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Bonding in the Diruthenium Molecule by ab Initio Calculations

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Abstract: In this study we present all-electron ab initio self-consistent field (SCF) and configuration interaction (CI) calculations of 112 electronic states resulting from interaction between two Ru atoms. The basis set used was of double-ζ quality in general, but the 4d orbital was represented by a triple-ζ function. The CI calculations of the ground state included octuple excitations from a reference configuration. Some important results of the study are that the Ru_2 molecule is stable although the calculated equilibrium distance, 5.13 au, dissociation energy, 0.64 eV, and vibrational frequency, 116 cm^{-1}, indicate a weaker bond than might have been expected. The ground state is a $^7\Delta_u$ state with the natural orbital populations: $(4d\sigma_g)^{1.67}$ $(4d\pi_u)^{3.31}$ $(4d\delta_g)^{2.73}$ $(4d\delta_u)^{2.42}$ $(4d\pi_g)^{2.60}$ $(4d\sigma_u)^{1.27}$ $(5s\sigma_g)^{1.94}$ $(5s\sigma_u)^{0.06}$. The bond strength is derived in considerable measure from 4d–4d interaction, in contrast to M_2 molecules of the first transition series where the bonding is due almost exclusively to a 4sσ interaction. We believe that this increased bonding role for the d orbitals is characteristic of the change from the first to the second (and presumably third) transition series. It is also estimated that because of inadequacies of the calculation the bond distance and dissociation energy are underestimated. The actual bond distance is predicted to be 4.80–4.90 au (2.54–2.59 Å).

The study of bonding between atoms of the transition metals is now an extensive field including (a) metal atom cluster compounds of the metal carbonyl type,[1] (b) metal atom clusters containing metal atoms in higher oxidation states,[2] (c) dinuclear compounds containing multiple bonds,[3] and (d) "naked" metal clusters, including diatomic molecules.[4] Species in category (d) are of interest for several reasons, one of which is that for the theoretician they provide examples of metal–metal bonding free from complications introduced by the additional presence of metal–ligand and perhaps intraligand bonding. It may be hoped that any theoretical understanding of the "naked" metal clusters will also contribute to our understanding of metal–metal bonding in the other three classes of compounds. It was partly with this hope in mind that the present authors, both separately and jointly, have examined the electronic structures of several diatomic molecules, M_2. Detailed all-electron ab initio calculations are very scarce for diatomic transition-metal molecules. Presently, results are known for the molecules Ni_2,[5a] Fe_2,[5b] NiCu,[5c] NiFe,[5d] and Mo_2.[5e] In addition, ab initio pseudopotential calculations have been published for Ni_2[5f,g] and Cr_2.[5h]

In this report we describe calculations of the ab initio type, i.e., Hartree–Fock calculations with inclusion of configuration interaction, for the molecule Ru_2. Previous experience with M_2 molecules had indicated to us that this might be a relatively tractable case, for the following reasons. For molecules with atoms of the first transition series, electron correlation is so great that enormous amounts of configuration interaction must be included, whereas for those derived from the third transition series, relativistic corrections will be required. Thus, the second transition series seems most attractive; in the second transition series it appears that correlation may not be excessively severe and it is safe to neglect relativistic effects which can be included via a perturbational calculation later on.

Table I. Relative Energies (in au) of the Lowest Lying Terms Originating from Different Orbital Configurations

	calcd	exptl[a]
$^5F(4d)^7(5s)^1$	0.0000	0.0000
$^5D(4d)^6(5s)^2$	0.0458	0.0319
$^3F(4d)^8$	0.0831	0.0401

[a] Center of gravity of each multiplet has been calculated from data of Moore (Moore, C. E. *Natl. Bur. Stand.* (*U.S.*)*Circ.* 1952, *3*, No. 467).

Accordingly, we have used the Hartree–Fock–Roothaan formalism[6] followed by a limited configuration interaction (CI) treatment at various internuclear distances to estimate the equilibrium internuclear distance, which is not yet known experimentally for Ru_2. The necessary integrals were evaluated by using the program MOLECULE[7] while the self-consistent field (SCF) and CI calculations were performed by using the ALCHEMY program system[8] in conjunction with some newer programs.[9]

Procedures

Details of Basis Set and Atomic Calculations. The basis set consisted of Gaussian-type functions, and it is essentially Huzinaga's,[10] but it has been extended by addition of two p functions with exponents 0.18 and 0.08. The additional p functions are needed to describe the 5p orbital, and their exponents were determined by using a method described by Raffenetti.[11] Furthermore, the exponents of the most diffuse s functions were altered from 0.101 273 07 and 0.036 775 425 to 0.11 and 0.05, respectively. This contracts the radial charge distribution. The original functions have their maxima of radial charge distributions at 2.22 au and 3.69 au, respectively; the maxima for the modified functions are at 2.13 and 3.16 au. These alterations result in a better description of the valence region in the molecule.

The primitive basis (17s, 13p, 8d) was contracted to (10s, 8p, 5d) by using a segmented contraction scheme. The coefficients of the contracted functions were determined from calculations on the $^5F(4d)^7(5s)^1$ term of the Ru atom. The 4d orbital is represented by a triple-ζ function in the contracted basis. All other orbitals including 5p are represented by double-ζ functions. For the first-row transition-metal atoms, it is well-known that there are discrepancies between experimental and calculated

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[1] Johnson, B. F. G., Ed. "Transition Metal Clusters"; New York, 1980.

[2] (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 26. (b) Simon, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1. (c) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1980**, *19*, 132.

[3] Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms", Wiley: New York, 1982.

[4] Faraday Discussions of the Royal Society of Chemistry, Faraday Symposium No. 14, 1980, entitled "Diatomic Metals and Metallic Clusters".

[5] (a) Shim, I.; Dahl, J. P.; Johansen, H. *Int. J. Quantum Chem.* **1979**, *15*, 311. (b) Shim, I.; Gingerich, K. A. *J. Chem. Phys.*, in press. (c) Shim, I. *Theor. Chim. Acta* **1980**, *54*, 113. (d) Shim, I. *Ibid.* **1981**, *59*, 413. (e) Bursten, B. E.; Cotton, F. A.; Hall, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 6348. (f) Upton, T. H.; Goddard, W. A., III. *Ibid.* **1978**, *100*, 5659. (g) Noell, J. O.; Newton, M. D.; Hay, P. J.; Martin, R. L.; Bobrowicz, F. W. *J. Chem. Phys.* **1980**, *73*, 2360. (h) Goodgame, M. M.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 215.

[6] Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

[7] Almlöf, J. In "Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry"; Max-Planck-Institute: München, 1973; p 14.

[8] The ALCHEMY program system was produced at the IBM Research Laboratory in San Jose, CA, by Drs. P. S. Bagus, B. Liu, M. Yoshimine, A. D. McLean, and U. Wahlgren.

[9] Sarma, C. R.; Rettrup, S. *Theor. Chim. Acta* **1977**, *46*, 63. Rettrup, S.; Sarma, C. R. *Ibid.* **1977**, *46*, 73.

[10] Huzinaga, S. *J. Chem. Phys.* **1977**, *66*, 4245.

[11] Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.

0002-7863/82/1504-7025$01.25/0

splittings between terms originating from different orbital configurations. Thus, for some of these atoms even the ground terms as calculated in the HF approximation have a different symmetry than the experimentally known ground terms. This has been discussed by Claydon and Carlson.[12] This difficulty is not present for the Ru atom. As illustrated in Table I, the correct order of the lowest lying terms arising from different orbital configurations is obtained in HF calculations. Furthermore, the calculated and the experimental splittings are in reasonable agreement as to order of magnitude.

General Strategy. Even with the contracted basis set (10s, 8p, 5d) just described, the number of two-electron integrals needed for Ru_2 is about 4.6×10^6, which are grouped into about 1.1×10^6 supermatrix elements for use in SCF calculations. Moreover, as in all calculations on molecules containing transition-metal atoms, the presence of partly filled inner shells means that a large number of Slater determinants of comparable energy are needed, and this number increases rapidly as the number of holes in the d shell increases, reaching a maximum value when the d shell is half-full.

The ground-state configuration of Ru is $(4d)^7(5s)^1$. Assuming the 5s orbitals of the two Ru atoms form a bonding molecular orbital in Ru_2, the number of Slater determinants due to the holes in the d shell is still $\binom{20}{14} = 38\,760$. It is not only a practical impossibility but an unenlightening exercise to perform SCF calculations on all states arising from 38 760 determinants.

Since our main interest is in the electronic structure of the low-lying states, our procedure has been to determine a single set of molecular orbitals in an SCF calculation and then to perform CI calculations to determine all states that arise when two atoms interact in their ground term. This procedure, of course, does not provide the optimum description of each state, individually, but we believe it results in a balanced description of the many low-lying electronic states.

SCF Calculations on Ru_2. The SCF calculations were performed to determine a set of molecular orbitals that can be utilized in CI calculations describing all low-lying states of the molecule. For initiation of the SCF calculations, a configuration is to be chosen having an SCF wave function that describes a bound state, that is, so that the total energy of the molecule at a reasonable internuclear distance is lower than the sum of the energies of the free atoms in their ground states. However, this criterion is more easily stated than fulfilled. On the basis of experience with other M_2 molecules, we first assumed that the molecular orbital $5s\sigma_g$ would play an important role in the bonding in Ru_2, and we therefore primarily considered configurations in which $5s\sigma_g$ was doubly occupied.

Of the many possible configurations arising because of the d orbital part of the wave function, 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 there is an even distribution of electrons in bonding and antibonding molecular orbitals; such an arrangement will lead to correct atomic configurations in the dissociation limit. Our previous work on V_2, Fe_2, Co_2, and Ni_2 has shown that it is essential to choose the wave function so that the d orbital part dissociates correctly, at least for these dimers of the first transition-metal row. This might, however, be less critical for Ru_2 since the maxima of charge distributions are considerably further away from the nuclei in the 4d orbitals of the second-row transition metals than in the corresponding 3d orbitals of the first-row transition metals. Thus, the maximum of the charge distribution for the 4d orbital of Ru is at 1.18 au while it is at 0.74 au for the 3d orbital of Fe.[13] It was considered one of the goals of the work to find out how Ru_2 would behave in this respect.

We performed a number of SCF calculations on Ru_2 at the internuclear distance 5.006 au, which is slightly shorter than the nearest-neighbor distance, 5.060 au, in the metal. We first treated a $^1\Sigma_g^+$ state arising from the $(4d\sigma_g)^2 (4d\pi_u)^4 (4d\delta_g)^4 (4d\delta_u)^4 (5s\sigma_g)^2$ configuration; this seemed a reasonable choice, since, from an elementary viewpoint, the $4d\delta_u$ orbital should be less antibonding than the $4d\pi_g$ and the $4d\sigma_u$ orbitals. However, SCF calculations on this state resulted in an energy approximately 0.5 au (13.6 eV) above the dissociation limit. Other states of the same kind, that is, with all bonding orbitals fully occupied and the remaining electrons distributed among other antibonding orbitals, also had energies far above the dissociation limit.

In Table II we have listed results of SCF calculations on a few selected states of Ru_2. It can be seen that only the states capable of giving correct dissociation of the 4d shell have energies close to or below the dissociation limit. The last two calculations in Table II were not performed on pure states but were averaged over different orbital angular momenta.

Table II. SCF Calculations on Ru_2 at the Internuclear Distance 5.006 au

state	configuration						energy, au[a]
	$4d\sigma_g$	$4d\pi_u$	$4d\delta_g$	$4d\delta_u$	$4d\pi_g$	$4d\sigma_u$	
$^7\Delta_u$	2	4	3	2	2	1	0.234 072
$^7\Sigma_u^+$	1	4	2	2	4	1	0.012 919
b	2	2	3	3	2	2	−0.005 847
b	1	3	3	3	3	1	−0.000 661

[a] Energy of Ru_2 minus energy of two Ru atoms both in the $^5F(4d)^7(5s)^1$ ground state. [b] Calculations performed on configurations averaged over orbital angular momenta.

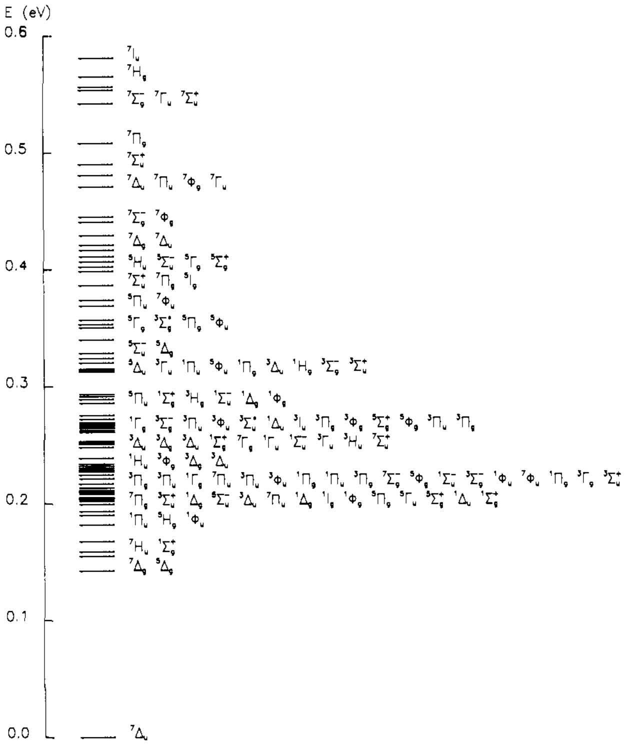

Figure 1. Relative energies in eV of the 112 low-lying states of Ru_2 at an internuclear distance of 5.006 au. States are listed in order of increasing energy.

Two sets of orbitals, one optimized for the configuration $(4d\sigma_g)^1 (4d\pi_u)^3 (4d\delta_g)^3 (4d\delta_u)^3 (4d\pi_g)^3 (4d\sigma_u)^1 (5s\sigma_g)^2$ and the other set for $(4d\sigma_g)^2 (4d\pi_u)^4 (4d\delta_g)^3 (4d\delta_u)^2 (4d\pi_g)^2 (4d\sigma_u)^1 (5s\sigma_g)^2$, were utilized in CI calculations describing all low-lying states. The calculations allowed full reorganization within the 4d shells. This is equivalent to including sextuple excitations relative to a reference configuration, and it assures correct dissociation of the d orbital part of the wave function. Since the $5s\sigma_g$ orbital, however, was kept doubly occupied, the total wavefunction does not dissociate correctly in these calculations. This is probably of minor importance for the relative energies of the low-lying states at an internuclear distance close to the equilibrium distance of the molecule.

Results

In Figure 1 we have shown all 112 low-lying states resulting from interaction between two Ru atoms in the $^5F(4d)^7(5s)^1$ term. The calculations were carried out at the internuclear distance 5.006 au. The calculations were performed in the subgroup D_{2h} of the full symmetry group $D_{\infty h}$ of the Ru_2 molecule. The number of configurations included within each symmetry species of D_{2h} varies from approximately 30 in the septet states to approximately 870 in the triplet states. The calculations were performed with each of the previously mentioned optimum sets of orbitals because we wanted to investigate the influence of the orbitals in the final results. The ground state resulting from both sets of calculations was a $^7\Delta_u$ state, which originates from similar occupations of the natural orbitals, namely $(4d\sigma_g)^{1.66} (4d\pi_u)^{3.28} (4d\delta_g)^{2.72} (4d\delta_u)^{2.44} (4d\pi_g)^{2.62} (4d\sigma_u)^{1.28}$ and $(4d\sigma_g)^{1.72} (4d\pi_u)^{3.36} (4d\delta_g)^{2.71} (4d\delta_u)^{2.37} (4d\pi_g)^{2.57} (4d\sigma_u)^{1.27}$. The first state, which has a slightly larger

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(12) Claydon, C. R.; Carlson, K. D. *J. Chem. Phys.* **1968**, *49*, 1331.

(13) Mann, J. B. La-3691 "Atomic Structure Calculations II, Hartree-Fock Wavefunctions and Radial Expectation Values: Hydrogen to Lawrencium"; Los Alamos Scientific Laboratory 196.

Table III. Energies and Major Configurations of the Wave Functions of the Ground $^7\Delta_u$ State of Ru_2 as Resulting from CI Calculations Employing Two Different Sets of Orbitals

	contribution, %	
configuration	$(\sigma_g)^1 (\pi_u)^3 (\delta_g)^3 (\delta_u)^3 (\pi_g)^3 (\sigma_u)^{1\,a}$ −8882.229 434 au	$(\sigma_g)^2 (\pi_u)^4 (\delta_g)^3 (\delta_u)^2 (\pi_g)^2 (\sigma_u)^{1\,a}$ −8882.223 181 au
1 $(\sigma_g)^2 (\pi_u)^4 (\delta_g)^3 (\delta_u)^2 (\pi_g)^2 (\delta_u)^1$	46.05	51.85
2 $(\sigma_g)^1 (\pi_u)^2 (\delta_g)^2 (\delta_u)^3 (\pi_g)^4 (\sigma_u)^2$	13.26	11.92
3 $(\sigma_g)^2 (\pi_u)^3 (\delta_g)^2 (\delta_u)^3 (\pi_g)^3 (\sigma_u)^1$	12.62	13.35
4 $(\sigma_g)^1 (\pi_u)^3 (\delta_g)^3 (\delta_u)^2 (\pi_g)^3 (\sigma_u)^2$	8.92	8.37
5 $(\sigma_g)^1 (\pi_u)^3 (\delta_g)^3 (\delta_u)^3 (\pi_g)^3 (\sigma_u)^1$	7.45	4.12
6 $(\sigma_g)^2 (\pi_u)^3 (\delta_g)^2 (\delta_u)^2 (\pi_g)^3 (\sigma_u)^2$	3.85	4.56
7 $(\sigma_g)^2 (\pi_u)^2 (\delta_g)^3 (\delta_u)^4 (\pi_g)^2 (\sigma_u)^1$	2.89	2.26
8 $(\sigma_g)^1 (\pi_u)^2 (\delta_g)^4 (\delta_u)^3 (\pi_g)^2 (\sigma_u)^2$	1.80	1.25

[a] Starting Configuration.

population in the antibonding orbitals, is based on orbitals optimized for the $(4d\sigma_g)^1 (4d\pi_u)^3 (4d\delta_g)^3 (4d\delta_u)^3 (4d\pi_g)^3 (4d\sigma_u)^1 (5s\sigma_g)^2$ configuration. The last-mentioned state is based on orbitals optimized for $(4d\sigma_g)^2 (4d\pi_u)^4 (4d\delta_g)^3 (4d\delta_u)^2 (4d\pi_g)^2 (4d\sigma_u)^1 (5s\sigma_g)^2$.

In Table III we have listed the energies and the percent contributions from all major configurations in the $^7\Delta_u$ ground state resulting from CI calculations employing the different sets of orbitals. From this table it is clear that the wave functions based on the different orbitals are in qualitative agreement, which is, of course, a very encouraging result. It is now apparent that the orbitals in the first case were optimized for a minor configuration (no. 5 in Table III) of the wave function, while they were optimized for the predominant configuration in the second case. However, it will be noted that the orbitals optimized for the minor configuration resulted in the lower energy of the $^7\Delta_u$ state.

The lowest excited state resulting from either calculation was $^7\Delta_g$, with the energy difference between the ground state and the lowest excited state being 1152 cm^{-1} in the first case and 1543 cm^{-1} in the second case. In general, the spacing between the 112 states calculated from orbitals optimized for the d shell configuration $(\sigma_g)^2 (\pi_u)^4 (\delta_g)^3 (\delta_u)^2 (\pi_g)^2 (\sigma_u)^1$ are greater than the spacing between the states based on orbitals optimized for the $(\sigma_g)^1 (\pi_u)^3 (\delta_g)^3 (\delta_u)^3 (\pi_g)^3 (\sigma_u)^1$ configuration. This is not surprising, since the higher lying states involve a growing population in the antibonding orbitals.

Of course, it is probably a practical impossibility to reach a quantitatively correct description of all 112 low-lying states, but we believe the results presented here offer a realistic qualitative description of the many low-lying states. However, spin–orbit coupling, which is not considered in the present work, would doubtless cause mixing and reordering of the states shown in Figure 1. The principal objective of our work has been to gain insight into the bonding in Ru_2 and similar molecules. The present results provide a point of departure for further calculations, in which spin–orbit coupling as well as polarization functions should be included so as to obtain a definitive ordering of the states and a more quantitative potential energy curve.

The Fe_2 molecule,[5b] which is isoelectronic to Ru_2, also has a $^7\Delta_u$ ground state, but with a somewhat different occupation of the d shell: $(\sigma_g)^{1.57} (\pi_u)^{3.06} (\delta_g)^{2.53} (\delta_u)^{2.47} (\pi_g)^{2.89} (\sigma_u)^{1.47}$. Relative to the configuration of Ru_2 the configuration of Fe_2 has an increased population in the antibonding orbitals, approaching equal distributions of electrons in bonding and antibonding orbitals: There is a net excess of only 0.33 bonding electrons. This is consistent with the essentially nonbonding character of the 3d electrons in Fe_2. Furthermore, for Fe_2 all 112 low-lying states form a dense band without an energy gap between the ground state and the first excited state.

Table IV. Mulliken Population Analysis of the Valence Orbitals of the $^7\Delta_u$ Ground State of Ru_2 As Determined in a CI Calculation at an Internuclear Distance of 5.006 au

		orbital analyses, %			
orbital	overlap population	s	p	d	occupation no.
σ_g	0.67	92	4	4	1.94
σ_g	0.15	5	0	95	1.67
σ_u	−0.16	3	0	97	1.27
σ_u	−0.06	82	18	0	0.06
π_u	0.22	0	0	100	3.31
π_g	−0.13	0	1	99	2.60
δ_g	0.03	0	0	100	2.73
δ_u	−0.03	0	0	100	2.42
total	0.69				

Table V. Total Energies and Spectroscopic Constants of the Ru_2 Molecule in Its $^7\Delta_u$ Ground State As Resulting from Three Different CI Calculations

	calculation			
full reorg within	total energy at 5.006 au, au	equilib dis, au	dissoc energy, eV	vibrat freq, cm^{-1}
4d shell	−8882.229 435	5.17	0.42	107
4p and 4d shells	−8882.236 363	5.12	0.60	110
4d and 5s shells	−8882.237 503	5.13	0.64	116

To investigate the ground state of Ru_2 further, we performed the following additional calculations. Orbitals were optimized for the configuration $(4d\sigma_g)^1 (4d\pi_u)^3 (4d\delta_g)^3 (4d\delta_u)^3 (4d\pi_g)^3 (4d\sigma_u)^1 (5s\sigma_g)^2$ at the internuclear distances 4.25, 4.50, 4.75, 5.60, and 8.0908 au. The resulting orbitals were utilized in CI calculations allowing full reorganization within the 4d and 5s shells. This is equivalent to including octuple excitations relative to a reference configuration and, since the $5s\sigma_u$ orbital is included in the CI calculation, allows for proper dissociation of the total wave function into two ground-state atoms. In terms of a valence bond description we include covalent as well as ionic structures, and through CI calculations we optimize their relative contributions to the wave function. The final CI calculation included 1152 configurations, and it resulted in a $^7\Delta_u$ ground state with the natural orbital population $(4d\sigma_g)^{1.67} (4d\pi_u)^{3.31} (4d\delta_g)^{2.73} (4d\delta_u)^{2.42} (4d\pi_g)^{2.60} (4d\sigma_u)^{1.27} (5s\sigma_g)^{1.94} (5s\sigma_u)^{0.06}$. It is noted that inclusion of the 5s orbitals in the CI calculation causes only an insignificant increase in population of the bonding orbitals.

Table IV shows Mulliken population analysis of the $^7\Delta_u$ ground state as determined in the CI calculations described above. The major overlap population is due to the $5s\sigma_g$ molecular orbital, although the overlap populations due to the d orbitals are larger than for Fe_2. Furthermore, the hybridization is insignificant except for in the $5s\sigma_u$ orbital, but this has only a very small population.

Since it has been shown that for the Ti atom the calculated term splittings are significantly improved by including excitations from the 3s and 3p orbitals,[14] we performed CI calculations on the $^7\Delta_u$ ground state of Ru_2 allowing full reorganization between the 4p and the 4d orbitals while the $5s\sigma_g$ orbital was kept doubly occupied. The calculation included 1038 configurations. It resulted in a $^7\Delta_u$ ground state with the d shell occupation $(\sigma_g)^{1.69} (\pi_u)^{3.30} (\delta_g)^{2.72} (\delta_u)^{2.42} (\pi_g)^{2.62} (\sigma_u)^{1.28}$ at 5.006 au. This configuration is almost identical with the configuration of the $^7\Delta_u$ state as resulting from the CI calculations allowing full reorganization between the 4d and 5s shells. Comparison of the total energies resulting from the two calculations (Table V) indicates that excitations between 4p and 4d orbitals are just as important as excitations between 4d and 5s orbitals. This indicates that for an optimum result both types of excitations should be included. However, such a calculation would entail nearly a million configurations and we do not contemplate carrying it out.

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(14) Freed, K. F., private communication.

Table VI. Configuration of the $^7\Delta_u$ Ground State of Ru_2 as a Function of Internuclear Distance

	configuration							
dist, au	$d\sigma_g$	$d\pi_u$	$d\delta_g$	$d\delta_u$	$d\pi_g$	$d\sigma_u$	$s\sigma_g$	$s\sigma_u$
4.25	1.86	3.68	2.83	2.20	2.31	1.13	1.96	0.04
4.50	1.80	3.57	2.79	2.27	2.40	1.18	1.96	0.05
4.75	1.74	3.44	2.75	2.34	2.50	1.22	1.95	0.05
5.006	1.67	3.31	2.73	2.42	2.60	1.27	1.94	0.06
5.60	1.55	3.10	2.71	2.57	2.74	1.33	1.90	0.11
8.0908	1.01	3.00	2.99	2.99	3.00	1.01	1.31	0.69

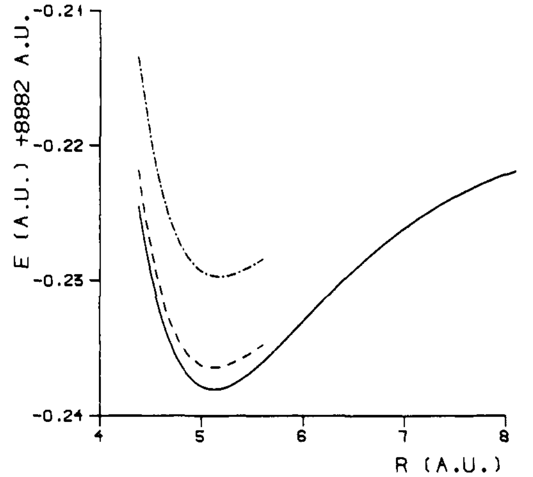

Figure 2. Potential energy curves for the $^7\Delta_u$ ground state of Ru_2 as resulting from three different CI calculations. The solid curve results from full reorganization within the 4d and 5s shells. The dashed curve shows the result of full reorganization within the 4p and 4d shells, and the dashed-dotted curve is the result of full reorganization within the 4d shells.

In Table V we compare spectroscopic constants of the Ru_2 molecule in the ground $^7\Delta_u$ state as determined in three different CI calculations. The equilibrium distance and the vibrational frequency has been determined by approximating the potential energy curves with Morse curves. The dissociation energies were determined as differences between the energies of the Ru_2 molecule at the equilibrium distance and the sum of the HF energies of the atoms in their ^5F ground term. This procedure is internally consistent because the CI wave functions include only molecular correlation, which vanishes when the atoms are separated.

The potential energy curves for the $^7\Delta_u$ ground state of Ru_2 as obtained by the three CI calculations are shown in Figure 2. The similarity of the spectroscopic constants pertaining to each of these curves (Table V) is surprising since it is only the wave function resulting from full reorganization within the 4d and 5s shells that dissociates correctly to two ground-state atoms. We had, therefore, expected a smaller curvature of the potential energy curve in this case. The similarity is probably due to the diffuseness of the 5s orbitals, which enhances the ionic character of the wave function at internuclear distances near the equilibrium value.

Unpublished calculations we have performed on the Nb_2 molecule reveal that the minima of the potential energy curves are located at shorter internuclear distances for low spin states than for high spin states. This indicates that the equilibrium distance of the molecule decreases with an increasing d-orbital participation in bonding. These results made us wonder if we would find a similar effect for the Ru_2 molecule, and we therefore performed additional CI calculations on the low spin states as functions of the internuclear distance, but no such effect was observed for the Ru_2 molecule.

Discussion

Experimental studies of transition-metal diatomic molecules and related small molecules are currently being pursued in many laboratories, and data are being accumulated rapidly. The Ru_2 molecule, however, has not yet been observed; the results of our calculations cannot, therefore, be compared to known values of the molecular parameters, but instead our work provides a genuine test of the predictive power of ab initio calculations for molecules of this sort. In comparing the computational results with experimental values that will doubtless become available in the future, several qualifications should be kept in mind.

First, let us discuss the estimated internuclear distance. For several reasons, the value we have obtained, 5.13 au (2.71 Å), must be considered an upper limit, and we can make an estimate of the likely error. One reason we have overestimated the distance is because relativistic effects have been neglected. Although the outer orbitals in the heavier atoms are themselves nonrelativistic, the relativistic contraction of the inner orbitals causes a shift in the charge distribution of the outer orbitals.[15] Thus, due to the relativistic effects, the 5s orbital of Ru contracts, so the maximum in its charge distribution moves 0.14 au closer in the nucleus. The Ru 4d orbital, however, expands slightly; its maximum of charge distribution gets removed 0.01 au from the nucleus.[16]

A recent pseudopotential calculation on Ag_2[17] resulted in a bond shortening of 0.2 au due to relativistic effects. The data above indicate that the calculated bond length in Ru_2 would be likely to undergo a comparable shortening in a relativistic calculation.

It is also pertinent that in a very recent pseudopotential calculation[18] on Cu_2 it was found that an extensive perturbational CI calculation shortened the bond by 0.29 au, thus bringing the calculated distance nearly into agreement with the experimental value.

On the basis of these considerations, we would hazard the prediction that the experimental internuclear distance for Ru_2 will be 0.20 to about 0.35 au shorter than the value given by our calculation. Thus, we forecast a value in the range of 4.80–4.90 au (2.54–2.59 Å) for the internuclear distance in Ru_2. This is still considerably longer than the values found in various compounds containing (formally) the Ru_2^{5+} ion, where the distances[19] are in the range 2.25–2.30 Å. However, the bonding in the latter is quite different,[20] depending mainly on 4d–4d interactions, with the 4d orbitals considerably contracted by the ionization of the dinuclear unit. The predicted internuclear distance of 4.80–4.90 au is less than that known for ruthenium metal,[21] 5.06 au, which we think is a reasonable relationship.

While there is no experimentally determined value for the dissociation energy of Ru_2 there are several estimates based on empirical rules.[22,23] These rules, which have been successful for other transition metal molecules, give for Ru_2 the values 3.04 eV[22] and 3.19 eV,[23] which are much greater than the calculated value presented in Table V. Of course, we would expect the calculated dissociation energy to be too low, since we do not include extensive correlation of the bonding electrons in our calculations. In the present study we were not striving to obtain spectroscopic constants of high accuracy, but rather we were aiming at reaching a deeper understanding of the nature of the chemical bond between the two Ru atoms.

Let us turn now to the description of the bond between the ruthenium atoms. Although it is evident from the population analysis in Table IV that the $5s\sigma_g$ molecular orbital is important for formation of the chemical bond between the two Ru atoms, the 4d electrons also play an important part in bond formation. This is reflected in the comparatively large population in the bonding d orbitals relative to the antibonding orbitals in the $^7\Delta_u$ ground state. Here again, as in the case of Mo_2[5e], we see that for M_2 molecules in the second transition series we have a qualitatively different situation from that in the first transition series, where the M–M bonds, if they are significant at all, are

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(15) Desclaux, J. P.; Kim, Y. K. *J. Phys. B* **1975**, *8*, 1177.

(16) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.

(17) Basch, H., ref 4; p 149.

(18) Pelissier, M. *J. Chem. Phys.* **1981**, *75*, 775.

(19) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.

(20) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

(21) Donahue, J. "The Structures of the Elements", Wiley: New York, 1974; p 214.

(22) Gingerich, K. A. *Symp. Faraday Soc.* **1980**, *14*, 109.

(23) Brewer, L.; Winn, J. S. *Symp. Faraday Soc.* **1980**, *14*, 126.

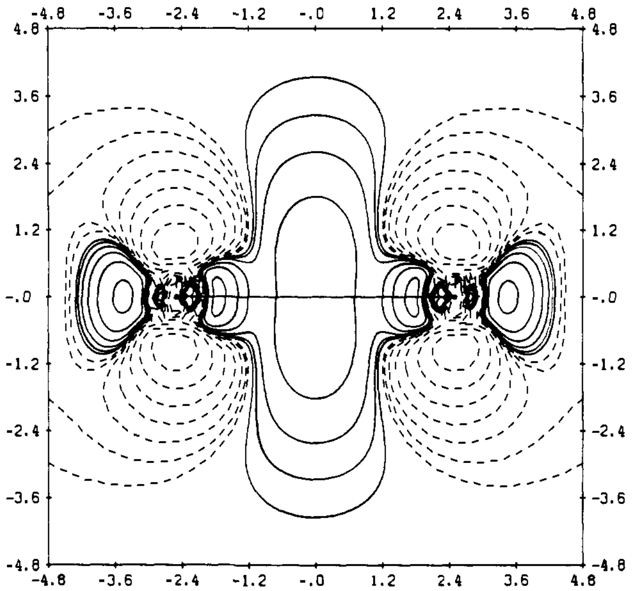

Figure 3. Deformation electron density map for Ru_2. Solid contours show enhanced electron charge relative to the superpositioned atoms; dashed contours show diminished charge. The smallest contour value is 0.000625 e/au^3. Adjacent contours differ by a factor of 2.

due almost entirely to a $4s\sigma_g$ electron pair. In the molecules of the second transition series (and, presumably, also the third), the role of the d orbitals is greatly enhanced.

Previous treatments[24,25] of the Mo_2 molecule by the SCF-Xα-SW method gave a simple orbital picture of the bonding, in which the following pattern of filled and lowest unfilled Mo's was obtained.

$$(4d\sigma_g)^2\,(4d\pi_u)^4\,(4d\delta_g)^4\,(5s\sigma_g)^2\,(4d\delta_u)^0\,(4d\pi_g)^0\,...$$

This corresponds to six pairs of bonding electrons. A reasonable extrapolation to Ru_2, which has four more electrons, would add these to one or more antibonding orbitals, thus giving a net bond order of 4. However, an ab initio calculation, with the inclusion of an amount of CI comparable to that included here in the Ru_2 calculation, gave a natural orbital population of

$$(4d\sigma_g)^{1.88}\,(4d\pi_u)^{3.78}\,(4d\delta_g)^{3.42}\,(5s\sigma_g)^{1.92}\,(5s\sigma_u)^{0.08}\,(4d\delta_u)^{0.58}\,(4d\pi_g)^{0.22}\,(4d\sigma_u)^{0.12}$$

which corresponds to a net of only 5.00 bonding electron pairs.

From the information in Tables II and III, however, it follows that it is even less accurate to try to describe the Ru_2 molecule in a simple molecular orbital picture. Although the leading configuration of the wave function contributes about 50%, it does not, by itself, adequately describe the molecule since the total energy of the molecule obtained with this configuration is far above the dissociation limit. Only through interaction with the additional configurations listed in Table III do we obtain a wave function that describes a bound molecule. Compared to the leading configuration, $(4d\sigma_g)^2\,(4d\pi_u)^4\,(4d\delta_g)^3\,(4d\delta_u)^2\,(4d\pi_g)^2\,(4d\sigma_u)^1\,(5s\sigma_g)^2$, the wave function resulting from the CI calculations shows a considerable transfer of electrons from the bonding to the antibonding d orbitals. Thereby the net bonding effect of the d electrons is decreased, while their localization on the individual atoms is enhanced. For the configuration that best describes the $^7\Delta_u$ ground state at 5.006 Å (vide supra), we have a net of 1.69 bonding electron pairs.

Finally, we have calculated a deformation electron density map, in which the sum of the two atomic charge distributions is subtracted from the molecular charge distribution calculated for the $^7\Delta_u$ ground state. This is shown in Figure 3. This shows clearly that bond formation results in a considerable buildup of charge between the two atoms.

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Registry No. Ru_2, 12596-99-5.

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(24) Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987.

(25) Bursten, B. E.; Cotton, F. A., in ref 4.