zeta functions, and all the occupied s and p orbitals

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★MOLECULE has been written by J. Almlöf, and has been described in »Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry« (Max-Planck Institut, München, 1973), p. 14.

★★The ALCHEMY program system is written at IBM Research Laboratory in San Jose, Ca. by P. S. Bagus, B. Liu, M. Yoshimine, and A. D. McLean.

★★★The program ENERGY has been written by S. Rettrup, and is described in C. R. Sarma and S. Rettrup, Theor. Chim. Acta (Berlin) 46, 63 (1977); S. Rettrup and C. R. Sarma, ibid. 46, 73 (1977).

as well as the empty 4p orbitals are represented by double zeta functions.

For the second row transition metal dimers Ru_2, Rh_2, Ag_2, and Nb_2 the basis sets used are essentially Huzinaga's 1977, but extended by addition of two p functions. The additional p functions are needed to describe the 5p orbitals, and their exponents have been determined using the even tempered method described by Raffenetti 1973. Equivalent to the first row transition metal atoms the exponents of the most diffuse s functions have been altered to contract the radial charge densities. The primitive basis sets (17s, 13p, 8d) were contracted to (10s, 8p, 5d) by using segmented contraction schemes. The coefficients of the contracted functions have been determined in HF calculations on the ground terms of the atoms. In the contracted basis sets all the occupied s and p orbitals and the empty 5p orbitals have been represented by double zeta functions. The 3d orbitals are represented by double zeta functions while the 4d orbitals by triple zeta functions.

The basis set utilized for the Pd atom is similar to Huzinaga's 1977, and it has been described in detail by Shim and Gingerich 1984.

In Table II we compare the relative energies of the lowest lying terms originating from different orbital configurations with the corresponding experimental values, and also with those derived in the numerical HF calculations performed by Martin and Hay 1981. It is observed that we obtain the right ordering of the terms except in the case of the Ni atom for which the $^3F(3d)^8(4s)^2$ term is found 1.28 eV below the $^3D(3d)^9(4s)^1$ term whereas it should be 0.03 eV above. The calculated splittings between terms originating from the different orbital configurations differ to some extent from the experimental values. This is a well-known deficiency of HF calculations and it has been discussed in considerable detail for the first row transition metal atoms by Claydon and Carlson 1968.

It is noted that our calculated splittings are in reasonable agreement with those derived in the numerical HF calculations both for the first and the second row transition metal atoms. This indicates that our basis sets are of good qualities.

In all calculations of electronic structures of molecules containing transition metal atoms, the partly filled inner shells, that is the 3d and the 4d shells for the first and the second row transition metal atoms, respectively, give rise to severe complications. Thus, for the diatomic molecules their presence causes great uncertainties as to electronic ground state assignments, because a considerable number of Slater determinants will have comparable energies. This number increases rapidly as the

Table II. Relative energies (eV) of the low-lying terms for the "d electron rich" transition metal atoms of the first and the second transition metal series.

Atom	Term	Calculated		Experimental [a]
		HF [b]	NHF [c]	
Cu	$^2S(3d)^{10}(4s)^1$	0.00	0.00	0.00
	$^2D(3d)^9(4s)^2$	0.38	0.37	1.49
	$^2P(3d)^{10}(4p)^1$	4.33		3.81
Ni	$^3D(3d)^9(4s)^1$	0.00	0.00	0.00
	$^3F(3d)^8(4s)^2$	-1.28	-1.27	0.03
	$^1S(3d)^{10}$	4.14	4.20	1.74
Co	$^4F(3d)^7(4s)^2$	0.00	0.00	0.00
	$^4F(3d)^8(4s)^1$	1.52	1.53	0.42
	$^2D(3d)^9$	6.98	7.04	3.36
Fe	$^5D(3d)^6(4s)^2$	0.00	0.00	0.00
	$^5F(3d)^7(4s)^1$	1.85	1.80	0.87
	$^3F(3d)^8$	7.59	7.46	4.07
Ag	$^2S(4d)^{10}(5s)^1$	0.00	0.00	0.00
	$^2D(4d)^9(5s)^2$	4.77	4.91	3.97
	$^2P(4d)^{10}(5p)^1$	3.82		3.74
Pd	$^1S(4d)^{10}$	0.00	0.00	0.00
	$^3D(4d)^9(5s)^1$	0.23	0.75	0.95
	$^1D(4d)^9(5s)^1$	0.62		1.45
	$^3F(4d)^8(5s)^2$	3.08	3.76	3.38
Rh	$^4F(4d)^8(5s)^1$	0.00	0.00	0.00
	$^2D(4d)^9$	1.49	0.95	0.34
	$^4F(4d)^7(5s)^2$	2.03	2.19	1.63
Ru	$^5F(4d)^7(5s)^1$	0.00	0.00	0.00
	$^5D(4d)^6(5s)^2$	1.25	1.42	0.87
	$^3F(4d)^8$	2.26	1.69	1.09

number of holes in the d shell increases, and it reaches a maximum value of 184 756, when the d shell is half full.

As has been studied in detail by Shim, Johansen and Dahl 1979 the chemical bond between two Ni atoms is formed when the atoms interact in the $(3d)^9(4s)^1$ configuration. Thus, in the cases of the molecules Ni_2 and Pd_2 the holes in the d shells give rise to $\binom{20}{18} = 190$ Slater determinants. For the molecules Co_2 and Rh_2 this number increases to $\binom{20}{16} = 4845$, and for Fe_2 and Ru_2 to $\binom{20}{14} = 38\ 760$. For the Nb_2 molecule the number is $\binom{20}{8} = 125\ 970$.

It is of course not only practically impossible but also undesirable to perform HF calculations on all the states arising from the large numbers of Slater determinants. Since our goal is determination of all the low-lying electronic states of the molecules investigated, we have chosen to perform HF or hyper-HF (HHF) calculations as introduced by Slater et al. 1969 to derive unique sets of molecular orbitals suitable for utilization in CI calculations to describe all the low-lying states. This procedure, of course, does not provide the optimum description of each state individually, but we believe it results in balanced descriptions of the many low-lying states.

For all the open shell molecules we have performed HF or HHF calculations in search for wave functions that could describe bound molecules, that is, the total energies of the molecules at reasonable internuclear distances should be lower than the sum of the energies of the free atoms in their ground terms. As a starting point we have chosen to doubly occupy the $s\sigma_g$ molecular orbital originating from the combination of the outermost s orbitals of the two atoms. Of the many possible configurations arising because of the d orbital part of the wave functions, there are two fundamentally different types. In one type the bonding molecular orbitals are first fully occupied, and the remaining electrons are then distributed in the antibonding orbitals. In the second type the electrons are distributed evenly in the bonding and in the antibonding orbitals; such an arrangement is required for a correct description of the molecules in the dissociation limit, and it also allows the electrons to localize around the nuclei. For all the open shell transition metal dimers investigated, it turned out that only wave functions with equal numbers

◊ a) Center of gravity of each multiplet has been derived from data of C. E. Moore, Nat. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D.C. 1952, 1958) vols. 2 and 3. – b) Preset work. – c) Results of Numerical HF calculations by Martin and Hay 1981.

of electrons in bonding and antibonding molecular orbitals could describe bound molecules. All the wave functions considered with excess of electrons in bonding orbitals relative to the antibonding orbitals have energies far above the dissociation limits of the molecules.

A variety of HF or HHF calculations have been performed for the transition metal dimers at internuclear distances app. equal to the distance between nearest neighbours in the bulk metals. The resulting molecular orbitals have been utilized in CI calculations to describe all the low-lying electronic states of the molecules. The calculations allowed at least full reorganization within the valence d shells, ensuring that the d orbital part of the wave functions is described correctly in the dissociation limit. The calculations have been performed in the subgroup D_{2h} of the full symmetry group $D_{\infty h}$ of the transition metal dimers.

Theoretical investigations of transition metal dimers

In the following we present results of ab initio studies of the homonuclear dimers consisting of atoms from the first and second transition metal series. The homonuclear dimers of the first transition metal series have all been investigated by Harris and Jones 1979 using a local spin density method, and by Wolf and Schmidtke 1980 using the restricted HF method. Only occasionally we discuss the results of these investigations, because both methods are essentially single determinant methods, and thus unable to describe the physics of the open shell molecules.

»d electron rich« transition metal dimers

Cu₂. The Cu atom has a completely filled 3d shell in its $^1S(3d)^{10}(4s)^1$ ground term, and therefore the Cu_2 molecule represents the simplest possible transition metal dimer. Unlike other transition metal dimers there is no ambiguity regarding the electronic ground state which is a $^1\Sigma_g^+$ state. Furthermore, at internuclear distances reasonably close to the equilibrium distance of the molecule the $^1\Sigma_g^+$ ground state is well described in the HF approximation by a single Slater determinant.

As reviewed by Huber and Herzberg 1979, the Cu_2 molecule is the transition metal dimer for which the equilibrium distance and the vibrational frequency of the electronic ground state have been accurately de-

termined earliest. For this reason and because no low-lying electronic states contribute to the partition function of the Cu_2 molecule the dissociation energy derived from high temperature mass spectrometric data is more reliable for this molecule than for other transition metal dimers.

The Cu_2 molecule has been the subject of many theoretical investigations, and Table III summarizes the spectroscopic data of the molecule as obtained in various calculations with a brief description of the methods used.

The early all-electron ab initio calculations mentioned in Table III employed either minimal basis sets or minimal basis sets with split valence orbitals. The apparent better agreement between the calculated and the experimental spectroscopic data obtained in these investigations relative to those obtained in the more elaborate calculations is fortuitous and stems from basis set superposition errors. However, the calculations by Bachmann et al. 1978, 1980 and by Tatewaki et al. 1980, 1981 were not primarily aimed at studying the Cu_2 molecule, but rather at obtaining basis sets manageable in calculations involving larger clusters.

Some of the difficulties associated with theoretical investigations of transition metal dimers are apparent in Table III, where it is observed that the calculated spectroscopic data vary considerably. Even the most elaborate calculations, which include those of Bauschlicher 1983 involving CI calculations with app. 225 000 functions and also those of Pelissier 1981 involving perturbational CI with contributions from app. 400 000 determinants do not lead to accurate spectroscopic data for the Cu_2 molecule.

The less sophisticated $X\alpha$ type calculations are more successful in deriving spectroscopic constants for the Cu_2 molecule, but these methods are in general only applicable to systems, where the wave functions can be represented by a single Slater determinant as shown by Ziegler 1984. Thus, the $X\alpha$ methods are not suitable for accurate descriptions of the electronic structures of the open shell transition metal dimers that have been the main emphases of our investigations.

The description of the chemical bond in the Cu_2 molecule also differs in the $X\alpha$ and in the HF-CI methods. In the $X\alpha$ methods substantial mixing or hybridization occurs between the 3d and the 4s orbitals. In the HF-CI calculations no such mixing occurs as is illustrated in Table IV, which shows the Mulliken population analyses for the Cu_2 molecule at the experimental internuclear distance. The bond between the two Cu atoms is primarily due to the delocalized doubly occupied $4s\sigma_g$ molecular orbital, and the largest contributions in the CI expansion, apart from the

HF function, arise from angular and left-right correlation of the bonding electrons as discussed in detail by Shim et al. 1983a. The deformation density map in Fig. 1 reveals that the bonding between the two atoms results in a build up of charge in the internuclear region.

Table III. Experimental and calculated spectroscopic constants for the Cu_2 molecule.

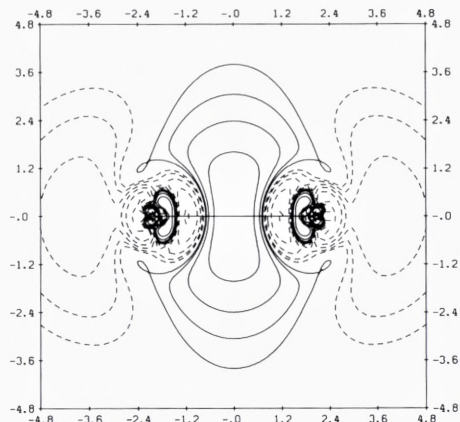|	Method	Basis set Type; primitive-contracted	Spectroscopic constants r_e(a.u.)	ω_e(cm^{-1})	D_e(eV)
	Experimental		4.1947[1]	264.55[1]	2.04±0.13[2]
	All electron ab initio calculations				
3)	CI(2×2)	STO; minimal + 4d and 4p	4.24		1.75
4)	HF	GTO; (12s,7p,5d)-(5s,3p,2d)	4.43	248	0.84
5)	HF	GTO; (12s,6p,3d)-(4s,2p,1d) optimized	4.48	194	0.42
	HF	GTO; (13s,7p,4d)-(5s,3p,2d)	4.55	220	0.37
6)	MCSCF($4s\sigma_g^2$,$4s\sigma_u^2$)	GTO; (12s,7p,5d)-(5s,3p,2d)	4.61	338	1.16
7)	HF	GTO; (14s,11p,5d)-(8s,6p,2d)	4.54	190	
	HF	GTO; (14s,13p,5d)-(8s,8p,2d)	4.38	210	
8)	HF	GTO; (12s,7p,4d)-(5s,4p,2d)	4.39	252	1.09
	HF	GTO; (14s,10p,7d)-(8s,6p,4d)	4.62	201	0.52
9)	CI	GTO; (12s,9p,4d)-(5s,6p,2d)	4.19	263	1.75
10)	HF	GTO; (14s,11p,6d)-(8s,6p,4d)	4.59		
	HF	GTO; (14s,11p,6d,3f)-(8s,6p,4d.1f)	4.53		
	CI	GTO; (14s,11p,6d)-(8s,6p,4d)	4.42		
	CI	GTO; (14s,11p,6d,3f)-(8s,6p,4d,1f)	4.39		
11)	MCSCF($4s\sigma_g^2,4s\sigma_u^2,4p\pi_u^2,4p\sigma_g^2$)	GTO; (14s,11p,6d,3f)-(8s,6p,4d,1f)	4.62	184	1.25
	CI(SD)	as above	4.42	220	1.51
	CI	as above	4.45	227	1.99
12)	HF	GTO; (14s,11p,6d)-(6s,5p,3d)	4.57	191	0.54
	MCSCF($4s\sigma_g^2,4s\sigma_u^2$)	as above	4.68	162	0.83
	HF + rel.perturbations	as above	4.48	206	0.61
	MCSCF + rel. perturbations	as above	4.58	176	0.90
13)	HF	GTO; (14s,11p,6d)-(8s,6p,3d)	4.56	197	0.68
	CI(18×18)	as above	4.62	179	0.83
	CI(378×378)	as above	4.60	186	1.27
	CI(2928×2928)	as above	4.54	200	2.07
14)	HF	GTO; (13s,7p,5d)-(4s,2p,1d)	4.74	155	
	HF	GTO; (13s,7p,5d)-(5s,3p,2d)	4.60	170	
	Pseudopotential calculations				
15)	CI	GTO; (6s,3d)-(2s,2d)	4.20		1.84
16)	MCSCF	GTO; (3s,1p,5d)-(2s,1p,2d)	4.71	282	0.76
	CI	as above	4.40	340	1.30
17)	HF	GTO; (4s,3p,6d)-(3s,2p,3d)	4.54	190	
	CI	as above	4.38	210	
	Xα type calculations				
18)	Xα-SW		4.10	272	2.86
19)	Local spin density		4.30	280	2.30
20)	Xα-LCAO	STO; valence triple zeta	4.23	274	2.30
	Xα-LCAO, relativistic	as above	4.27	268	2.21

Fig. 1. Deformation density map of the Cu_2 molecule at the internuclear distance 4.1947 a.u. The superpositioned atomic charge densities have been subtracted from the molecular charge density as derived in CI calculations with 18 functions. Solid contours show enhanced electron charge relative to the superpositioned atoms, dashed contours show diminished charge. The smallest contour value is 0.000625 $e/a.u.^3$. Adjacent contours differ by a factor of 2.

The main purpose of our investigation of the Cu_2 molecule was not to derive spectroscopic constants of high accuracy which in any case seem fortuitous, but rather to study the nature of the chemical bond of the molecule. We have carried out CI calculations of various accuracies. The CI calculation with 18 functions allowed full reorganization within the 3d and 4s shells and therefore leads to a correct description of the molecule in the dissociation limit. All other CI calculations performed included additional excitations on top of the full reorganization within the 3d and 4s shells. Thus, the calculation with 378 functions represents complete correlation of the bonding $4s\sigma_g$ electrons within the space spanned by the basis set. Our largest calculation with 2928 functions included selected single and double excitations from the $4s\sigma_g$ and the 3d orbitals.

The calculated spectroscopic constants as derived from the various CI calculations for this simple transition metal dimer have been utilized to estimate the accuracy of the calculated spectroscopic data of the much more complicated open shell transition metal dimers for which experimental data are more scarce.

◊ 1) Huber and Herzberg 1979. – 2) D_o^o, Gingerich 1980. – 3) Joyes and Leleyter 1973. – 4) Bachmann, Demuynck, and Veillard 1978. – 5) Tatewaki and Huzinaga 1980; Tatewaki, Sakai, and Huzinaga 1981a. – 6) Basch 1980a – 7) Wolf and Schmidtke 1980. – 8) Tatewaki, Sakai, and Huzinaga 1981b. – 9) Witko and Beckmann 1982. – 10) Bauschlicher, Walch, and Siegbahn 1982. – 11) Bauschlicher 1983. – 12) Martin 1983. – 13) Shim and Gingerich 1983a. – 14) Cingi, Clemente, and Foglia 1984. – 15) Dixon and Robertson 1978. – 16) Basch 1980a. – 17) Pelissier 1981. – 18) Ozin, Huber, McIntosh, Mitchell, Norman Jr., and Noodleman 1979. – 19) Harris and Jones 1979. – 20) Ziegler, Snijders, and Baerends 1981.

Table IV. Mulliken population analyses of the valence orbitals of the Cu_2 molecule as derived in CI calculations with 18 functions at the internuclear distance 4.1947 a.u.

Orbital	Overlap population	Orbital analyses			Occupation number
		s	p	d	
$4s\sigma_g$	0.75	0.94	0.04	0.00	1.97
$3d\sigma_g$	0.09	0.00	0.00	1.00	2.00
$3d\pi_u$	0.14	0.00	0.00	2.00	4.00
$3d\delta_g$	0.03	0.00	0.00	2.00	4.00
$3d\delta_u$	-0.03	0.00	0.00	2.00	4.00
$3d\pi_g$	-0.12	0.00	0.00	2.00	4.00
$3d\sigma_u$	-0.08	0.01	0.00	0.99	2.00
$4s\sigma_u$	-0.04	0.01	0.00	0.00	0.03

Ag₂. The Ag atom has a $^1S(4d)^{10}(5s)^1$ ground term that is well separated from the higher lying terms. Two Ag atoms interact by forming a stable Ag_2 molecule with a closed shell $^1\Sigma_g^+$ ground state. The ground state is well described in the HF approximation by a single Slater determinant at the equilibrium internuclear distance.

Just as for the Cu_2 molecule, the ground state of the Ag_2 molecule is well characterized experimentally. In Table V we have listed the spectroscopic constants for the Ag_2 molecule together with a summary of the calculated values as derived in the various theoretical investigations. It is noted that the calculated spectroscopic constants differ considerably from the experimental values. Thus, all the calculated equilibrium distances are too long even those derived from the calculations that take relativistic effects into account. It appears that the spectroscopic constants derived from electronic structure calculations of transition metal compounds with the presently known computational techniques are questionable in an absolute sense. It is, however, apparent from Table I that only very little experimental information is available for the second

row transition metal dimers, and therefore we have utilized our calculated spectroscopic constants for the Ag_2 molecule to judge the spectroscopic constants derived in equivalent calculations for the other transition metal dimers of the second transition metal series.

For the Ag_2 molecule we have carried out two sets of CI calculations, Shim and Gingerich 1983a. One set is completely equivalent to some of the calculations performed for the Cu_2 molecule. In these calculations we have included the 18 functions arising from all rearrangements of the electrons within the 4d and the 5s shells. Such wave functions allow correct description of the molecule in the dissociation limit. In the second set of CI calculations with 684 functions we also included all single and double excitations from the 4d and the 5s shells into the lowest lying virtual σ and π orbitals.

Table V. Experimental and calculated spectroscopic constants for the Ag_2 molecule.

	Method	Basis set Type; primitive-contracted	Spectroscopic constants		
			r_e(a.u.)	ω_e(cm^{-1})	D_e(eV)
	Experimental		4.69[1]	192.4[2]	1.65±0.5[3]
	All electron ab initio calculations				
4)	MCSCF($5s\sigma_g^2,5s\sigma_u^2$)	GTO;(19s,11p,8d)-(6s,4p,3d)	5.37	218	0.76
5)	HF	GTO;(17s,13p,8d)-(10s,8p,5d)	5.24	134	0.89
	CI(18×18)	as above	5.32	120	1.05
	CI(684×684)	as above	5.21	134	
6)	HF	STO;(11s,9p,5d)	5.27	129	0.38
	MCSCF	as above	5.41	108	0.67
	CI(6091×6091)	as above	5.15		1.13
7)	HF	GTO;(14s,8p,7d)-(5s,3p,2d)	5.2	120	
	Pseudopotential calculations				
8)	MCSCF($5s\sigma_g^2,5s\sigma_u^2$)	GTO;(3s,1p,5d)-(2s,1p,2d)	5.46	164	0.51
	CI	as above	5.12	226	0.95
	MCSCF($5s\sigma_g^2,5s\sigma_u^2$), relativistic	as above	5.22	222	0.61
	CI, relativistic	as above	4.95	242	1.12
9)	MCSCF($5s\sigma_g^2,5s\sigma_u^2$)	GTO;(3s,2p,5d)-(2s,2p,1d)	5.07	131	0.94
10)	HF	GTO;(8s,4p,5d)-(4s,4p,3d)	5.29	130	
	HF, relativistic	as above	5.16	145	
	Xα type calculations				
11)	Xα-SW		5.37	187	1.56
12)	Xα-LCAO	STO; valence triple zeta	5.05	184	1.73
	Xα-LCAO, relativistic	as above	4.76	203	2.04

1) Srdanov and Pešić 1981. – 2) Huber and Herzberg 1979. – 3) D_0^o, Gingerich 1980. – 4) Basch 1980a. – 5) Shim and Gingerich 1983. – 6) McLean 1983. – 7) Cingi, Clemente, and Foglia 1984. – 8) Basch 1980a. – 9) Basch 1981. – 10) Klobukowski 1983. – 11) Ozin, Huber, McIntosh, Mitchell, Norman Jr., and Noodleman 1979. – 12) Ziegler, Snijders, and Baerends 1981.

Fig. 2. Deformation density map of the Ag_2
molecule at the internuclear distance 5.20 a.u.
The superpositioned atomic charge densities ha-
ve been subtracted from the molecular charge
density as derived in CI calculations with 18
functions. Solid contours show enhanced elec-
tron charge relative to the superpositioned
atoms, dashed contours show diminished char-
ge. The smallest contour value is 0.000625
$e/a.u.^3$. Adjacent contours differ by a factor of
2.
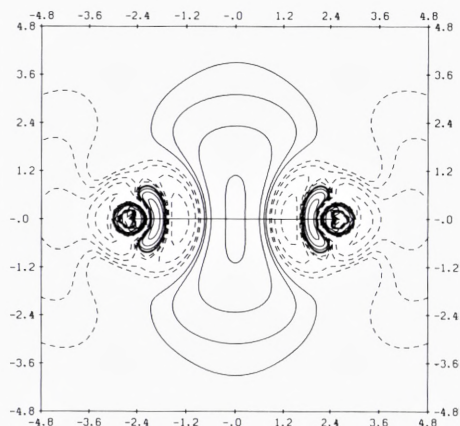
The chemical bond in the Ag_2 molecule resembles that of the Cu_2 molecule considerably. The 4d electrons tend to localize around the individual nuclei and only participate slightly in the formation of the bond. The bond is primarily due to the doubly occupied delocalized $5s\sigma_g$ molecular orbital. This is reflected in the Mulliken population analyses presented in Table VI. It is noted that the overlap population is chiefly due to the $5s\sigma_g$ molecular orbital and, as is the case for the Cu_2 molecule, hardly any hybridization occurs between the s and the d orbitals.

The CI calculations with 684 functions reveal that the major config-urations, apart from the HF configuration, originate from double excita-tions from the $5s\sigma_g$ orbital into the $5p\pi_u$ and $5s\sigma_u$ orbitals. Such config-urations are attributed to angular and left-right correlation, respectively, of the bonding $5s\sigma_g$ electrons.

Fig. 2 shows a deformation density map for the Ag_2 molecule at the internuclear distance 5.20 a.u. It is noted that the chemical bond mani-fests itself through a build up of charge in the region between the two nuclei.

Ni_2. The element just prior to Cu in the periodic system is Ni that has a ground term arising from a non-closed 3d shell. This causes considerable complications in the theoretical investigations of the dimer because it gives rise to many different possibilities for assigning symmetry and configuration of the electronic ground state of Ni_2. As a consequence fewer theoretical investigations have appeared for Ni_2 than for Cu_2 as is evident from Table VII, where we have summarized the spectroscopic constants of the Ni_2 molecule derived in the various calculations.

According to Moore's Tables 1952 the lowest lying level of the Ni atom is $^3F_4(3d)^8(4s)^2$, but after averaging over the spin–orbit components of the lowest lying terms it turns out that the average energy of the $^3D(3d)^9(4s)^1$ term is slightly below that of the $^3F(3d)^8(4s)^2$ term. In our previous work, Shim et al. 1979, we have shown that interaction between two Ni atoms in the $^3F(3d)^8(4s)^2$ term is repulsive, while two Ni atoms interacting in the $^3D(3d)^9(4s)^1$ term results in formation of a stable molecule. The chemical bond in Ni_2 proved to be primarily due to the delocalized doubly occupied $4s\sigma_g$ molecular orbital. The 3d electrons localize around the individual nuclei giving rise to a hole in the 3d shell of each atom. The hole can be in an orbital of either σ, π, or δ symmetry, and the low–lying electronic states of Ni_2 can be characterized by the symmetry of the holes.

The results presented below have been derived in a new investigation of the Ni_2 molecule. The new results confirm our earlier work as to the description of the chemical bond and also regarding the existence of a

Table VI. Mulliken population analyses of the valence orbitals of the Ag_2 molecule as derived in CI calculations with 18 functions at the internuclear distance 5.20 a.u.

Orbital	Overlap population	Orbital analyses			Occupation
		s	p	d	number
$5s\sigma_g$	0.66	0.93	0.04	0.00	1.95
$4d\sigma_g$	0.10	0.00	0.00	1.00	2.00
$4d\pi_u$	0.09	0.00	0.00	2.00	4.00
$4d\delta_g$	0.01	0.00	0.00	2.00	4.00
$4d\delta_u$	-0.01	0.00	0.00	2.00	4.00
$4d\pi_g$	-0.07	0.00	0.01	1.99	4.00
$4d\sigma_u$	-0.08	0.01	0.01	0.98	2.00
$5s\sigma_u$	-0.05	0.02	0.00	0.00	0.05

Table VII. Experimental and calculated spectroscopic constants of the Ni_2 molecule

Method	Basis set Type; primitive-contracted	State	Spectroscopic constants r_e(a.u.)	ω_e(cm^{-1})	D_e(eV)
Experimental			4.16[3]	380.9[2]	2.38[1]
All electron ab initio calculations					
[4] CI(252×252)	GTO; (14s,11p,5d)-(8s,6p,3d)	$^1\Sigma_g^+(\delta\delta)$	4.15	289	1.76
[5] CI	GTO;(12s,6p,4d)-(5s,2p,1d)	$^1\Gamma_g(\delta\delta)$	4.46		0.52
[6] Restricted HF	GTO;(14s,11p,5d)-(8s,6p,2d)	$^1\Sigma_g^+$	4.31	240	
[7] CI (252×252)	GTO;(14s,11p,6d)-(8s,6p,3d)	$^1\Sigma_g^+(\delta\delta)$	4.68	185	0.95
CI (3219×3219)	as above	$^1\Sigma_g^+(\delta\delta)$	4.67	186	
Pseudopotential calculations					
[8] CI (GVB)	GTO;(4s,4p,5d)-(3s,2p,2d)	$^1\Gamma_g(\delta\delta)$	3.86	344	2.93
[9] CI	GTO;(4s,2p,5d)-(4s,2p,2d)		4.27		1.88
Xα type calculations					
[10] Local spin density		$^3\Sigma_g^-$	4.12	320	2.70
[11] Xα-LCAO	GTO;(14s,10p,6d,1f)	$^3\Pi_u$	3.84	356	2.91

1) D_0^o from Kant 1964. – 2) Ahmed and Nixon 1979. – 3) Morse, Hansen, Langridge-Smith, Zheng, Geusic, Michalopoulos, and Smalley 1984. – 4) Shim, Dahl, and Johansen 1979. – 5) Wood, Doran, Hillier, and Guest 1980. – 6) Wolf and Smidtke 1980. – 7) Present work. – 8) Upton and Goddard 1978. – 9) Noell, Newton, Hay, Martin, and Bobrowicz 1980. – 10) Harris and Jones 1979. – 11) Dunlap and Yu 1980.

»band« consisting of 30 low-lying electronic states, but some of the states in the middle of the »band« have been reversed. The calculated spectroscopic constants deviate from those of our previous work. This is not surprising since the spectroscopic constants are very sensitive to the calculational details as has been noted for Cu_2.

In connection with the present work we have added a diffuse d function to the basis set of the Ni atom, and we have also carried out a counterpoise correction analysis as suggested by Kolos 1979. This has shown that basis set superposition errors are negligible in the present investigation.

HF calculations on Ni_2 at the internuclear distance 4.709 a.u. showed that states with holes in localized σ, π, or δ orbitals of each of the two atoms all have energies below the sum of the separated atoms. In the molecular orbital picture these states are arising from holes in the orbital

pairs $3d\sigma_g, 3d\sigma_u$ or $3d\pi_u, 3d\pi_g$ or $3d\delta_g, 3d\delta_u$, respectively. We have utilized the molecular orbitals from the three above-mentioned configurations in CI calculations to describe all the low-lying electronic states of the Ni_2 molecule. It turned out that the inclusion of the diffuse d function in the basis set caused the sequence of the low-lying electronic states resulting from the CI calculations to be dependent on the state chosen for optimization of the molecular orbitals. However, the CI calculations based on the molecular orbitals optimized for the $(\delta\delta)$ hole state gave rise to the lowest total energies, and therefore we report only the results of these calculations.

Figs. 3 and 4 show results of CI calculations allowing full reorganization within the 3d and 4s shells. In Fig. 3 the 30 low-lying electronic states of the Ni_2 molecule are depicted at the nearest neighbour internuclear distance in bulk Ni, 4.709 a.u. Table VIII reveals the 3d shell configurations of the low-lying states. It is noted that the 6 lowest lying states all have a hole in the $3d\delta$ subshell of each of the two atoms. After that follows 8 states with a hole in the $3d\delta$ orbital of one atom and in the $3d\pi$ orbital of the other atom. Thereafter 4 states with holes in the $3d\delta$ and in $3d\sigma$ orbitals of the two atoms, respectively. Then 6 $(\pi\pi)$ hole states followed by 4 $(\pi\sigma)$ hole states, and finally at the highest energies the 2 $(\sigma\sigma)$ hole states. From Table VIII it is also seen that mixing of states originating from holes with different symmetries is negligible. Fig. 4 shows the potential energy curves obtained by fitting the calculated points of the

Table VIII. Energy ranges and the d shell configuration for low-lying states of Ni_2 at the internuclear distance 4.709 a.u.

Energy range (eV)		States	d shell population		
			σ	π	δ
0.000	- 0.012	$^1\Sigma_g^+, {}^1\Gamma_g, {}^1\Sigma_u^-, {}^3\Sigma_g^-, {}^3\Sigma_u^+, {}^3\Gamma_u$	4.00	8.00	6.00
0.176	- 0.203	$^3\phi_u, {}^1\Pi_u, {}^1\phi_g, {}^3\Pi_u, {}^1\Pi_g, {}^1\phi_u, {}^3\Pi_g, {}^3\phi_g$	4.00	7.00	7.00
0.241	- 0.261	$^1\Delta_g, {}^3\Delta_g, {}^1\Delta_u, {}^3\Delta_u$	3.00	8.00	7.00
0.350	- 0.418	$^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+, {}^1\Sigma_u^-, {}^3\Delta_u, {}^3\Sigma_u^+$	4.00	6.00	8.00
0.424	- 0.492	$^3\Pi_u, {}^1\Pi_u, {}^1\Pi_g, {}^3\Pi_g$	3.00	7.00	8.00
0.513	- 0.576	$^1\Sigma_g^+, {}^3\Sigma_u^+$	2.00	8.00	6.00

Fig. 3. Relative energies in eV of the 30 low-lying states of the Ni_2 molecule at the internuclear distance 4.709 a.u. States are listed in order of increasing energy.
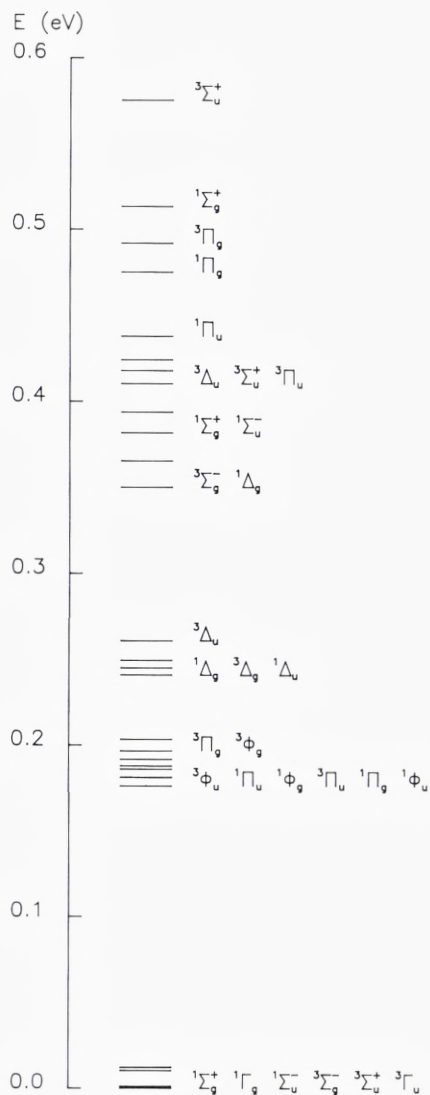
potential energies to Morse curves. It is noted that the shapes of the potential energy curves are very similar although the equilibrium distances increase slightly and the vibrational frequencies decrease for the higher lying states.

In Table IX we present the Mulliken population analyses of the valence orbitals of Ni_2. The total overlap population is almost entirely due to the $4s\sigma_g$ molecular orbital. The 3d electrons are practically non bonding, and analogous with the Cu_2 molecule hardly any mixing of the 3d and the 4s orbitals occurs.

Table IX. Mulliken population analyses of the valence orbitals for the $^1\Sigma_g^+$ ground state of the Ni_2 molecule resulting from CI calculations with 252 functions at the internuclear distance 4.709 a.u.

Orbital	Overlap population	Orbital analyses			Occupation number
		s	p	d	
$4s\sigma_g$	0.70	0.93	0.04	0.00	1.94
$3d\sigma_g$	0.06	0.00	0.00	1.00	2.00
$3d\pi_u$	0.12	0.00	0.00	2.00	4.00
$3d\delta_g$	0.02	0.00	0.00	1.51	3.01
$3d\delta_u$	-0.02	0.00	0.00	1.49	2.98
$3d\pi_g$	-0.11	0.00	0.00	2.00	4.00
$3d\sigma_u$	-0.05	0.01	0.00	0.99	2.00
$4s\sigma_u$	-0.04	0.02	0.00	0.00	0.06
Total	0.68	6.96	12.05	8.98	

A picture of the bonding interaction between two Ni atoms emerges from the calculational results: As the two atoms approach each other an axial symmetry is introduced, and this causes the 3d orbitals to split into σ, π, and δ orbitals associated with different energies. One should expect that the holes in the 3d shells of the Ni atoms would reside in the 3dσ subshells, because this should give rise to the formation of a 3dσ bond at closer approach. However, it turns out that the system is more stable when the holes are localized in the 3dδ subshells. This indicates that each atom experiences the other as a positive unit, and therefore the Ni_2 molecule can be regarded as two Ni^+ ions kept together by the de-localized charge cloud originating from the 4s electrons. The 3d electrons localize around the nuclei, and their interaction can be interpreted as a Heisenberg exchange coupling as discussed by Shim 1980a. The interaction between the 3d electrons gives rise to the small energy split-tings between the many low lying potential energy curves. The $^1\Sigma_g^+$

Fig. 4. Potential energy curves of the low-lying electronic states of the Ni_2 molecule as derived in CI calculations.
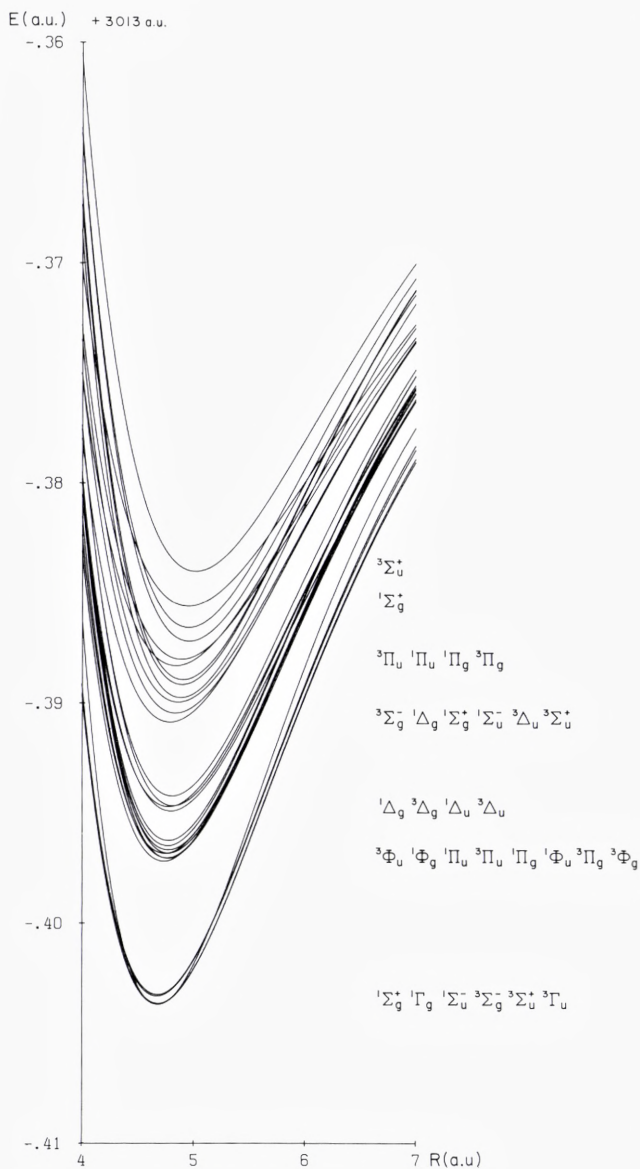
ground state of the Ni_2 molecule has the natural orbital configuration $(3d\sigma_u)^{2.00}(3d\pi_u)^{4.00}(3d\delta_g)^{3.01}(3d\delta_u)^{2.98}(3d\pi_g)^{4.00}(3d\sigma_g)^{2.00}(4s\sigma_g)^{1.94}$ $(4s\sigma_u)^{0.06}$ at the internuclear distance 4.709 a.u.

The $^1\Sigma_g^+$ ground state of the Ni_2 molecule has been investigated further by performing CI calculations which included all single and double excitations into the $4p\sigma_g$, $5s\sigma_g$ and $4p\pi_u$ orbitals from the $4s\sigma_g$ orbital and

Table X.   Major configurations of the wave functions decribing the $^1\Sigma_g^+$ ground state of the
Ni$_2$ molecule at the internuclear distance 4.709 a.u.

Configuration											Contribution (%) in CI with	
											252	3219
$4s\sigma_g$	$4s\sigma_u$	$3d\sigma_g$	$3d\pi_u$	$3d\delta_g$	$3d\delta_u$	$3d\pi_g$	$3d\sigma_u$	$4p\sigma_g$	$4p\pi_u$	$5s\sigma_g$	configurations	
2	0	2	4	4	2	4	2	0	0	0	49.19	47.92
2	0	2	4	2	4	4	2	0	0	0	47.43	46.07
0	2	2	4	4	2	4	2	0	0	0	1.16	0.72
0	2	2	4	2	4	4	2	0	0	0	1.13	0.70
1	1	2	4	3	3	4	2	0	0	0	0.95	0.59
0	0	2	4	4	2	4	2	0	2	0	-	1.36
0	0	2	4	2	4	4	2	0	2	0	-	1.31

from the 3d shells of the 12 functions having the $4s\sigma_g$ orbital doubly occupied and allowing all rearrangements within the 3d shells. This resulted in a CI matrix of dimension 3219.

In Table X we present the major configurations of the wave functions for the $^1\Sigma_g^+$ ground state of Ni$_2$ as derived in CI calculations at the internuclear distance 4.709 a.u. The two dominating configurations in both calculations account for the localization of the holes in the $3d\delta$ subshells of each atom. This is evident when noting that the two configurations have approximately equal weight and in one configuration the $3d\delta_g$ orbitals are fully occupied while the $3d\delta_u$ orbitals are fully occupied in the other. The two configurations contributing slightly more than 1% in the smaller calculation introduces left-right correlation of the bonding $4s\sigma_g$ electrons. In the larger calculation the angular correlation of the $4s\sigma_g$ electrons is introduced through the configurations derived from double excitations from the $4s\sigma_g$ to the $4p\pi_u$ orbitals. It is noted that the configurations accounting for the angular correlation of the $4s\sigma_g$ electrons contribute more to the wave function than those accounting for the left-right correlation. This is analogous with our findings for the molecules Cu$_2$ and Ag$_2$.

Since the electronic states of the Ni$_2$ molecule are very closely spaced it is evident that spin-orbit coupling might cause considerable mixing of the states. Consequently we have undertaken a study of this effect based on the perturbational Hamiltonian $H^1 = \sum_i \xi(r_i)\, \mathbf{l}_i \cdot \mathbf{s}_i$. The method employed for treating the spin-orbit coupling in the Ni$_2$ molecule is analogous to that used in our previous work concerning the NiCu molecule, Shim

1980b. We have applied the following approximations: The overlap integrals between 3d orbitals centered at different nuclei have been neglected, since the 3d orbitals are well localized. We have also utilized that hybridization between the 3d, 4s, and 4p orbitals is negligible. Finally, we have assumed that the radial integrals $\xi(r_i)$ arising when evaluating the matrix elements of the spin-orbit coupling operator are all equal, and the value of 603 cm^{-1} for the appropriate radial integral has been taken from work by Laporte and Inglis 1930.

The energies of the LS states have been added to the appropriate diagonal elements of the matrices representing the spin-orbit coupling for each value of Ω, and the spin-orbit coupled states have been derived by diagonalization of the matrices.

As anticipated the spin-orbit coupling causes the low-lying electronic states to mix considerably resulting in a spreading of the »band« of low-lying electronic states. At the internuclear distance 4.709 a.u. all the low-lying states without considering spin-orbit coupling are found in an energy range of app. 0.58 eV. When spin-orbit coupling is taken into account the states cover an energy range of app. 0.84 eV.

Fig. 5 shows the potential energy curves for the spin-orbit coupled states derived by fitting the calculated points of the potential energies to Morse curves. The three lowest lying states in order of increasing energy are 0_g^+, 0_u^- and 5_u. These states are all characterized as having holes in the 3dδ subshells of the two atoms. The higher lying states gradually mix in states originating from different hole symmetries and they can, therefore, not be described by the symmetries of the holes in a simple manner. The spin-orbit coupling does not change the description of the chemical bond in Ni_2. This is not surprising since the effect as treated in the present investigation is basicly atomic.

Table VII reveals that the spectroscopic constants of the Ni_2 molecule derived in our work from 1979 are considerably closer to the experimental values than those derived in our present investigation. This is at least partly due to the basis set superposition errors, which apparently compensate for other deficiencies in our ealier work. The general trends in the calculated spectroscopic constants of the Ni_2 molecule coincide with those of the Cu_2 molecule, that is, the agreement between the calculated and the experimental spectroscopic constants becomes worse as the calculations get more elaborate. The calculated equilibrium distances become too long and the vibrational frequencies too low. Furthermore, only a fraction of the dissociation energy is accounted for.

More important, however, Morse et al. 1984 have recently found the

first experimental evidence in support of the characteristic features of the electronic structures of the transition metal dimers, namely the existence of the many low-lying electronic states. In their spectroscopic studies of the Ni_2 molecule they have found a much higher density of spectroscopic transitions than is usual in a diatomic molecule, and this is considered as confirmation of the large number of low-lying electronic states.

Pd_2. Both experimental and theoretical investigations are very scarce for the Pd_2 molecule. Besides the high temperature mass spectrometric investigations by Gingerich 1967, by Lin et al. 1969a, and by Shim and Gingerich 1984, only matrix isolation study has been reported by Klotzbücher et al. 1980b. These authors claim to have observed the Pd_2 molecule in an Ar matrix, but no spectral assignment whatsoever could be derived from their observations. Previous ab initio studies concerning the Pd_2 molecule are limited to two pseudopotential calculations. Garcia – Prieto et al. 1980 dealt especially with the basis set superposition errors, while Basch et al. 1980b have performed MCSCF calculations for a few of the low-lying states.

The ground term of the Pd atom is the closed shell $^1S(4d)^{10}$ term. In accordance with our expectations the interaction between two Pd atoms in their ground term does not lead to the formation of a stable molecule. However, it has been necessary to carry out a counterpoise correction analysis of our HF results to verify this, Shim and Gingerich 1984.

Formation of a chemical bond between two Pd atoms occurs, when the atoms interact in the $^3D(4d)^9(5s)^1$ term. The interaction between the Pd atoms is very similar to that of the Ni atoms. When the Pd atoms approach each other the 4d orbitals split into σ, π, and δ orbitals with different energies. The split orbitals exchange couple, and this gives rise to the small splittings between the 30 low-lying potential energy curves. At the internuclear distance 5.19788 a.u. which is the nearest neighbour internuclear distance in bulk Pd, the 30 low-lying electronic states cover an energy range of only 0.37 eV as shown in Fig. 6. The 4d electrons localize around the nuclei, and the chemical bond in the Pd_2 molecule is primarily due to the delocalized $5s\sigma_g$ molecular orbital.

Analogous to the electronic structure of Ni_2, the 6 lowest lying states of Pd_2 all have a hole in the $4d\delta$ subshell of each atom. States arising from holes in the $4d\pi$ subshells are found at higher energies, and the highest lying states originate from holes in the $4d\sigma$ subshells. The ground state of the Pd_2 molecule is a $^1\Sigma_g^+$ state, and it has the natural orbital

configuration $(4d\sigma_g)^{2.00}$ $(4d\pi_u)^{4.00}$ $(4d\delta_g)^{3.03}$ $(4d\delta_u)^{2.98}$ $(4d\pi_g)^{3.99}$ $(4d\sigma_u)^{2.00}$ $(5s\sigma_g)^{1.93}$ $(5s\sigma_u)^{0.07}$ at the internuclear distance 5.19788 a.u.

The calculated equilibrium distance and vibrational frequency for the Pd_2 molecule in its $^1\Sigma_g^+$ ground state is 5.30 a.u. and 132 cm^{-1}, respectively. Correction for basis set superposition errors causes the equilibrium distance to increase to 5.49 a.u. and the vibrational frequency to decrease to 104 cm^{-1}.

The calculated equilibrium distance is too long, and on basis of our results for the transition metal dimers Cu_2, Ni_2, and Ag_2 we estimate the true equilibrium distance of Pd_2 to be app. 4.7 a.u. Half of the bond contraction, that is app. 0.3 a.u., will presumably arise from relativistic effects while the other half is attributable to correlation. The magnitude of the relativistic bond contraction is estimated on basis of the relativistic contractions of the 5s orbitals in the second row transition metal series as determined by Desclaux 1973. Ziegler et al. 1981 and Pyykkö et al. 1981 have shown that the relativistic bond contraction is a first order effect and consequently not a result of the orbital contraction. However, the calculational works by Ziegler 1981 on Ag_2 and by McLean 1983 on AgH indicate that the known orbital contractions offer a reasonable measure of the bond contractions.

It is not possible to give a reliable estimate of the true vibrational frequency of the Pd_2 molecule from our calculated value. This is due to the fact that counteracting effects have to be considered. Thus, our calculated vibrational frequency is too low for a Pd_2 molecule dissociating into two Pd atoms in the $^3D(4d)^9(5s)^1$ term, but a real Pd_2 molecule will dissociate into two atoms in the $^1S(4d)^{10}$ ground term, and this will lower the vibrational frequency.

The calculated dissociation energy of Pd_2 is 1.18 eV relative to two Pd atoms in the $^3D(4d)^9(5s)^1$ term, and this value is reduced to 0.93 eV when the basis set superposition errors are taken into account. When the experimental energy splitting between the $^3D(4d)^9(5s)^1$ term and the $^1S(4d)^{10}$ ground term is considered, it turns out that the Pd_2 molecule in our description is unbound by 0.72 eV or 0.97 eV excluding and including corrections for basis set superposition errors, respectively. However, in view of our results for the molecules Cu_2 and Ag_2 we can only expect to account for about half of the dissociation energy of Pd_2 relative to two Pd atoms in the $^3D(4d)^9(5s)^1$ term in our present work. Therefore, it seems likely that more extensive CI calculations based on our sets of molecular orbitals would cause the Pd_2 molecule to be bound relative to two Pd atoms in their $^1S(4d)^{10}$ ground term.
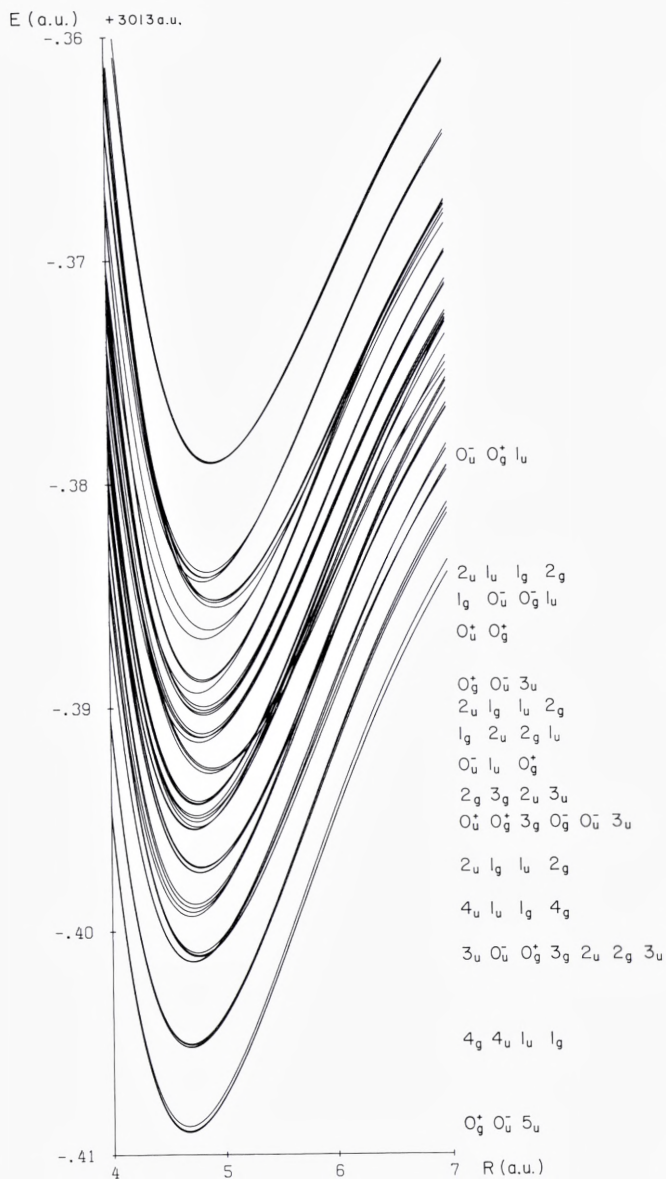
E (a.u.)   +3013 a.u.

Fig. 5. Potential energy curves of the low-lying electronic states of the Ni_2 molecule taking into account the effect of spin-orbit coupling.
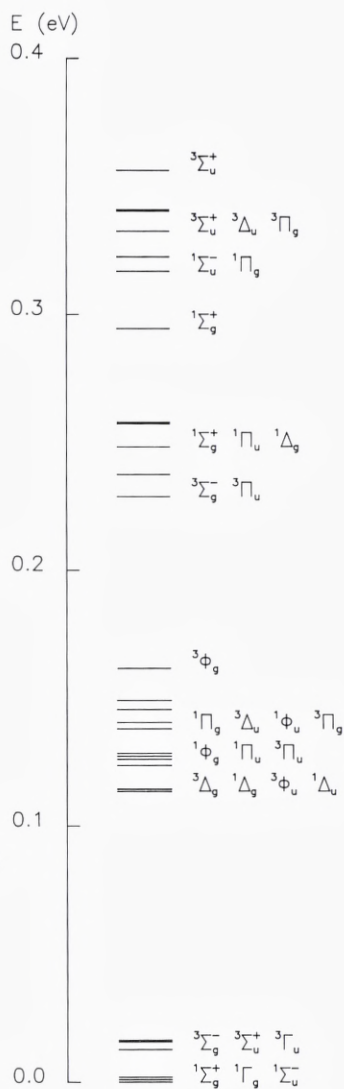
Fig. 6. Relative energies in eV of the 30 low-lying electronic states of the Pd_2 molecule at the internuclear distance 5.19788 a.u. States are listed in order of increasing energy.

In the light of the fact that the more elaborate calculations for the molecules Cu_2 and Ag_2 have not changed the qualitative description of the bonding in these molecules, we believe that our calculations on Pd_2 in general offer an appropriate description of the electronic structure and of the chemical bond in this molecule.

Finally, we have considered the effect of spin–orbit coupling on the low-lying electronic states by applying the same approximations as those described above for the Ni_2 molecule. The »band« of low-lying states is, however, more narrow for Pd_2 than for Ni_2, and the atomic spin–orbit coupling constant is 1412 cm^{-1} for Pd, Laporte and Inglis 1930, relative to 603 cm^{-1} for Ni. Therefore the spin–orbit coupling causes considerable more spreading of the low-lying electronic states for Pd_2 than for Ni_2. At the internuclear distance 5.19788 a.u. the energy range of the »band« of low-lying states changes from app. 0.37 eV to app. 1.17 eV due to spin–orbit coupling. The three lowest lying states in order of increasing energy are 0_g^+, 5_u, 0_u^-, and these states are all characterized by a hole in the $3d\delta$ subshell of each of the Pd atoms. The 0_g^+ and the 0_u^- states consist both of app. equal amounts of the $^1\Sigma_g^+$ and the $^3\Sigma_g^-$ ($\delta\delta$) hole states, while the 5_u state is a pure $^3\Gamma_{u5}$ state. The higher lying states mix considerably and cannot be described by the symmetry of the holes in a simple manner. The spin–orbit coupling as treated in our work is of atomic nature, and it therefore does not change the description of the chemical bond in the Pd_2 molecule.

Co_2. The Co_2 molecule has been observed by Kant and Strauss 1964 in their high temperature mass spectrometric studies. The only experimental data available for Co_2 are the dissociation energy derived by Kant and Strauss 1964 and a vibrational frequency that has been determined in a matrix isolation investigation as quoted by DiLella et al. 1982.

Prior to our theoretical work, Shim and Gingerich 1983b, Harris and Jones 1979 have investigated the Co_2 molecule using a local spin density method. They predicted a $^5\Delta_g$ ground state with the configuration $(3d\sigma_g)^2(3d\pi_u)^4(3d\delta_g)^4(3d\delta_u)^3(3d\pi_g)^2(3d\sigma_u)^1(4s\sigma_g)^2$. They derived the equilibrium distance of the $^5\Delta_g$ state as 3.92 a.u., the vibrational frequency as 360 cm^{-1}, and the dissociation energy as 3.35 eV.

According to Moore's Tables 1952 the ground term of the Co atom is $^4F(3d)^7(4s)^2$. In light of the repulsive interaction between two Ni atoms in the $^3F(3d)^8(4s)^2$ term we presumed that two Co atoms in their ground term also will interact repulsively. However, the Co atom has a

$^4F(3d)^8(4s)^1$ term 0.42 eV above the ground term, and this gives rise to the bonding interaction between the two Co atoms.

Due to the additional hole in the 3d shell of atomic Co relative to Ni it is considerably more difficult to determine the electronic ground state of the Co_2 molecule than of the Ni_2 molecule. As a first attempt we performed HF calculations on the $^5\Delta_g$ state which Harris and Jones have predicted to be the ground state of the Co_2 molecule. Our results have revealed that this state is unbound by app. 0.5 a.u. in the HF approximation.

Of all the configurations we tried out in HF calculations only two had energies below the sum of the energies of the separated atoms. These are $(3d\sigma_g)^1 (3d\pi_u)^4 (3d\delta_g)^3 (3d\delta_u)^3 (3d\pi_g)^4 (3d\sigma_u)^1 (4s\sigma_g)^2$ and $(3d\sigma_g)^2 (3d\pi_u)^3$ $(3d\delta_g)^3 (3d\delta_u)^3 (3d\pi_g)^3 (3d\sigma_u)^2 (4s\sigma_g)^2$, respectively. Orbitals from both of these configurations have been utilized in CI calculations to describe all low-lying electronic states, but the latter configuration gave rise to the lowest total energies, and only the results based on this configuration are reported.

The molecular orbitals have been utilized in CI calculations that allowed full reorganization within the 3d shells. This insures that the d orbital part of the wave function is described correctly in the dissociation limit. The $4s\sigma_g$ orbital was kept doubly occupied and therefore the total wave functions do not behave correctly in the dissociation limit. This should, however, be of minor importance for the relative energies of the low-lying states at internuclear distances close to the equilibrium distance of the molecule.

Fig. 7 shows all the 84 low-lying electronic states resulting from CI calculations at the internuclear distance 4.72 a.u. The 9 lowest lying states all have holes in orbital pairs $3d\delta$, $3d\pi$ of each of the two atoms. In the 9 highest lying states the holes are in the $3d\delta$ and in the $3d\sigma$ subshells of each of the two atoms, respectively. Most of the remaining states cannot be described by the symmetry of the holes in a simple manner. The interaction between two Co atoms is of a similar nature as the interaction between two Ni atoms. Thus, the chemical bond in Co_2 is mainly due to the delocalized doubly occupied $4s\sigma_g$ molecular orbital. At the internuclear distance 4.72 a.u. the populations in the bonding and in the antibonding 3d orbitals are approximately equal. This indicates that the 3d electrons hardly participate in the bonding, but localize around the nuclei. The interaction between the 3d electrons of the two Co atoms occurs as a Heisenberg exchange coupling resulting in the small energy splittings between the 84 low-lying potential energy curves. Thus, of the 9 lowest lying states all with holes in the orbital pairs $3d\delta$, $3d\pi$ of each
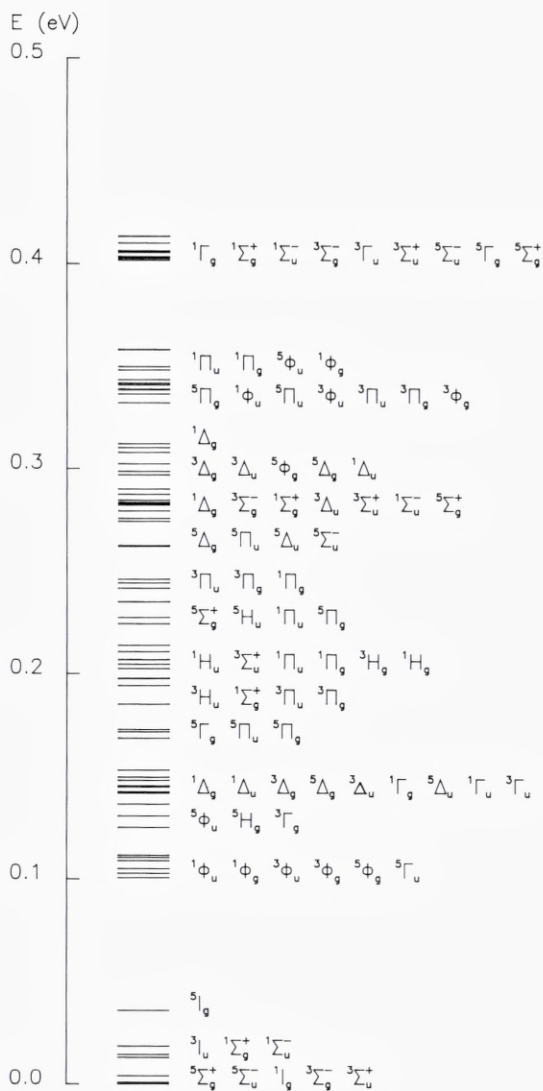
Left diagram (Fig. 7):

E (eV)

- 0.5
- 0.4 — $^1\Gamma_g$ $^1\Sigma_g^+$ $^1\Sigma_u^-$ $^3\Sigma_g^-$ $^3\Gamma_u$ $^3\Sigma_u^+$ $^5\Sigma_u^-$ $^5\Gamma_g$ $^5\Sigma_g^+$
- $^1\Pi_u$ $^1\Pi_g$ $^5\Phi_u$ $^1\Phi_g$
- $^5\Pi_g$ $^1\Phi_u$ $^5\Pi_u$ $^3\Phi_u$ $^3\Pi_u$ $^3\Pi_g$ $^3\Phi_g$
- $^1\Delta_g$
- 0.3 — $^3\Delta_g$ $^3\Delta_u$ $^5\Phi_g$ $^5\Delta_g$ $^1\Delta_u$
- $^1\Delta_g$ $^3\Sigma_g^-$ $^1\Sigma_g^+$ $^3\Delta_u$ $^3\Sigma_u^+$ $^1\Sigma_u^-$ $^5\Sigma_g^+$
- $^5\Delta_g$ $^5\Pi_u$ $^5\Delta_u$ $^5\Sigma_u^-$
- $^3\Pi_u$ $^3\Pi_g$ $^1\Pi_g$
- $^5\Sigma_g^+$ ^5H_u $^1\Pi_u$ $^5\Pi_g$
- 0.2 — ^1H_u $^3\Sigma_u^+$ $^1\Pi_u$ $^1\Pi_g$ ^3H_g ^1H_g
- ^3H_u $^1\Sigma_g^+$ $^3\Pi_u$ $^3\Pi_g$
- $^5\Gamma_g$ $^5\Pi_u$ $^5\Pi_g$
- $^1\Delta_g$ $^1\Delta_u$ $^3\Delta_g$ $^5\Delta_g$ $^3\Delta_u$ $^1\Gamma_g$ $^5\Delta_u$ $^1\Gamma_u$ $^3\Gamma_u$
- $^5\Phi_u$ ^5H_g $^3\Gamma_g$
- 0.1 — $^1\Phi_u$ $^1\Phi_g$ $^3\Phi_u$ $^3\Phi_g$ $^5\Phi_g$ $^5\Gamma_u$
- ^5I_g
- ^3I_u $^1\Sigma_g^+$ $^1\Sigma_u^-$
- 0.0 — $^5\Sigma_g^+$ $^5\Sigma_u^-$ ^1I_g $^3\Sigma_g^-$ $^3\Sigma_u^+$

Fig. 7. Relative energies in eV of the 84 low-lying electronic states of the Co_2 molecule at the internuclear distance 4.72 a.u. States are listed in order of increasing energy.

Right diagram (Fig. 8):

E (eV)

- 0.5 — $^5\Sigma_u^-$ $^5\Delta_g$ $^5\Gamma_g$ $^5\Sigma_g^+$
- 0.4 — $^5\Phi_u$
- $^5\Pi_g$ $^3\Sigma_g^-$ $^3\Gamma_u$ $^3\Sigma_u^+$ $^5\Pi_u$
- $^1\Phi_g$
- $^1\Pi_u$ $^1\Gamma_g$ $^1\Pi_g$ $^1\Sigma_g^+$ $^1\Sigma_u^-$
- $^5\Pi_u$ $^3\Pi_u$ $^3\Pi_g$ $^1\Delta_g$ $^3\Phi_g$ $^5\Sigma_g^+$
- 0.3 — ^5H_u $^3\Phi_u$ $^1\Delta_u$
- $^1\Sigma_u^-$ $^3\Sigma_u^+$ $^5\Sigma_g^+$ $^1\Phi_u$ $^3\Delta_u$ $^5\Sigma_u^-$
- $^1\Sigma_g^+$ $^5\Delta_u$ $^5\Delta_g$ $^3\Sigma_g^-$ $^3\Delta_u$ $^3\Delta_g$
- ^1H_g $^1\Delta_g$ $^1\Pi_g$ $^3\Pi_g$
- $^5\Gamma_g$ $^5\Pi_g$ $^3\Pi_u$ $^5\Phi_g$
- ^3H_g $^1\Pi_u$ $^3\Sigma_u^+$
- $^1\Pi_g$
- 0.2 — $^5\Phi_u$ $^3\Pi_u$ $^3\Pi_g$ $^1\Sigma_g^+$ $^1\Pi_u$
- $^1\Gamma_u$ $^3\Gamma_u$ ^1H_u
- $^5\Phi_g$ $^3\Delta_g$ $^3\Delta_u$ ^3H_u
- $^3\Gamma_g$ $^3\Phi_g$ $^1\Delta_g$ $^1\Delta_u$ $^5\Delta_u$ $^1\Gamma_g$
- $^1\Phi_g$ $^3\Phi_u$
- 0.1 — $^5\Pi_u$ $^5\Delta_g$ $^5\Pi_g$ $^1\Phi_u$ ^5I_g
- $^5\Gamma_u$
- $^1\Sigma_u^-$
- $^1\Sigma_g^+$ $^3\Sigma_g^-$ $^3\Sigma_u^+$ ^3I_u
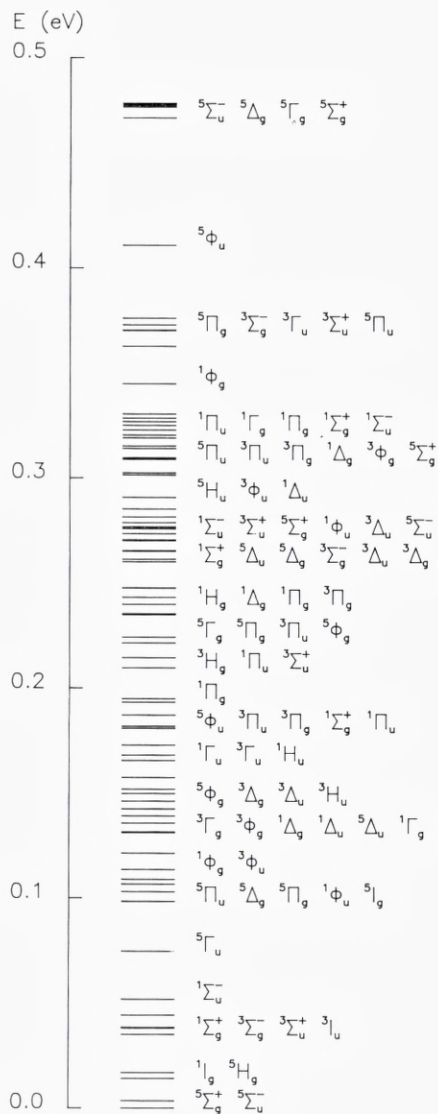- ^1I_g ^5H_g
- 0.0 — $^5\Sigma_g^+$ $^5\Sigma_u^-$

Fig. 8. Relative energies in eV of the 84 low-lying electronic states of the Rh_2 molecule at the internuclear distance 5.082 a.u. States are listed in order of increasing energy.

atom, the Σ states are ferromagnetic coupled while the I states are antiferromagnetic coupled. The exchange coupling constant for the Σ states is 23 cm^{-1} and that for the I states is -43 cm^{-1} at the internuclear distance 4.72 a.u. The 9 highest lying states arising from holes in the orbital pairs $3d\delta$, $3d\sigma$ of each atom are all antiferromagnetic coupled. The exchange coupling constants are -15 cm^{-1} for the Σ^+ states, -8 cm^{-1} for the Σ^- states, and -16 cm^{-1} for the Γ states, respectively.

The spin-orbit coupling which has not been considered for the Co_2 molecule would cause considerable mixing of the low-lying states, but as for Ni_2 and Pd_2 it would not alter the description of the chemical bond.

The $^5\Sigma_g^+$ ground state of Co_2 has been investigated further by performing CI calculations that allowed full reorganization within both the 3d and the 4s shells. The natural orbital configuration of the $^5\Sigma_g^+$ ground state determined in these calculations is $(3d\sigma_g)^{2.00}$ $(3d\pi_u)^{3.09}$ $(3d\delta_g)^{3.02}$ $(3d\delta_u)^{2.98}$ $(3d\pi_g)^{2.91}$ $(3d\sigma_u)^{2.00}$ $(4s\sigma_g)^{1.94}$ $(4s\sigma_u)^{0.06}$ at the internuclear distance 4.72 a.u.

The calculated points of the potential energies for the $^5\Sigma_g^+$ ground state of Co_2 have been fitted to a Morse curve from which we have derived the equilibrium distance as 4.84 a.u. and the vibrational frequency as 162 cm^{-1}. The calculated equilibrium distance is presumably too long by 0.4–0.5 a.u. as is the case for Cu_2 and Ni_2 in equivalent calculations. The calculated vibrational frequency is considerably lower than the experimental value of 290 cm^{-1} quoted by DiLella et al. 1982.

In the present description the dissociation energy relative to two Co atoms in the $^4F(3d)^8(4s)^1$ term is 0.81 eV. but relative to two Co atoms in their $^4F(3d)^7(4s)^2$ ground term the Co_2 molecule is unbound by app. 0.02 eV. However, in the light of our experience with the Cu_2 molecule we are confident that larger CI calculations based on our sets of molecular orbitals would result in a bound Co_2 molecule relative to the atoms in their ground term. Furthermore, it is unlikely that such additional calculations, which would demand considerable resources, would give rise to any significant change in the description of the chemical bond or in the picture of the many low-lying electronic states.

Rh₂. The only experimental investigations of the Rh_2 molecule known are the high temperature mass spectrometric measurements by Gingerich and Cocke 1972, Cocke and Gingerich 1974, and by Piacente et al. 1974. The present work constitutes the first theoretical investigation of the Rh_2 molecule.

According to Moore's Tables 1952 the ground term of the Rh atom is

$^4F(4d)^8(5s)^1$, and therefore no ambiguity arises as to which term gives rise to a bonding interaction. Two Rh atoms interacting in their ground term will lead to the formation of a stable molecule.

In search for a state that would be able to describe a bound molecule, we have performed HF calculations for many different configurations at the internuclear distance 5.082 a.u. which is the nearest neighbour distance in bulk Rh. Only one of the configurations we tried out, namely $(4d\sigma_g)^2(4d\pi_u)^3(4d\delta_g)^3(4d\delta_u)^3(4d\pi_g)^3(4d\sigma_u)^2(5s\sigma_g)^2$ was associated with an energy below the sum of the energies of the separated atoms. It is noted that this configuration is equivalent with the configuration used for optimization of the molecular orbitals for the Co_2 molecule.

The molecular orbitals optimized for the above-mentioned configuration have been utilized in CI calculations to describe all the low-lying states of the Rh_2 molecule. The CI calculations performed are equivalent to those performed for the Co_2 molecule, that is, full reorganization within the 4d shells is allowed, but the $5s\sigma_g$ orbital has been kept fully occupied. In Fig. 8 we show the energies of the 84 low-lying states at the internuclear distance 5.082 a.u.

The 3 lowest lying states $^5\Sigma_g^+$, $^5\Sigma_u^-$, ^1I_g have holes in the orbital pairs $4d\pi$, $4d\delta$ of each of the Rh atoms, and thus they are equivalent to the 3 lowest lying states of the Co_2 molecule. However, contrary to our findings for Co_2 the lowest lying electronic states of the Rh_2 molecule cannot be described as simple Heisenberg exchange couplings. This is clearly recognized from the fact that the energy of the lowest lying $^1\Sigma_g^+$ state is in between those of the lowest lying $^5\Sigma_g^+$ and $^3\Sigma_u^+$ states.

The $^5\Sigma_g^+$ ground state of Rh_2 has been investigated further in CI calculations allowing full reorganization within the 4d as well as the 5s shells. This gave rise to CI matrices of dimension 1084. In an additional set of CI calculations also excitations from the $5s\sigma_g$ into the $5p\pi_u$ orbitals have been included resulting in matrices of dimension 1682.

In Table XI we present the major contributions to the wave functions describing the $^5\Sigma_g^+$ ground state of the Rh_2 molecule. The principal contribution to the chemical bond is due to the delocalized $5s\sigma_g$ molecular orbital. It is noted that the wave function with 1084 configurations introduces left–right correlation of the bonding electrons through double excitations from the $5s\sigma_g$ into the $5s\sigma_u$ orbital. In the largest calculation the left–right correlation of the $5s\sigma_g$ electrons is reduced in favour of the angular correlation. This trend is in agreement with our results for the molecules Cu_2 and Ag_2.

The configurations of the 4d shells have not been specified in detail in

Table XI. Major contributions to the wave functions describing the $^5\Sigma_g^+$ ground state of the Rh$_2$ molecule at the internuclear distance 5.082 a.u.

Occupations						Contributions in (%) in CI with		
						32	1084	1682
$5s\sigma_g$	$5s\sigma_u$	$5p\pi_u$	$4d\sigma_g+4d\sigma_u$	$4d\pi_u+4d\pi_g$	$4d\delta_g+4d\delta_u$	functions		
2	0	0	4	6	6	97.85	92.77	91.16
2	0	0	3	6	7	1.53	1.52	2.32
1	1	0	4	6	6	-	1.28	0.62
0	2	0	4	6	6	-	1.94	1.29
0	0	2	4	6	6	-	-	3.07

Table XI. If this had been done, it would have revealed that larger contributions stem from configurations with excess of electrons in the bonding 4d orbitals relative to configurations with excess of electrons in the antibonding 4d orbitals. This indicates that the 4d electrons do not localize completely, but to some extent participate in the formation of the chemical bond in the Rh$_2$ molecule.

The $^5\Sigma_g^+$ ground state of Rh$_2$ as resulting from the CI calculations with 1084 functions arises from the configuration $(4d\sigma_g)^{1.98} (4d\pi_u)^{3.20} (4d\delta_g)^{3.07}$ $(4d\delta_u)^{2.97} (4d\pi_g)^{2.79} (4d\sigma_u)^{1.98} (5s\sigma_g)^{1.94} (5s\sigma_u)^{0.06}$ at the internuclear distance 5.082 a.u.

The calculated energies for the $^5\Sigma_g^+$ ground state have been fitted to a Morse curve, and the spectroscopic constants have been derived. The equilibrium distance is determined as 5.40 a.u. and the vibrational frequency as 118 cm^{-1}. The calculated dissociation energy is only 0.85 eV as compared to the experimental value of 2.92 eV.

The calculated spectroscopic constants of the Rh$_2$ molecule are presumably encumbered with similar deficiencies as those of the other transition metal dimers. In analogy with our results for the Ag$_2$ molecule we estimate the true equilibrium distance of Rh$_2$ to be in the range 4.7–4.8 a.u.

In the present work we have refrained from treating the spin–orbit

coupling. Due to the participation of the 4d electrons in the bonding the spin–orbit coupling is not solely an atomic effect, and therefore more difficult to treat adequately. It certainly would cause considerable mixing of the low-lying electronic states, but probably not influence the description of the chemical bond significantly.

Fe$_2$. Of the open shell transition metal dimers the Fe$_2$ molecule is one of the most widely studied experimentally. Thus, Lin and Kant 1969b, and also Shim and Gingerich 1982 have performed high temperature mass spectrometric measurements to determine the Fe$_2^+$ / Fe$^+$ ratios over liquid Fe. Matrix isolation techniques have been utilized in work by de Vore et al. 1975 to obtain a UV-visible spectrum, and by Moskovits and DiLella 1980 to observe resonance Raman spectra. Barrett et al. 1970, McNab et al. 1971, Montano et al. 1976, Montano 1980, and Nagarathna et al. 1983 have investigated the Fe$_2$ molecule using matrix isolation techniques in conjunction with Mössbauer spectroscopy. Furthermore, Montano and Shenoy 1980, and Purdum et al. 1982 have performed extended X-ray absorption fine structure measurement on Fe and Fe$_2$ isolated in an Ar and a Kr matrix, respectively.

Nonempirical theoretical calculations have previously been performed by Harris and Jones 1979 using a local spin density approximation. They predicted the ground state of the Fe$_2$ molecule to be a $^7\Delta_u$ state with the configuration $(3d\sigma_g)^2 (3d\pi_u)^4 (3d\delta_g)^3 (3d\delta_u)^2 (3d\pi_u)^2 (3d\sigma_u)^1 (4s\sigma_g)^2$. From their calculations they derived the equilibrium distance as 3.96 a.u., the vibrational frequency as 390 cm^{-1}, and the dissociation energy as 3.45 eV.

Guenzburger and Saitovitch 1981 have reported results of discrete variational Xα type calculations on various electronic configurations of Fe$_2$ at the internuclear distance 3.53 a.u. These authors compared their calculated hyperfine parameters with the experimental values, and on this basis they concluded that the most likely ground state configuration of Fe$_2$ is $(3d\sigma_g)^2 (3d\pi_u)^4 (3d\delta_g)^2 (3d\delta_u)^2 (3d\pi_g)^3 (3d\sigma_u)^1 (4s\sigma_g)^2$.

Nagarathna et al. 1983 have performed Xα-SW calculations on five different configurations of the Fe$_2$ molecule. The lowest lying state in their calculations is a $^7\Delta_u$ state with the same configuration as found by Harris and Jones, but they find that other configurations give rise to quadrupole splittings in closer agreement with their experimental work.

The ground term of the Fe atom is $^5D(3d)^6(4s)^2$. The closed 4s shell of the Fe atom will prevent a bonding interaction between two Fe atoms in their ground term. However, a $^5F(3d)^7(4s)^1$ term is found 0.88 eV above

the ground term, and interaction between two Fe atoms in this term will result in formation of a stable molecule.

In our previous work on Fe_2, Shim and Gingerich 1982, we have employed Wachters' basis set which does not include a diffuse d function for the Fe atom. The molecular orbitals have been optimized for a $^7\Sigma_u^+$ state with the configuration $(3d\sigma_g)^1$ $(3d\pi_u)^4$ $(3d\delta_g)^2$ $(3d\delta_u)^2$ $(3d\pi_g)^4$ $(3d\sigma_u)^1$ $(4s\sigma_g)^2$. The resulting orbitals have been utilized in CI calculations that allowed full reorganization within the 3d shells while the $4s\sigma_g$ orbital was kept doubly occupied. The resulting 112 low-lying electronic states are shown in Fig. 9 at the internuclear distance 4.691 a.u. which is the nearest neighbour distance in bulk Fe.

The ground state of the Fe_2 molecule is a $^7\Delta_u$ state with the configuration $(3d\sigma_g)^{1.57}$ $(3d\pi_u)^{3.06}$ $(3d\delta_g)^{2.53}$ $(3d\delta_u)^{2.47}$ $(3d\pi_g)^{2.89}$ $(3d\sigma_u)^{1.49}$ $(4s\sigma_g)^{2.00}$ at the internuclear distance 4.691 a.u. The principal bonding orbital is the delocalized $4s\sigma_g$ molecular orbital. The 3d electrons localize around the nuclei and give rise to the small energy splittings between the potential energy curves. The larger number of holes in the 3d shells of Fe_2 relative to the other transition metal dimers treated give rise to an increasing number of low-lying electronic states, and this of course makes a simple interpretation of the calculational results more difficult. Although the 3d electrons hardly participate in the bonding it is recognized from the configuration of the $^7\Delta_u$ ground state that there is an increased population of the natural orbitals arising from the bonding 3d orbitals relative to those arising from the antibonding 3d orbitals.

Recently we have performed additional calculations on the Fe_2 molecule using a basis set that included a diffuse d function. The molecular orbitals have been optimized for the configuration $(3d\sigma_g)^1$ $(3d\pi_u)^3$ $(3d\delta_g)^3$ $(3d\delta_u)^3$ $(3d\pi_g)^3$ $(3d\sigma_u)^1$ $(4s\sigma_g)^2$ and utilized in CI calculations allowing full reorganization within both the 3d and the 4s shells. The new results confirm our previous work as to the description of the chemical bond including the existence of the »band« consisting of 112 low-lying electronic states. The configuration of the $^7\Delta_u$ ground state is $(3d\sigma_g)^{1.50}$ $(3d\pi_u)^{3.08}$ $(3d\delta_g)^{2.72}$ $(3d\delta_u)^{2.59}$ $(3d\pi_g)^{2.78}$ $(3d\sigma_u)^{1.33}$ $(4s\sigma_g)^{1.97}$ $(4s\sigma_u)^{0.03}$ at the internuclear distance 4.691 a.u. It is noted that this configuration is slightly different from that of our earlier work. The net excess of electrons in the bonding 3d orbitals relative to the antibonding 3d orbitals is 0.60 compared to 0.31 in our previous work. This indicates participation of the 3d electrons in the bonding, but the Mulliken population analyses in Table XII reveal that the total overlap population is almost entirely due to the $4s\sigma_g$ orbital.

Fig. 9. *Relative energies in eV of the 112 low-lying electronic states of the Fe₂ molecule at the internuclear distance 4.691 a.u. States are listed in order of increasing energy.*

The potential energies of the $^7\Delta_u$ ground state as obtained in the CI calculations with the different basis sets have been fitted to Morse curves, and the spectroscopic constants of the Fe₂ molecule have been derived. The calculations with the smaller basis set resulted in an equilibrium distance of 4.54 a.u. and a vibrational frequency of 204 cm⁻¹ while the corresponding values with the larger basis set are 4.99 a.u. and 134

cm^{-1}. The dissociation energy relative to two Fe atoms in the $^5F(3d)^7(4s)^1$ term is 0.69 eV when derived from the calculations with the smaller basis set, but only 0.04 eV based on the calculations with the larger basis set. Relative to two Fe atoms in their ground term the Fe_2 molecule is unbound in both sets of calculations. However, we expect that larger CI calculations would make the molecule bound without changing significantly the description of the chemical bond.

We expect that our calculated equilibrium distance using the smaller basis set, 4.54 a.u., is close to the true equilibrium distance of the Fe_2 molecule, since the experimental equilibrium distance for Ni_2, within the error limits given, has turned out to be identical to our value derived in the equivalent set of calculations. In addition, the deviation of 0.44 a.u. from the calculated value based on the larger basis set is consistent with our findings for the Cu_2 molecule. However, based on extended X-ray absorption fine structure measurements Montano et al. 1980, and Purdum et al. 1982 have derived the equilibrium distance of Fe_2 isolated in

Table XII. Mulliken population analyses of the valence orbitals for the $^7\Delta_u$ ground state of the Fe_2 molecule resulting from a CI calculation with 1152 functions at the internuclear distance 4.691 a.u.

Orbital	Overlap population	Orbital analyses			Occupation number
		s	p	d	
$4s\sigma_g$	0.73	0.93	0.05	0.01	1.97
$3d\sigma_g$	0.06	0.01	0.00	0.74	1.50
$3d\pi_u$	0.14	0.00	0.00	1.54	3.08
$3d\delta_g$	0.03	0.00	0.00	1.36	2.72
$3d\delta_u$	-0.03	0.00	0.00	1.30	2.59
$3d\pi_g$	-0.11	0.00	0.01	1.38	2.78
$3d\sigma_u$	-0.05	0.00	0.00	0.66	1.33
$4s\sigma_u$	0.00	0.01	0.01	0.00	0.03
Total	0.77	6.95	12.07	6.99	

an Ar matrix as only 3.53 a.u. and in a Ne matrix as 3.82 a.u., respectively. These distances appear to be very short perhaps indicating a different structure of Fe_2 in the matrix than in the gas phase.

Montano 1980 has reported the quadrupole splitting of Fe_2 as 4.05 ±0.04 mm/s, and he also found that the electric field gradient at the Fe nucleus is negative. Based on our calculated wavefunctions for the $^7\Delta_u$ ground state of Fe_2 we also estimate that the electric field gradient at the nucleus is negative. The electric field gradient is estimated by assuming that the major contributions are the one-center contributions due to the 3d electrons. It turns out that the one-center contributions from the 3d electrons to the electric field gradient are negative for all the states below 0.09 eV in Fig. 9, whereas they are positive for the highest lying states. Of course, it is necessary to perform accurate calculations to derive numerical values of the electric field gradient and of the quadrupole splitting, since the neglected contribution to the electric field gradient due to core polarization and two-center terms might be sizable as found in the work by Guenzburger and Saitovitch 1981.

To us, however, it appears rather meaningless to argue as to whether the ground state of the Fe_2 molecule is a $^7\Delta_u$ or a $^7\Sigma_g$ state as done by Nagarathna et al. 1983. The spin-orbit coupling that has been neglected in the present work will certainly mix the low-lying electronic states considerably and only leave Ω as a good quantum number.

Ru_2. The ab initio work by Cotton and Shim 1982 is the only known investigation of the Ru_2 molecule.

The ground term of the Ru atom is $^5F(4d)^7(5s)^1$, and two Ru atoms interacting in their ground term will lead to the formation of a stable molecule. HHF calculations revealed two configurations with energies below the sum of the energies of the separated atoms. The molecular orbitals optimized for these configurations: $(4d\sigma_g)^1$ $(4d\pi_u)^3$ $(4d\delta_g)^3$ $(4d\delta_u)^3$ $(4d\pi_g)^3$ $(4d\sigma_u)^1$ $(5s\sigma_g)^2$ and $(4d\sigma_g)^2$ $(4d\pi_u)^2$ $(4d\delta_g)^3$ $(4d\delta_u)^3$ $(4d\pi_g)^2$ $(4d\sigma_u)^2$ $(5s\sigma_g)^2$ have been utilized in CI calculations allowing full reorganization within the 4d shells. Both sets of calculations predict a $^7\Delta_u$ ground state with just slightly different configurations. The lowest energies have been obtained in the calculations based on orbitals optimized for the former configuration, and only these results will be presented.

In Fig. 10 we show the 112 low-lying electronic states resulting from interaction between two ground term Ru atoms at the internuclear distance 5.006 a.u. It is noted that there is a distinct energy gap between the ground state and the low-lying excited states. This has not been found
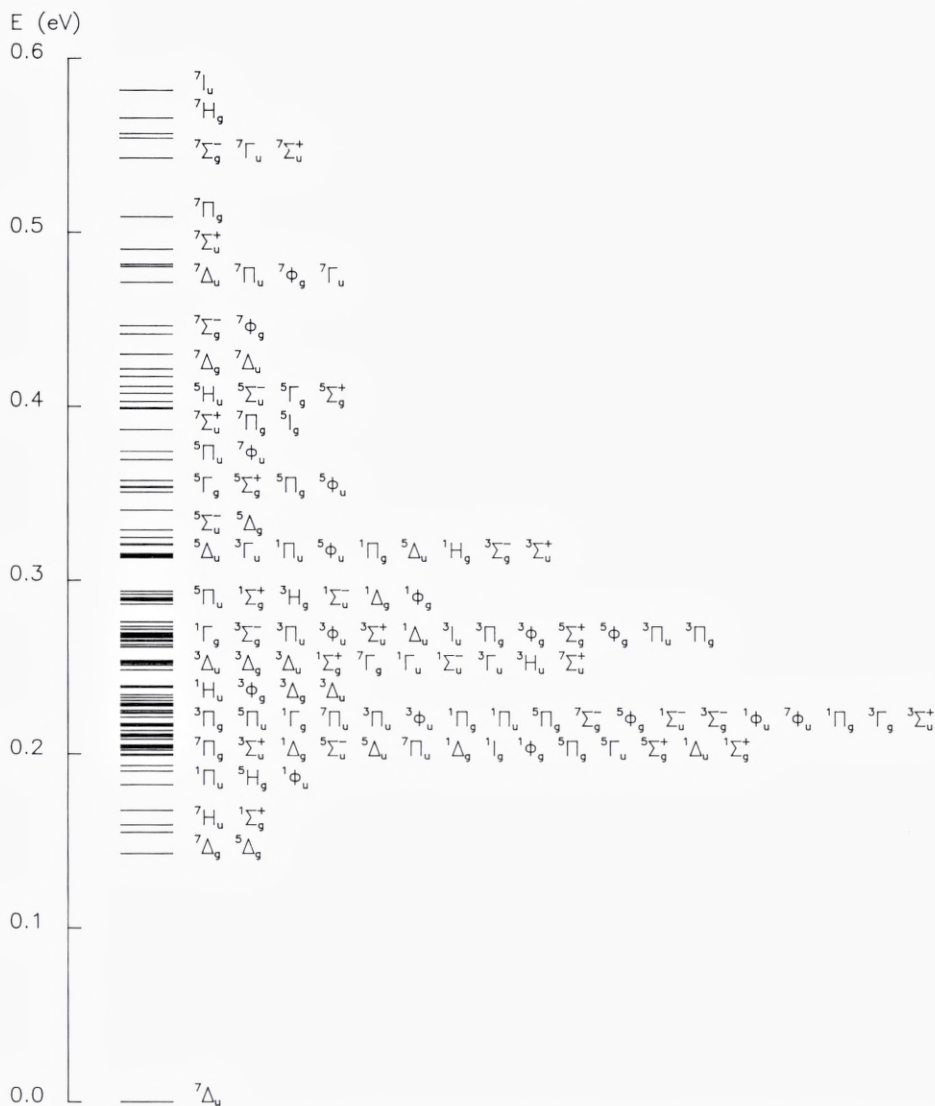
E (eV)

$$
\begin{array}{ll}
0.6 & \\
 & \rule{1cm}{0.4pt} \quad {}^7I_u \\
 & \rule{1cm}{0.4pt} \quad {}^7H_g \\
 & \rule{1cm}{0.4pt} \quad {}^7\Sigma_g^- \ {}^7\Gamma_u \ {}^7\Sigma_u^+ \\[4pt]
0.5 & \rule{1cm}{0.4pt} \quad {}^7\Pi_g \\
 & \rule{1cm}{0.4pt} \quad {}^7\Sigma_u^+ \\
 & \rule{1cm}{0.4pt} \quad {}^7\Delta_u \ {}^7\Pi_u \ {}^7\phi_g \ {}^7\Gamma_u \\[4pt]
 & \rule{1cm}{0.4pt} \quad {}^7\Sigma_g^- \ {}^7\phi_g \\
 & \rule{1cm}{0.4pt} \quad {}^7\Delta_g \ {}^7\Delta_u \\
0.4 & \rule{1cm}{0.4pt} \quad {}^5H_u \ {}^5\Sigma_u^- \ {}^5\Gamma_g \ {}^5\Sigma_g^+ \\
 & \rule{1cm}{0.4pt} \quad {}^7\Sigma_u^+ \ {}^7\Pi_g \ {}^5I_g \\
 & \rule{1cm}{0.4pt} \quad {}^5\Pi_u \ {}^7\phi_u \\
 & \rule{1cm}{0.4pt} \quad {}^5\Gamma_g \ {}^5\Sigma_g^+ \ {}^5\Pi_g \ {}^5\phi_u \\
 & \rule{1cm}{0.4pt} \quad {}^5\Sigma_u^- \ {}^5\Delta_g \\
 & \rule{1cm}{0.4pt} \quad {}^5\Delta_u \ {}^3\Gamma_u \ {}^1\Pi_u \ {}^5\phi_u \ {}^1\Pi_g \ {}^5\Delta_u \ {}^1H_g \ {}^3\Sigma_g^- \ {}^3\Sigma_u^+ \\
0.3 & \rule{1cm}{0.4pt} \quad {}^5\Pi_u \ {}^1\Sigma_g^+ \ {}^3H_g \ {}^1\Sigma_u^- \ {}^1\Delta_g \ {}^1\phi_g \\
 & \rule{1cm}{0.4pt} \quad {}^1\Gamma_g \ {}^3\Sigma_g^- \ {}^3\Pi_u \ {}^3\phi_u \ {}^3\Sigma_u^+ \ {}^1\Delta_u \ {}^3I_u \ {}^3\Pi_g \ {}^3\phi_g \ {}^5\Sigma_g^+ \ {}^5\phi_g \ {}^3\Pi_u \ {}^3\Pi_g \\
 & \rule{1cm}{0.4pt} \quad {}^3\Delta_u \ {}^3\Delta_g \ {}^3\Delta_u \ {}^1\Sigma_g^+ \ {}^7\Gamma_g \ {}^1\Gamma_u \ {}^1\Sigma_u^- \ {}^3\Gamma_u \ {}^3H_u \ {}^7\Sigma_u^+ \\
 & \rule{1cm}{0.4pt} \quad {}^1H_u \ {}^3\phi_g \ {}^3\Delta_g \ {}^3\Delta_u \\
 & \rule{1cm}{0.4pt} \quad {}^3\Pi_g \ {}^5\Pi_u \ {}^1\Gamma_g \ {}^7\Pi_u \ {}^3\Pi_u \ {}^3\phi_u \ {}^1\Pi_g \ {}^1\Pi_u \ {}^5\Pi_g \ {}^7\Sigma_g^- \ {}^5\phi_g \ {}^1\Sigma_u^- \ {}^3\Sigma_g^- \ {}^1\phi_u \ {}^7\phi_u \ {}^1\Pi_g \ {}^3\Gamma_g \ {}^3\Sigma_u^+ \\
0.2 & \rule{1cm}{0.4pt} \quad {}^7\Pi_g \ {}^3\Sigma_u^+ \ {}^1\Delta_g \ {}^5\Sigma_u^- \ {}^5\Delta_u \ {}^7\Pi_u \ {}^1\Delta_g \ {}^1I_g \ {}^1\phi_g \ {}^5\Pi_g \ {}^5\Gamma_u \ {}^5\Sigma_g^+ \ {}^1\Delta_u \ {}^1\Sigma_g^+ \\
 & \rule{1cm}{0.4pt} \quad {}^1\Pi_u \ {}^5H_g \ {}^1\phi_u \\
 & \rule{1cm}{0.4pt} \quad {}^7H_u \ {}^1\Sigma_g^+ \\
 & \rule{1cm}{0.4pt} \quad {}^7\Delta_g \ {}^5\Delta_g \\[20pt]
0.1 & \\[20pt]
0.0 & \rule{1cm}{0.4pt} \quad {}^7\Delta_u
\end{array}
$$

Fig. 10. *Relative energies in eV of the 112 low-lying electronic states of the Ru$_2$ molecule at the internuclear distance 5.006 a.u. States are listed in order of increasing energy.*

for any of the other transition metal dimers considered, and it presumably arises from the increased participation of the d electrons in the bond formation.

The $^7\Delta_u$ ground state has been subject to further investigations in CI calculations allowing full reorganization within both 4d and 5s shells.

These CI calculations included 1152 functions, and resulted in a $^7\Delta_u$ ground state with the natural orbital configuration $(4d\sigma_g)^{1.67}$ $(4d\pi_u)^{3.31}$ $(4d\delta_g)^{2.73}$ $(4d\delta_u)^{2.42}$ $(4d\pi_g)^{2.60}$ $(4d\sigma_u)^{1.27}$ $(5s\sigma_g)^{1.94}$ $(5s\sigma_u)^{0.06}$ at the internuclear distance 5.006 a.u.

Analogous with the other transition metal dimers investigated, the chemical bond in the Ru_2 molecule is mainly due to the delocalized $5s\sigma_g$ molecular orbital. However, there is an excess of 1.42 electrons in the natural orbital arising from the 4d bonding relative to the antibonding 4d molecular orbitals. We consider this as a manifestation of the participation of the 4d electrons in the bond formation although it hardly contributes to the overlap population in the Mulliken population analyses.

The calculated points of the potential energies of the $^7\Delta_u$ ground state have been fitted to a Morse curve, and the spectroscopic data have been derived. The equilibrium distance has been determined as 5.13 a.u., the vibrational frequency as 116 cm^{-1}, and the dissociation energy as 0.64 eV.

The calculated spectroscopic constants for the Ru_2 molecule presumably have similar defects as those of the other transition metal dimers. Judging from our results for the Ag_2 molecule we estimate the true equilibrium distance of Ru_2 to be app. 4.5 a.u. This value is quite close to the range 4.25–4.35 a.u. which was found by Bino et al. 1979 to cover the equilibrium distances in various compounds containing the formally Ru_2^{5+} ion. We expect that the calculated vibrational frequency and also the dissociation energy are too low, but we refrain from making any estimates of the true values at this point.

The spin–orbit coupling has not been considered in the present work. This effect, of course, would give rise to mixing of the close lying electronic states. However, contrary to the other open shell transition metal dimers, we expect that the spin–orbit coupling only will have minor effect on the $^7\Delta_u$ ground state of the Ru_2 molecule, since this state is quite well separated from the higher lying states.

The Mn_2 molecule

Mn₂. Kant et al. 1968 observed of the Mn_2 molecule in their high temperature mass spectrometric studies, but already prior to that Nesbet 1964 investigated the molecule theoretically. Nesbet's work represents the very first ab initio investigation performed for any transition metal dimer.

Nesbet utilized a minimal Slater type basis set, but including a 4p function, in his HF calculations on the closed shell $^1\Sigma_g^+$ $(3d\sigma_g)^2$ $(3d\pi_u)^4$ $(3d\delta_g)^4$ $(4s\sigma_g)^2$ $(4s\sigma_u)^2$ state of the Mn_2 molecule. Thereafter, he made use of the optimized molecular orbitals to calculate the energies of other states derived by successive replacement of the bonding 3d orbitals with β spins in the Slater determinant by the corresponding antibonding 3d orbitals with α spins. In this way he achieved localization of some of the 3d electrons around the nuclei, and he identified a $^9\Sigma_g^+(3d\sigma_g)^2$ $(3d\pi_u)^2$ $(3d\delta_g)^2$ $(3d\delta_u)^2$ $(3d\pi_g)^2$ $(4s\sigma_g)^2$ $(4s\sigma_u)^2$ state that was bound by 0.758 eV at the internuclear distance 5.5 a.u.

The configuration of the $^9\Sigma_g^+$ state reveals that the chemical bond in the Mn_2 molecule essentially is due to the delocalized $3d\sigma_g$ molecular orbital. The remaining 3d electrons are localized, and they give rise to a net spin of 2 on each Mn atom. Finally Nesbet determined the molecular ground state by calculating the energies of the states arising when the localized atomic spins were coupled to molecular spin states.

The ground state of the Mn_2 molecule as derived in Nesbet's calculations is a $^1\Sigma_g^+$ state resulting from antiferromagnetic coupling of the localized spins. The equilibrium distance of the molecule was determined as 5.44 a.u., and the dissociation energy as 0.79 eV. Furthermore, he also derived a value for the Heisenberg exchange parameter J in the phenomenological Hamiltonian $-J\mathbf{S}_1\cdot\mathbf{S}_2$ as -8 cm^{-1} at the equilibrium internuclear distance.

Nesbet's predictions of the nature of bonding in the Mn_2 molecule has recently been confirmed by experimental investigations by Van Zee et al. 1981, Rivoal et al. 1982, and by Baumann et al. 1983. In these investigations the exchange coupling constant of Mn_2 has been determined as -8 cm^{-1}, -10.3 cm^{-1}, and -9 cm^{-1}, respectively.

Harris and Jones 1979 have performed calculations on the Mn_2 molecule using a local spin density method. They identified two states with essentially identical energies, namely $^{11}\Pi_u$ $(3d\sigma_g)^1$ $(3d\pi_u)^3$ $(3d\delta_g)^2$ $(3d\delta_u)^2$ $(3d\pi_g)^2$ $(3d\sigma_u)^1$ $(4s\sigma_g)^2$ $(4s\sigma_u)^1$ and $^{11}\Sigma_u^+$ $(3d\sigma_g)^2$ $(3d\pi_u)^2$ $(3d\delta_g)^2$ $(3d\delta_u)^2$ $(3d\pi_g)^2$ $(3d\sigma_u)^1$ $(4s\sigma_g)^2$ $(4s\sigma_u)^1$.
The spectroscopic constants associated with the $^{11}\Pi_u$ state are $r_e=5.03$ a.u., $\omega_e=220$ cm^{-1}, and $D_e=1.25$ eV, and with the $^{11}\Sigma_u^+$ state: $r_e=5.10$ a.u., $\omega_e=210$ cm^{-1}, and $D_e=1.25$ eV. In addition, Wolf and Schmidtke 1980 have performed restricted HF calculations on the closed shell $^1\Sigma_g^+$ state investigated by Nesbet.

None of these later calculations, however, match the physical insight into the bonding of the Mn_2 molecule gained by Nesbet's work.

»d electron deficient« transition metal dimers

Cr₂. The Cr atom has a $^7S(3d)^5(4s)^1$ ground term well separated from the higher lying terms, and therefore, the possible molecular states arising from coupling of the angular momenta of two interacting Cr atoms are limited to $^{13}\Sigma_g^+$, $^{11}\Sigma_u^+$, $^9\Sigma_g^+$, $^7\Sigma_u^+$, $^5\Sigma_g^+$, $^3\Sigma_u^+$, and $^1\Sigma_g^+$. A priori, it is to be expected that the Cr_2 molecule has a $^1\Sigma_g^+$ ground state that is well described by a single Slater determinant with the configuration $(3d\sigma_g)^2$ $(3d\pi_u)^4$ $(3d\delta_g)^4$ $(4s\sigma_g)^2$ corresponding to a »sixtuple« bond between the two atoms.

Such a description would be in accordance with the experimental investigations of the Cr_2 molecule which have revealed, beyond reasonable doubt, that the molecule has an extremely short equilibrium distance, 3.18 a.u. The determination of the equilibrium distance byEfremov et al. 1974, 1978, and especially its confirmation by Michalopoulos et al. 1982, and by Bondybey et al. 1983 have given rise to enhanced activity of the theoretical investigations of the Cr_2 molecule. This is evident from Table XIII, where we have summarized the spectroscopic constants derived in the various calculations together with an abbreviated description of the methods used.

From Table XIII it is noted that two calculations have been reported for the $^1\Sigma_g^+$ $(3d\sigma_g)^2$ $(3d\pi_u)^4$ $(3d\delta_g)^4$ $(4s\sigma_g)^2$ state of Cr_2 in the restricted HF approximation. Wolf and Schmidtke 1980 used a reasonably large basis set consisting of Gaussian type functions, and McLean and Liu 1983 employed an extremely large basis set of Slater type functions. Qualitatively the two calculations are in agreement by resulting in too short bond distances and too high vibrational frequencies. The calculated dissociation energy has not been reported in Wolf and Schmidtke's work, but it would, without doubt, be negative of the same order of magnitude as found by McLean and Liu. In their work the energy associated with the $^1\Sigma_g^+$ $(3d\sigma_g)^2$ $(3d\pi_u)^4$ $(3d\delta_g)^4$ $(4s\sigma_g)^2$ state is app. 19 eV above the dissociation limit of the molecule at the calculated equilibrium distance.

Of the calculations going beyond HF, the one by Goodgame and Goddard 1981 including 1516 functions (GVB without inclusion of van der Waals terms) is almost equivalent with the MCSCF calculations with 3196 functions by Atha and Hillier 1982, and this presumably also holds for the basis sets used. It is noted that the spectroscopic constants derived in the two calculations are in close agreement, but far off the experimental values. As observed by Goodgame and Goddard, the bond in the Cr_2 molecule as resulting from their calculations, is due to an antifer-

le XIII.   Experimental and calculated spectroscopic constants of the Cr_2 molecule.

Method	Basis set Type; primitive-contracted	State	r_e(a.u)	ω_e(cm^{-1})	D_e(eV)
Experimental			3.184[3]	~470[2]	1.56[1]
All electron ab initio calculations					
MCSCF(APSG*)	GTO;(13s,7p,5d)-(6s,3p,2d)		3.59		~-4
Restricted HF	GTO;(14s,11p,5d)-(8s,6p,2d)	$^1\Sigma_g^+$	2.95	750	
GVB(1516 functions)	GTO;valence double zeta	$^1\Sigma_g^+$	6.14	70	0.13
GVB(6064 functions)	as above	$^1\Sigma_g^+$	5.78	110	0.35
MCSCF(APSG*)	GTO;(14s,11p,6d)-(8s,6p,3d) + bond centre functions s,p,d	$^1\Sigma_g^+$	3.50	355	-6.76
CI(3196×3196)	as above	$^1\Sigma_g^+$	6.56	58	-0.01
MCSCF(3196 functions)	as above	$^1\Sigma_g^+$	5.93	92	0.14
CI(3520×3520)	GTO;(11s,8p,5d)-(5s,4p,3d) + bond centre functions s,p,d	$^1\Sigma_g^+$	3.27	396	
MCSCF(3088 functions)	GTO;(14s,11p,6d,3f)-(8s,6p,4d,2f)				-1.4
Restricted HF	STO;(9s,6p,4d,3f,2g)		2.784	1181	-19.1
Xα type calculations					
Local spin density		$^{13}\Sigma_g^+$	6.92	55	0.20
Local spin density		$^{11}\Sigma_u^+$	5.37	200	-0.02
Xα-LCAO	GTO;(10s,6p,4d) + bond centre functions s,p,d	$^1\Sigma_g^+$	5.20	110	1.00
Xα-LCAO	as above	$^{13}\Sigma_g^+$	6.92	55	0.20
Local spin density		$^1\Sigma_g^+$	3.21	~450	1.80
Pseudopotential local spin density		$^1\Sigma_g^+$	3.21	470	2.8
Xα-LCAO; $\alpha\rho^{1/3}$-potential	GTO;(14s,11p,7d)-(9s,8p,5d)		4.01	106	1.4
Xα-LCAO;corr. potential	as above		3.72	423	5.0

Antisymmetric products of strongly orthogonal geminals.
) D_0°, Kant and Strauss 1966. – 2) Bondybey and English 1983. – 3) Efremov, Somoilo-
a, and Gurvich 1978. – 4) Wood, Doran, Hillier, and Guest 1980. – 5) Wolf and
chmidtke 1980. – 6) Goodgame and Goddard III 1981. – 7) Atha and Hillier 1982. – 8)
Kok and Hall 1983. – 9) Walch, Bauschlicher Jr., Roos, and Nelin 1983. – 10) McLean
nd Liu 1983. – 11) Harris and Jones 1979. – 12) Dunlap 1983. – 13) Delley, Freeman, and
Ellis 1983. – 14) Bernholc and Holzwarth 1983. – 15) Baykara, McMaster, and Salahub
984.

romagnetic coupling of localized spins of 3 on each of the Cr atoms. Thus, not even the 4s orbitals form a bonding molecular orbital at the calculated equilibrium distance. From their calculations, they determined the value of the exchange coupling constant as -93 cm^{-1} at the calculated equilibrium distance.

Kok and Hall 1983 have performed calculations that reproduce quite well the experimentally determined values of the equilibrium distance and the vibrational frequency for Cr_2. However, they do not report any value for the dissociation energy, and without doubt, the Cr_2 molecule is unbound in their description. The nice results obtained in their calculations, most likely, stem from basis set superposition errors combined with an inadequacy of their CI wave function to allow the molecule to dissociate properly into two Cr atoms in the ^7S ground term. The wave function determined by Kok and Hall arises from the natural orbital configuration $(3d\sigma_g)^{1.78}$ $(3d\pi_u)^{3.62}$ $(3d\delta_g)^{3.20}$ $(3d\delta_u)^{0.80}$ $(3d\pi_g)^{0.38}$ $(3d\sigma_u)^{0.22}$ $(4s\sigma_g)^{1.92}$ $(4s\sigma_u)^{0.08}$ at the internuclear distance 3.27 a.u. This configuration is very similar to those derived by Walch et al. 1983 in MCSCF calculations with 3088 functions. Thus, at the internuclear distance 3.0 a.u. their wave function has the natural orbital configuration $(3d\sigma_g)^{1.83}$ $(3d\pi_u)^{3.70}$ $(3d\delta_g)^{3.36}$ $(3d\delta_u)^{0.64}$ $(3d\pi_g)^{0.30}$ $(3d\sigma_u)^{0.16}$ $(4s\sigma_g)^{1.90}$ $(4s\sigma_u)^{0.11}$ and at 3.5 a.u. $(3d\sigma_g)^{1.60}$ $(3d\pi_u)^{3.32}$ $(3d\delta_g)^{2.58}$ $(3d\delta_u)^{1.42}$ $(3d\pi_g)^{0.68}$ $(3d\sigma_u)^{0.39}$ $(4s\sigma_g)^{1.85}$ $(4s\sigma_u)^{0.15}$.

This indicates the similarity of the descriptions of the Cr_2 molecule in Kok and Hall's and in Walch et al.'s calculations, but in Walch et al.'s calculations the Cr_2 molecule is unbound by 1.4 eV.

The Xα type calculations also result in diversified values of the spectroscopic constants as is seen from Table XIII.

It is recognized that in spite of the vast amount of theoretical work performed for the Cr_2 molecule no clear picture of the chemical bond in this molecule has emerged. It is possible, however, that internal CI calculations within the 3d and 4s shells, comparable to the calculations done by Goodgame and Goddard 1981 and by Atha and Hillier 1982, will provide a reasonable description of the nature of the chemical bond in the Cr_2 molecule when performed at the experimental internuclear distance.

This would be in agreement with the results obtained for the »d electron rich« transition metal dimers. For the molecules Cu_2 and Ni_2 the calculated spectroscopic constants derived from extensive CI calculations are in reasonable agreement with the experimental values. However, these calculations did not alter the qualitative description of the chemical

XIV. Experimental and calculated spectroscopic constants of the Mo_2 molecule.

Method	Basis set Type; primitive-contracted	State	r_e(a.u.)	ω_e(cm^{-1})	D_e(eV)
Experimental			3.666[3]	477.1[2]	4.18[1]
All electron ab initio					
MCSCF(APSG*)	GTO;(27s,13p,9d)-(8s,4p,3d)		3.97		~-1
CI(3212×3212)	GTO;(27s,13p,9d)-(9s,5p,4d)		3.89	392	
CI(3212×3212)	GTO;(27s,13p,9d)-(9s,5p,4d) + bond centre functions s,p,d		3.72	475	
GVB(6064 functions)	GTO ; valence double zeta + 1f	$^1\Sigma_g^+$	3.72	455	1.41
GVB	as above	$^3\Sigma_u^+$	3.91	325	0.60
Restricted HF	GTO;(18s,11p,9d)-(12s,5p,4d)	$^1\Sigma_g^+$	3.48	699	-9.35
	+ bond centre functions 2s,2p,1d				
MCSCF(APSG*)	as above	$^1\Sigma_g^+$	3.82	392	-3.10
CI(3196×3196)	as above	$^1\Sigma_g^+$	3.80	388	0.86
Restricted HF	STO;(11s,8p,6d,3f,2g)	$^1\Sigma_g^+$	3.400	717	-18.1
$X\alpha$ type calculations					
$X\alpha$-SW		$^1\Sigma_g^+$	4.3		
Local spin density		$^1\Sigma_g^+$	3.69	520	4.35
Pseudopotential local spin density		$^1\Sigma_g^+$	3.97	360	4.2
$X\alpha$-LCAO;$\alpha\rho^{1/3}$-potential	GTO;(17s,11p,9d)-(14s,9p,7d)		~5.1	92	0.4
$X\alpha$-LCAO; corr. potential	as above		3.17	441	2.6

* Antisymmetric products of strongly orthogonal geminals.

1) D_o^o, Gupta, Atkins, and Gingerich 1978. − 2) Efremov, Somoilova, Kozhukhovsky, and Gurvich 1978. − 3) Hopkins, Langridge-Smith, Morse, and Smalley 1983. − 4) Wood, Doran, Hillier, and Guest 1980. − 5) Bursten, Cotton, and Hall 1980. − 6) Goodgame and Goddard III 1982. − 7) Atha, Hillier, and Guest 1980; Atha and Hillier 1982. − 8) McLean and Liu 1983. − 9) Norman, Kolari, Gray, and Trogler 1977. − 10) Delley, Freeman, and Ellis 1983. − 11) Bernholc and Holzwarth 1983. − 12) Baykara, McMaster, and Salahub 1984.

bond derived from internal CI calculations within the 3d and 4s shells. A similar relationship for the »d electron deficient« transition metal dimers still needs to be proven.

Mo_2. Theoretical investigations of the Mo_2 molecule are up against similar difficulties as those encountered in the Cr_2 molecule. Like the Cr

atom, the ground term of the Mo atom is $^7S(4d)^5(5s)^1$ well separated from the higher lying terms. Intuitively, it is to be expected that the ground state of Mo_2 is a $^1\Sigma_g^+$ state, which should be well described in the molecular orbital picture by a one determinant wave function with all valence bonding orbitals fully occupied: $(4d\sigma_g)^2(4d\pi_u)^4(4d\delta_g)^4(5s\sigma_g)^2$. Furthermore, such a description is supported by the experimental findings of the very short bond distance, 3.666 a.u., and the high vibrational frequency, 477.1 cm^{-1}.

However, the data presented in Table XIV reveal that the accurate ab initio calculations based on the above assumptions lead to too short bond distances, too high vibrational frequencies and, more disturbing, the molecule is unbound by 9 eV in the calculations by Atha et al. 1980, 1982, and by 18 eV in McLean and Liu's 1983 calculations, which presumably are very close to the HF limit.

Contrary to the findings for Cr_2, however, reasonable spectroscopic constants have been obtained in the calculations going beyond HF. Basicly, the methods used in these calculations are very much alike, and they also lead to spectroscopic data in quantitative agreement.

Bursten et al. 1980 and Atha et al. 1980, 1982 have optimized their molecular orbitals in MCSCF type calculations, which included selected configurations within the space spanned by the 4d and 5s valence orbitals. Both groups utilized the optimized molecular orbitals in internal CI calculations within the 4d and 5s shells, but including only restricted excitations. Bursten et al. included all single and double excitations from the 64 determinants corresponding to perfect pairing in the GVB method. Atha et al. included all configurations in which the number of electrons in the 4dσ as well as in the 5sσ added up to 2 while those in the 4dπ and in the 4dδ added up to 4. These restrictions reduced the dimension of the CI matrix to 3212 and 3196, respectively, as compared to app. 35 000 for a full internal CI calculation within the 4d and 5s shells.

At the internuclear distance 3.78 a.u. the wavefunction derived by Bursten et al. has the configuration $(4d\sigma_g)^{1.92}(4d\pi_u)^{3.78}(4d\delta_g)^{3.42}$ $(4d\delta_u)^{0.58}(4d\pi_g)^{0.22}(4d\sigma_u)^{0.08}(5s\sigma_g)^{1.88}$ $(5s\sigma_u)^{0.12}$ and that of Atha et al. $(4d\sigma_g)^{1.86}(4d\pi_u)^{3.76}(4d\delta_g)^{3.33}(4d\delta_u)^{0.67}(4d\pi_g)^{0.24}(4d\sigma_u)^{0.14}(5s\sigma_g)^{1.87}$ $(5s\sigma_u)^{0.13}$.

The similarity of the configurations indicates that the wave function determined by Bursten et al. does describe a bound molecule with a dissociation energy similar to that obtained in Atha et al.'s work. The improvement of the spectroscopic data achieved by Bursten et al. by

inclusion of bond centre functions in their basis set probably reflects larger basis set superposition errors.

The calculations by Goodgame and Goddard 1982 are more elaborate than those by Bursten et al. and by Atha et al., but not much different in principle. Their wave functions are constructed by assigning the 4d and 5s electrons pairwise to either doubly occupied bonding orbitals, doubly occupied antibonding orbitals or one in a bonding and the other in the corresponding antibonding orbital. This gives rise to $3^6=729$ spatial configurations, or 1516 spin eigenfunctions for the $^1\Sigma_g^+$ state. On top of this they include excitations from the 5s orbitals into the $5p\sigma$ and the $5p\pi$ orbitals. The resulting wavefunctions consist of 6064 spin eigenfunctions and they are optimized in MCSCF type calculations. The improved spectroscopic constants derived in Goodgame and Goddard's work as compared to those derived by Bursten et al. and by Atha et al. are partly due to the better optimization of the orbitals and partly due to inclusion of correlation of the 5s electrons.

It is gratifying to experience that acceptable spectroscopic constants for the Mo_2 molecule can be derived from conceptually simple wave functions including external correlation only of the 5s electrons. In addition, this certainly implies that the method we have used, that is full internal CI based on molecular orbitals optimized in HHF like calculations, to describe the electronic structure of the »d electron rich« transition metal dimers is appropriate, indeed.

V_2. Recently, Langridge-Smith et al. 1984 have investigated the V_2 molecule spectroscopically in the gas phase. Their results indicate that the molecule has a $^3\Sigma_g^-$ ground state. Furthermore, they determined the equilibrium distance as 3.34 a.u., and the vibrational frequency as 535 cm^{-1}. From evidence of predissociation they derived the dissociation energy as 1.85 eV, and this is considerably less than the value, 2.47 eV, derived from high temperature mass spectrometric measurements.

The first theoretical investigation of the V_2 molecule has been performed by Harris and Jones 1979 using a local spin density method. Their calculations resulted in a $^9\Sigma_u^-$ ground state with the configuration $(3d\sigma_g)^1 (3d\pi_u)^2 (3d\delta_g)^2 (3d\delta_u)^2 (3d\sigma_u)^1 (4s\sigma_g)^2$, but they found numerous other states with similar energies. The calculated spectroscopic constants for the $^9\Sigma_u^-$ state were derived as $r_e=5.01$ a.u., $\omega_e=230$ cm^{-1}, and $D_e=1.00$ eV.

Apparently the experimental results by Langridge-Smith et al. inspired Walch et al. 1983 to perform theoretical investigations of a $^3\Sigma_g^-$

state of V_2. They performed MCSCF type calculations using two differ-
ent basis sets consisting of Gaussian type functions. Their smaller basis
set consisted of (14s, 11p, 6d) primitive functions which they contracted
to (8s, 6p, 4d). The larger basis set was derived from the smaller by
addition of 3 primitive f functions contracted to 2.

The ground term of the V atom is $^6D(3d)^3(4s)^2$, but the chemical bond
in V_2 probably arises from two V atoms interacting in the $^4F(3d)^4(4s)^1$
term that is only 0.25 eV above the ground term. In this case, a simple
molecular orbital picture suggests that the V_2 molecule has a $^3\Sigma_g^-$ ground
state with the configuration $(3d\sigma_g)^2 (3d\pi_u)^4 (3d\delta_g)^2 (4s\sigma_g)^2$.

In Walch et al.'s MCSCF calculations they constrained the configura-
tions included to those having 4 valence electrons in orbitals of σ sym-
metry, 2 valence electrons in π_x orbitals, 2 in π_y orbitals, 1 in δ_{xy}, and 1 in
$\delta_{x^2-y^2}$. The type of calculations Walch et al. have performed especially
takes into account the left-right correlation of the 3d and the 4s electrons.

In the calculations with the smaller basis set the V_2 molecule was found
to be bound relative to two V atoms in the $^4F(3d)^4(4s)^1$ term, but not
relative to two ground term V atoms. This is, however, achieved in the
calculation with the larger basis set. Presumably the two sets of calcula-
tions result in very similar descriptions of the chemical bond, but this
cannot be judged from the data given.

The spectroscopic constants derived from Walch et al.'s calculations
with the larger basis set are in good agreement with the experimental
values as to the equilibrium distance and the vibrational frequency. The
calculated equilibrium distance is 3.34 a.u., the vibrational frequency is
593.6 cm^{-1}, but the calculated dissociation energy is only 0.33 eV. At the
internuclear distance 3.00 a.u. the wave function has the configuration
$(3d\sigma_g)^{1.83} (3d\pi_u)^{3.80} (3d\delta_g)^{1.86} (3d\delta_u)^{0.14} (3d\pi_g)^{0.20} (3d\sigma_u)^{0.15} (4s\sigma_g)^{1.93}$
$(4s\sigma_u)^{0.09}$ and at 3.50 a.u. $(3d\sigma_g)^{1.81} (3d\pi_u)^{3.70} (3d\delta_g)^{1.74} (3d\delta_u)^{0.26} (3d\pi_g)^{0.30}$
$(3d\sigma_u)^{0.18} (4s\sigma_g)^{1.93} (4s\sigma_u)^{0.07}$. These configurations indicate considerable
participation of the 3d electrons in the bonding.

Thus, as in the case of Mo_2, spectroscopic constants for the V_2
molecule in reasonable agreement with the experimental values have
been obtained from conceptually simple wavefunctions.

Nb_2. From high temperature mass spectrometric measurements Gupta
and Gingerich 1979 determined the dissociation energy of the Nb_2

molecule to 5.21 eV. Recently Cotton and Shim 1985 have performed a theoretical investigation of the molecule using ab initio methods.
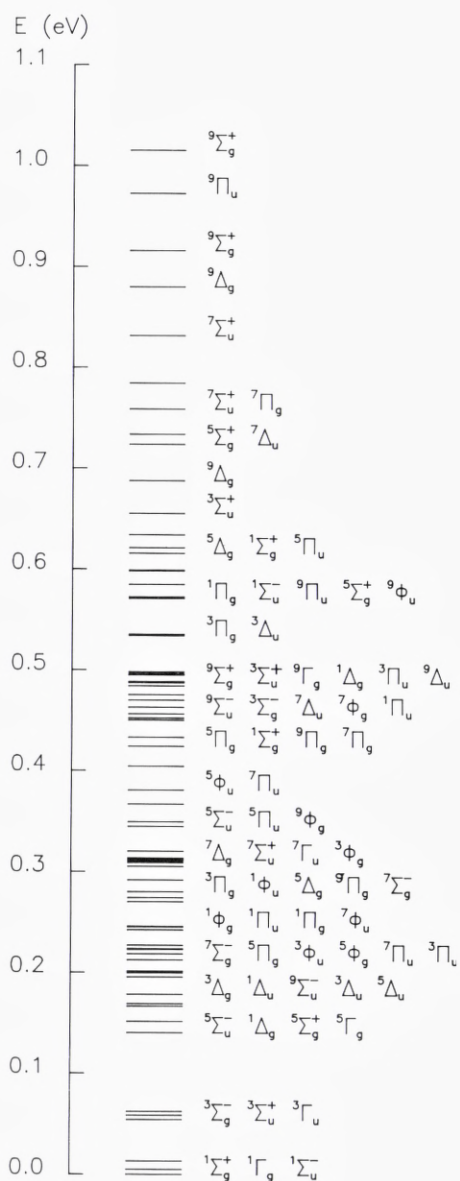
The ground term of the Nb atom is $^6D(4d)^4(5s)^1$, and it is expected that interaction between two Nb atoms in their ground term will result in formation of a stable molecule.

The numerous HF and HHF calculations we have performed at the internuclear distance 5.402 a.u. only revealed two configurations which are associated with energies below the sum of the energies of the separated atoms. These configurations are $(4d\sigma_g)^1$ $(4d\pi_u)^2$ $(4d\delta_g)^1$ $(4d\delta_u)^1$ $(4d\pi_g)^2$ $(4d\sigma_u)^1$ $(5s\sigma_g)^2$ and $(4d\sigma_g)^{1.0}$ $(4d\pi_u)^{1.5}$ $(4d\delta_g)^{1.5}$ $(4d\delta_u)^{1.5}$ $(4d\pi_g)^{1.5}$ $(4d\sigma_u)^{1.0}$ $(5s\sigma_g)^{2.0}$, respectively. The molecular orbitals optimized for the latter configuration have been utilized in CI calculations that allowed full reorganization within the 4d shells.

Fig. 11 shows all 75 low-lying electronic states of the Nb_2 molecule at the internuclear distance 5.402 a.u., which is the nearest neighbour distance in bulk Nb. It is noted that the six lowest lying states are separated from the dense manyfold of higher lying states by an energy gap of app. 0.1 eV. This is of the same order of magnitude as the energy gap separating the ground state from the higher lying states in the Ru_2 molecule. The ground state of the Nb_2 molecule is a $^1\Sigma_g^+$ state with the configuration $(4d\sigma_g)^{1.34}$ $(4d\pi_u)^{2.69}$ $(4d\delta_g)^{1.11}$ $(4d\delta_u)^{0.91}$ $(4d\pi_g)^{1.28}$ $(4d\sigma_u)^{0.67}$ $(5s\sigma_g)^{2.00}$ at the internuclear distance 5.402 a.u. Two other states, $^1\Gamma_g$ and $^1\Sigma_u^-$, lying very close to the ground state arise from almost identical configurations. The lowest lying $^3\Sigma_g^-$ state has the configuration $(4d\sigma_g)^{1.27}$ $(4d\pi_u)^{2.62}$ $(4d\delta_g)^{1.09}$ $(4d\delta_u)^{0.93}$ $(4d\pi_g)^{1.36}$ $(4d\sigma_u)^{0.73}$ $(5s\sigma_g)^{2.00}$, and this is almost identical to the configurations of the lowest lying $^3\Sigma_u^+$ and $^3\Gamma_u$ states. Thus, the six lowest lying states reveal substantial participation of the 4d electrons in the bonding. For the lowest lying singlet states, the excess of electrons in bonding 4d orbitals relative to antibonding 4d orbitals is 2.28, whereas it has decreased to 1.96 electrons for the lowest lying triplet states. Judging from Mulliken population analyses, the principal bonding orbital is the delocalized $5s\sigma_g$ molecular orbital. At 5.402 a.u. this orbital contributes 0.69 out of a total overlap population of 0.81.

The equilibrium distances derived from the calculated potential energy curves for the 75 low-lying states are scattered over app. 1 a.u., ranging from 5.6-6.6 a.u. This is in contrast to the findings for the »d electron rich« transition metal dimers. Thus, for the Pd_2 molecule the corresponding spread of the equilibrium distances is only 0.26 a.u. Due to the

Fig. 11. Relative energies in eV of the 75 low-lying elektronic states of the Nb$_2$ molecule at the internuclear distance 5.402 a.u. States are listed in order of increasing energy.

E (eV)

1.1

1.0 — $^9\Sigma_g^+$
— $^9\Pi_u$

0.9 — $^9\Sigma_g^+$
— $^9\Delta_g$
— $^7\Sigma_u^+$

0.8
— $^7\Sigma_u^+$ $^7\Pi_g$
— $^5\Sigma_g^+$ $^7\Delta_u$

0.7 — $^9\Delta_g$
— $^3\Sigma_u^+$
— $^5\Delta_g$ $^1\Sigma_g^+$ $^5\Pi_u$

0.6 — $^1\Pi_g$ $^1\Sigma_u^-$ $^9\Pi_u$ $^5\Sigma_g^+$ $^9\Phi_u$
— $^3\Pi_g$ $^3\Delta_u$

0.5 $^9\Sigma_g^+$ $^3\Sigma_u^+$ $^9\Gamma_g$ $^1\Delta_g$ $^3\Pi_u$ $^9\Delta_u$
$^9\Sigma_u^-$ $^3\Sigma_g^-$ $^7\Delta_u$ $^7\Phi_g$ $^1\Pi_u$
$^5\Pi_g$ $^1\Sigma_g^+$ $^9\Pi_g$ $^7\Pi_g$

0.4 — $^5\Phi_u$ $^7\Pi_u$
— $^5\Sigma_u^-$ $^5\Pi_u$ $^9\Phi_g$

0.3 — $^7\Delta_g$ $^7\Sigma_u^+$ $^7\Gamma_u$ $^3\Phi_g$
$^3\Pi_g$ $^1\Phi_u$ $^5\Delta_g$ $^9\Pi_g$ $^7\Sigma_g^-$
— $^1\Phi_g$ $^1\Pi_u$ $^1\Pi_g$ $^7\Phi_u$

0.2 $^7\Sigma_g^-$ $^5\Pi_g$ $^3\Phi_u$ $^5\Phi_g$ $^7\Pi_u$ $^3\Pi_u$
— $^3\Delta_g$ $^1\Delta_u$ $^9\Sigma_u^-$ $^3\Delta_u$ $^5\Delta_u$
— $^5\Sigma_u^-$ $^1\Delta_g$ $^5\Sigma_g^+$ $^5\Gamma_g$

0.1

— $^3\Sigma_g^-$ $^3\Sigma_u^+$ $^3\Gamma_u$

0.0 — $^1\Sigma_g^+$ $^1\Gamma_g$ $^1\Sigma_u^-$

appearence of shoulders in the potential energy curves for the 3 lowest lying states, the calculated potential energies of these states could not with sufficient accuracy be fitted to Morse curves. For the $^1\Sigma_g^+$ and the $^1\Sigma_u^-$ states the shoulders appear at app. 4.8 a.u., and for the $^1\Gamma_g$ state at app. 5.1 a.u. The equilibrium distances for the 3 states are app. 5.6 a.u.

In light of the very short bond distances found experimentally for the

molecules V_2, Cr_2, and Mo_2 we also expect that Nb_2 has a short bond distance. The change in equilibrium distance in going from Cr_2 to Mo_2 is identical with that of going from Cu_2 to Ag_2. If we invoke a similar relationship when going from the V_2 to the Nb_2 molecule we should expect an equilibrium distance of only 3.81 a.u. in Nb_2. This implies, by analogy with our findings for the Ag_2 molecule, that the calculated equilibrium distance for Nb_2 should be app. 4.36 a.u. The calculated equilibrium distance, however, is app. 5.6 a.u.

We expect that the major reason for the shoulders in the potential energy curves as well as for the large discrepancy between the calculated and the expected equilibrium distance is due to the lack of f functions in the basis set. Such functions are required to account properly for the 4d electrons, because they are deeply involved in the bonding.

Based on the simple molecular orbital picture the Nb_2 molecule should have a $^3\Sigma_g^-$ ground state with the configuration $(4d\sigma_g)^2$ $(4d\pi_u)^4$ $(4d\delta_g)^2$ $(5s\sigma_g)^2$. HF calculations reveal that this state does not describe a bound molecule, but it should be noted that the total number of $d\sigma$ and $d\delta$ electrons each add up to app. 2 for the $^1\Sigma_g^+$ ground state, just as the $d\pi$ electrons add up to app. 4. Walch et al. 1983 imposed such constraints onto their wavefunctions for the V_2 molecule. In our work no such constraints have been imposed, and therefore the number of electrons associated with each symmetry type is a genuine result of the calculations performed. This implies that the molecular orbital picture offers a useful guidance in determining the ground state of the Nb_2 molecule. A similar result has not been found for the »d electron rich« transition metal dimers, and it still needs to be investigated, if it is valid also for other »d electron deficient« transition metal dimers.

Sc_2. The Sc_2 molecule has been investigated by high temperature mass spectrometry by Verhaegen et al. 1964. However, the dissociation energy derived from the mass spectrometric data appears unreliable, since the original value 1.12 eV derived by Verhaegen et al. later on, without justification, has been changed to 1.65 eV as quoted in Table XV. Lately, the Sc_2 molecule has also been studied by matrix isolation techniques. This has resulted in determination of the ground state vibrational frequency as 238.91 cm^{-1}, and from the ESR studies by Knight et al. 1983 the symmetry of the ground state has been derived as $^5\Sigma$.

The first theoretical investigation of the Sc_2 molecule is a local spin density calculation performed by Harris and Jones 1979. Their calculations resulted in a $^5\Sigma_u^-(3d\sigma_g)^1(3d\pi_u)^2(3d\sigma_u)^1(4s\sigma_g)^2$ ground state with an

equilibrium distance of 5.10 a.u., a vibrational frequency of 200 cm^{-1}, and a dissociation energy of 1.80 eV. Furthermore, they also have reported the spectroscopic constants for a $^3\Sigma_g^-$ $(3d\pi_u)^2$ $(4s\sigma_g)^2$ $(4s\sigma_u)^2$ state as r_e=6.15 a.u., ω_e=235 cm^{-1}, and D_e=1.00 eV. Harris and Jones 1978 have determined the discrepancies in the local spin density method between the calculated and the experimental energy splittings of atomic states originating from different orbital configurations. Applying this correction to the dissociation energy for the $^5\Sigma_u^-$ state of Sc_2 reduces it to app. 0.4 eV. This is, however, still in disagreement with the results obtained in HF calculations by Wood et al. 1980. They found the $^5\Sigma_u^-$ $(3d\sigma_g)^1$ $(3d\pi_u)^2$ $(3d\sigma_u)^1$ $(4s\sigma_g)^2$ state unbound by app. 2 eV relative to the atomic limit $^2D(3d)^1(4s)^2+^4F(3d)^2(4s)^1$. At least for the transition metal dimers, this kind of relationship between dissociation energies derived in HF and Xα type calculations are common, and the reason for the discrepancy is presently not clear.

The most extensive theoretical investigation of the Sc_2 molecule has been carried out by Das 1982 using a pseudopotential method in conjunction with a large valence basis set consisting of Slater type functions. The conclusion of his work is that the Sc_2 molecule is a van der Waals dimer with a binding energy of app. 0.17 eV at the internuclear distance app. 9.4 a.u. His results, of course, are in sharp contrast to the available experimental data for the Sc_2 molecule.

The results by Das were essentially confirmed by Walch and Bauschlicher 1983a. They performed all electron ab initio calculations on a few selected states of the Sc_2 molecule and found that the states dissociating into two $^2D(3d)^1(4s)^2$ ground term Sc atoms were very weakly bound with equilibrium distances of app. 8 a.u. and dissociation energies of app. 0.06 eV. However, they also performed calculations on a $^5\Delta_u$ and a $^5\Sigma_u^-$ state that dissociate into one Sc atom in the $^2D(3d)^1(4s)^2$ ground term and the other in the $^4F(3d)^2(4s)^1$ excited term. Relative to this dissociation limit the $^5\Delta_u$ and the $^5\Sigma_u^-$ states were strongly bound by app. 0.8 eV.

The appearance of the experimental results by Knight et al. 1983 indicating the existence of a bound $^5\Sigma$ state for the Sc_2 molecule influenced Walch and Bauschlicher 1983b to reinvestigate the $^5\Sigma_u^-$ state. In their MCSCF calculations on the $^5\Sigma_u^-$ state they constrained the configurations included to those having a total of 4 valence electrons of σ symmetry and 2 of π symmetry. The optimized molecular orbitals were utilized in CI calculations that allowed single and double excitations from ten selected

e XV.   Experimental and calculated spectroscopic constants of the Sc_2 molecule.

Method	Basis set		State(atomic limit)	Spectroscopic constants		
	Type; primitive-contracted			r_e(a.u.)	ω_e(cm^{-1})	D_e(eV)
Experimental					238.91[2]	1.65[1]
All electron ab initio calculations						
MCSCF	GTO;(13s,7p,5d)-(6s,3p,2d)		$^5\Sigma_u^-(^2D(4s^23d^1)+^4F(4s^13d^2))$	4.86		0.30
CI	as above		$^5\Sigma_u^-(^2D(4s^23d^1)+^4F(4s^13d^2))$	4.91		1.12
Restricted HF	GTO;(14s,11p,5d)-(8s,6p,2d)		$^1\Sigma_g^+(3d\sigma_g)^2(3d\sigma_u)^2(4s\sigma_g)^2$	5.76	210	
Restricted HF	as above		$^1\Sigma_g^+(4s\sigma_g)^2(3d\pi_u)^4$	4.20	360	
CI	GTO;(14s,11p,6d)-(8s,6p,4d)		$^1\Sigma_g^+(^2D(4s^23d^1)+^2D(4s^23d^1))$	~8		0.045
CI	as above		$^3\Sigma_g^-(^2D(4s^23d^1)+^2D(4s^23d^1))$	~8		0.045
CI	as above		$^3\Sigma_u^+{}^2D(4s^23d^1)+^2D(4s^23d^1))$	~8		0.029
CI	GTO;(14s,11p,6d,1f)-(6s,6p,3d,1f)		$^3\Sigma_u^+(^2D(4s^23d^1)+^2D(4s^23d^1))$~8			0.046
CI	GTO;(14s,11p,6d)-(8s,6p,4d)		$^5\Delta_u(^2D(4s^23d^1)+^4F(4s^14p^13d^1))$	~7		0.8
CI	as above		$^5\Sigma_u^-(^2D(4s^23d^1)+^4F(4s^14p^13d^1))$	~6.5,~7		0.9
CI	GTO;(14s,11p,6d)-(8s,6p,4d)		$^5\Sigma_u^-(^2D(4s^23d^1)+^2D(4s^23d^1))$	5.27	184	0.12
CI, corrected	as above		as above	5.27	184	0.44
Pseudopotential calculations						
CI	STO;(3s,3p,4d,1f)		$^1\Sigma_g^+(^2D(4s^23d^1)+^2D(4s^23d^1))$	~9.4	61	0.17
Xα type calculations						
Local spin density			$^5\Sigma_u^-$	5.10	200	1.80
Local spin density			$^3\Sigma_g^-$	6.15	235	1.00

1) Drowart 1967. – 2) Moskovits, DiLella and Limm 1984. – 3) Wood, Doran, Hillier and Guest 1980. – 4) Wolf and Schmidtke 1980. – 5) Walch and Bauschlicher Jr. 1983a. – 6) Walch and Bauschlicher Jr. 1983b. – 7) Das 1982. – 8) Harris and Jones 1979.

reference configurations. From their calculations they derived an equilib-rium distance of 5.27 a.u., a vibrational frequency of 184 cm^{-1}, and a dissociation energy relative to two ground term atoms of 0.12 eV which they corrected to 0.44 eV by taking into account Davidson's correction, correction for errors in the asymptotic limit and also corrections for basis set insufficiencies.

Prior to the appearance of the experimental work by Knight et al. 1983, Wood et al. 1980 suggested a $^5\Sigma_u^-$ ground state of the Sc_2 molecule on basis of their MCSCF and CI calculations. Their calculations, how-

ever, were not convincing by themselves due to errors in the atomic limit, and substantial superposition errors associated with the basis sets used.

Conclusion

During the past two decades great efforts have been devoted to experimental and theoretical investigations trying to elucidate the natures of the chemical bonds in small molecules composed of transition metal atoms. In the present work we have reviewed the experimental and the theoretical knowledge of the dimers of the first and second transition metal series, and in addition, we have presented some new calculational results for the molecules Ni_2, Fe_2, and Rh_2. At present, it appears that a unified understanding of the transition metal dimers is emerging from the combined experimental and theoretical results, which for a long time have seemed contradictory

By now it must be considered proven that it is extremely difficult, from ab initio work, to derive spectroscopic constants for the transition metal dimers, which are in good agreement with the experimental values. Nevertheless, such good agreements have been achieved for a few transition metal dimers of the »d electron rich« and recently also of the »d electron deficient« types. In addition, the theoretical predictions of the many low-lying electronic states in the Ni_2 molecule have recently been confirmed by experimental work. Therefore, we are confident that ab initio methods in general provide physical insight into the complex chemical bonds of the transition metal dimers. In particular, it appears that adequate descriptions of the transition metal dimers are obtained in internal CI calculations involving only the valence d and s shells. Such calculations do not result in spectroscopic constants of high accuracy, but for the »d electron rich« transition metal dimers, it appears that the calculated equilibrium distances deviate systematically from the experimental values. For the »d electron deficient« transition metal dimers the theoretical data are still too scarce to reach a similar conclusion. In any case, it is far more difficult to achieve reasonable agreements for these molecules.

Due to the unfilled d shells of the transition metal atoms, the wave functions for the dimers usually consist of a large number of Slater determinants and therefore appear to be very complicated. In spite of

this, however, it has been possible to interpret the wave functions in simple physical pictures.

Thus, the chemical bonds in the »d electron rich« transition metal dimers, Cu_2, Ni_2, Co_2, and Fe_2 are mainly due to the delocalized $4s\sigma_g$ molecular orbitals. The 3d electrons localize around the nuclei and interact through Heisenberg exhange couplings. This gives rise to the small energy splittings between the many low-lying electronic states. The principal bonding orbitals in the corresponding dimers of the second transition metal series are the delocalized $5s\sigma_g$ molecular orbitals. The 4d electrons in Ag_2 and Pd_2 are well localized, but in the sequence Rh_2 to Ru_2 the 4d electrons become increasingly delocalized signifying their participation in the bonding. The d electrons in the »d electron deficient« transition metal dimers are considerably delocalized and strongly involved in the bonding of the molecules. In these molecules the combined contributions to the bonding from the d electrons are comparable to the contributions from the outermost $s\sigma_g$ molecular orbitals.

The chemical bonds in the transition metal dimers cannot be described in a molecular orbital picture, but at least in the case of the Nb_2 molecule, it appears that the simple picture still has a significance.

In summary, accurate spectroscopic constants for the transition metal dimers are not obtained from ab initio calculations, but it appears that the nature of the chemical bonds in such molecules are well described by the conceptually simple wave functions resulting from internal CI calculations within the valence d and s shells.

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