sorptivities (ca. 10^3 M^{-1} cm^{-1} at peak maxima) were difficult to estimate. The spectra are sensitive both to the solvent and to the extent of conjugation in the bridging ligand L and are thus assigned to metal-to-ligand (d to π^*) charge-transfer transitions. Again, as previously found for the system $[W(CO)_5]_2L$,[1] the π^* levels in the bridging ligands L can be placed in the relative order BPA > BPY > BPE.

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Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Electronic Structure of Octachloroditungstate(II)

Ramiro Arratia-Perez and David A. Case*

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The existence of quadruple bonds between atoms of transition metals has been recognized for about 20 years.[1] These systems are characterized by having singlet ground states, short metal-metal bond lengths, and eclipsed conformations for the M_2X_8 species. In general, the excited states and photoelectron spectra of these systems are in good agreement with results of Xα-scattered-wave (SW) calculations.[2-4] A large number of such calculations have been made, and in recent years attention has been paid to possible relativistic effects in multiple bonds of the third transition series, by using quasi-relativistic calculations on complexes of tungsten and rhenium.[5,6] These calculations include the mass-velocity and Darwin corrections but omit the spin-orbit effect.[7,8] Here we report the first fully relativistic SW calculation on a molecule containing a multiple metal-metal bond, comparing relativistic and nonrelativistic results for $W_2Cl_8^{4-}$.

Our computational method incorporates the same approximations as conventional SW calculations but uses the Dirac equation rather than the Schroedinger wave equation as a starting point. Hence, all relativistic effects at the one-electron level are included. The development and applications of this method have recently been reviewed.[4,9] A D_{4h} geometry was assumed, with W-W and W-Cl bond lengths of 2.257 and 2.429 Å, respectively, and a W-W-Cl angle of 103.5°.[10] Our chlorine sphere radius (1.41 Å) is the same as that used in an earlier nonrelativistic calculation by Cotton and Kalbacher (CK);[11] the tungsten sphere radius (1.35 Å) is slightly larger than that used in the CK calculation since we assume a longer W-W bond (2.26 vs. 2.20 Å). Our nonrelativistic results were obtained from the Dirac program by setting the speed of light to a very large value (10^{15} au); except for the small change in geometry, however, they are identical with the CK results. A Watson sphere of charge 5+ and radius equal to that of the outer sphere (4.34 Å) was used to neutralize the charge of the cluster. Each iteration of the self-consistent calculation required about 5 min on a Burroughs B7800 computer; 38 iterations were required to converge the potential to a relative uncertainty of 8×10^{-5}.

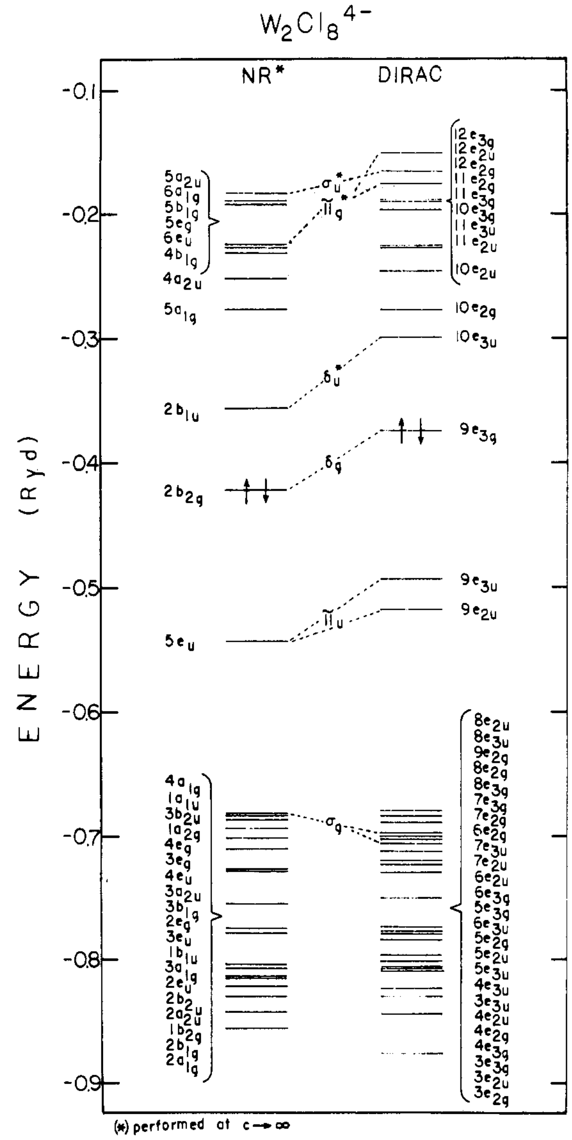

Figure 1. Nonrelativistic (NR) and relativistic (DIRAC) orbital energies for $W_2Cl_8^{4-}$.

Molecular orbital energies are shown in Figure 1. The principal relativistic shifts are similar to those seen in earlier quasi-relativistic studies:[5,6] the π_u, δ_g, and δ^*_u metal levels are shifted upward, while the metal σ_g bonding level is stabilized. The relative splittings among the upper three levels change only slightly (0.1-0.2 eV) upon incorporation of relativistic effects, whereas the relative distance between the σ_g and the upper levels increases by 0.8-0.9 eV. The predicted spin-orbit splitting of the π_u orbital is 0.33 eV, compared to a value of 0.4 eV seen in both $W_2Cl_4[P(CH_3)_3]_4$[5] and $W_2(mph)_4$.[12] These two compounds show a σ_g-π_u($j = {}^1/_2$) splitting of 2.61 and 2.9 eV, respectively (calculated 2.44 eV), and splittings

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Table I. Valence Populations for $W_2Cl_8{}^{4-}$

l	j	non rel		rel	
W: s	$^1/_2$	0.355		0.553	
p	$^1/_2$	0.177	2.00[a]	0.233	1.61[a]
	$^3/_2$	0.354		0.376	
d	$^3/_2$	1.935	1.50	2.136	1.20
	$^5/_2$	2.902		2.561	
f	$^5/_2$	0.114	1.33	0.110	1.42
	$^7/_2$	0.152		0.156	
total W		5.989		6.125	
Cl: s	$^1/_2$	1.959		1.960	
p	$^1/_2$	1.848	2.00	1.834	2.00
	$^3/_2$	3.696		3.674	
total Cl		7.503		7.468	

[a] Ratio of $j = l + {}^1/_2$ to $j = l - {}^1/_2$ populations.

of 1.24 and 2.0 eV for $\pi_u(j = {}^3/_2)$–δ_g (calculated 1.61 eV). Hence the spin–orbit and environmental splittings of the tungsten levels are in fairly good accord with values for comparable molecules.

Several unoccupied levels are also shown in Figure 1, along with the corresponding nonrelativistic results, which were not reported by CK. The δ_g–δ^*_u energy splitting is about the same in the nonrelativistic and Dirac calculations. All but four of the orbitals above δ^*_u have more than three-fourths of their charge density in the intersphere and outer-sphere regions. These very diffuse orbitals would probably change a lot in energy and character if a more realistic description of the crystalline environment were included in the calculations. The $10e_{3g}$, $12e_{2g}$, $12e_{2u}$, and $12e_{3g}$ orbitals are more localized and could represent the upper states in optical transitions. The last three of these orbitals are the π^*_g and σ^*_u combinations of tungsten d orbitals, while the $10e_{3g}$ state is a mixture of metal d orbitals and chlorine s orbitals; it is also fairly diffuse, with 31% of the charge distribution in the outer-sphere region. The existence of this "extra" orbital with significant δ_g character, plus the high density of other diffuse states, makes it clear that simple crystal field arguments are of limited use in describing the properties of these very highly excited states.

Total electron populations[13] are given in Table I. The trends seen upon adding relativistic effects can be understood by remembering that in the W *atom*, relativistic effects lower the s- and p-orbital energies and raise the valence d orbitals. Thus, in the molecule, the population in the 6s and 6p orbitals of tungsten increases while the 5d occupation decreases. These trends may also be seen in the orbital energies in Figure 1: the π and δ orbitals increase in energy, whereas the σ_g orbital (with about 7% W s character) decreases slightly. Within the d orbitals, the lower energy $d_{3/2}$ orbitals are favored over $d_{5/2}$: the $d_{5/2}$:$d_{3/2}$ population ratio is 1.2 in the DSW calculation; a value of 1.5 is required by symmetry in the nonrelativistic results. This bias in favor of $d_{3/2}$ is expected to have an important influence on the intensities and angular distributions seen in photoelectron spectra;[14] calculations of these properties are planned.

It is instructive to break the four-component spinors into their two-component (Pauli) counterparts. To do this, we neglect the third and fourth, "small", components and assume that the radial function is the same in the two large components.[9,15] In this way each molecular orbital may be decomposed into "spin-up" and "spin-down" parts, corresponding to its functional behavior in components one and two, respectively. Results of this decomposition for the metal-based orbitals are shown in Table II. In the nonrelativistic limit (not shown) pure spin states are obtained, and one measure of the extent of spin–orbit mixing is the amount of minority spin mixed into the relativistic orbital. Within the tungsten spheres, this contamination is always less than 2%, except for the $7e_{2g}$ (σ_g) and the unoccupied $10e_{3g}$ (π^*_g) orbitals, for which the minority spins are 4% and 12% of the majority spin, respectively. The upper (e_{3u}) component of the π_u orbital, which is spin–orbit coupled to functions of δ_u symmetry, contains about 5 times as much minority spin as the lower (e_{2u}) component, which mixes with functions of σ_u symmetry. This difference is in accord with the smaller π_u–δ^*_u energy difference compared to that of π_u–σ^*_u. More surprising behavior is seen for the chlorine components of the $7e_{2g}$ and $8e_{2g}$ orbitals, which together comprise the metal–metal σ bond. Here the spin-down W 5d orbitals mix with a combination of Cl 3p orbitals that are primarily spin-up. (The other row of the e_{2g} irreducible representation contains the opposite spin pattern.) Contour maps for the $8e_{2g}$ orbital are shown in Figure 2. The spin-down component of this orbital is virtually identical with the metal–metal σ bond in the nonrelativistic complex (cf. Figure 8 of ref 11), and a largely nonbonding set of chlorine p orbitals is seen in the spin-up component. This strong spin mixing is undoubtedly caused by the close spacing of the energy levels in this region of the spectrum (see Figure 1). It is not expected to have an important effect on the strength of the metal–metal bond, but it could make it difficult to identify the σ bond in the photoelectron spectrum.

In conclusion, we have reported the first fully relativistic molecular orbital calculation on a complex with a multiple metal–metal bond.[16] Except for the situation involving the

Table II. Pauli Decomposition for Individual Orbitals[a]

orbital character			$10e_{3u}$	$9e_{3g}$	$9e_{3u}$	$9e_{2u}$	σ_g	
			δ^*_u	δ_g	π_u	π_u	$8e_{2g}$	$7e_{2g}$
2 W:	s	↓	--	--	--	--	0.0810	0.0573
	p	↑	0.0060	0.0000	0.0455	0.0496	0.0018	0.0001
		↓	--	--	--	0.0000	0.0470	0.0396
	d	↑	0.0066	0.0055	0.8046	0.7951	0.0000	0.0144
		↓	0.9355	0.9114	0.0046	0.0008	0.3910	0.3015
	f	↑	0.0040	0.0003	0.0270	0.0277	0.0013	0.0019
		↓	0.0021	0.0080	0.0000	0.0000	0.0128	0.0107
total:		↑	0.0166	0.0058	0.8781	0.8724	0.0031	0.0164
		↓	0.9375	0.9194	0.0046	0.0008	0.5318	0.4091
8 Cl:[b]	p	↑	0.0004	0.0006	0.1148	0.1247	0.3382	0.5269
		↓	0.0540	0.0733	0.0020	0.0007	0.1262	0.0477

[a] See text for method of calculation; dashed lines indicate values that are zero because of symmetry. [b] Contributions from the Cl s orbitals are all less than 0.001.

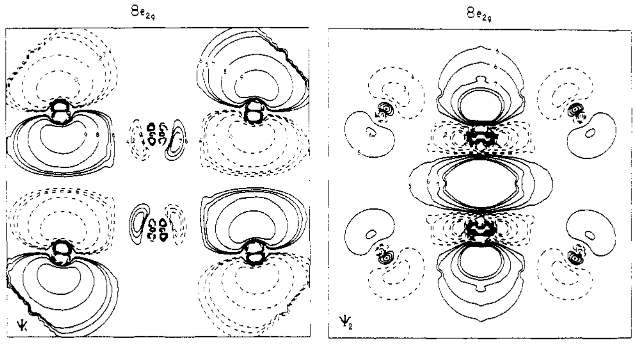

Figure 2. Contours of the $8e_{2g}$ orbital in a plane containing 2 W and 4 Cl atoms. Contour values in (electrons/bohr^3)$^{1/2}$: for ψ_1 (0,9), (1,8), (2,7), (3,5), (4,6) = ±0.040, ±0.020, ±0.010, ±0.008, ±0.006; for ψ_2 (0,9), (1,8), (2,7), (3,6), (4,5) = ±0.080, ±0.068, ±0.044, ±0.022, ±0.011.

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(13) Values in Tables I and II include contributions from the intersphere and outer-sphere regions partitioned according to the algorithm given in: Case, D. A.; Karplus, M. *Chem. Phys. Lett.* **1976**, *39*, 33.

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metal σ orbital, described in the previous paragraph, the relativistic level shifts are small and are apparently well described by the simpler quasi-relativistic calculations. This is an important point, since it helps to validate the use of these simpler calculations in other molecules with metal–metal bonds. For detailed conclusions on photoelectron intensities and angular distributions, however, it is expected that results of the type described here will be most useful.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 81-17101. D.A.C. is an Alfred P. Sloan Foundation Fellow. We thank Cary Yang for useful discussions.

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Contribution from the School of Chemistry,
University of Western Australia,
Nedlands, Western Australia 6009, Australia

Use of the Bireciprocal Length–Energy Relationship To Predict the Structures of Boron Hydrides and the Structural Analogy between Boron Hydrides and Other Atom Clusters

D. J. Fuller and D. L. Kepert*

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Recently we[1] developed a new approach for the prediction of the structures of *closo*-boron hydrides $B_nH_n^{2-}$, in which each boron atom is considered to bond directly to all other boron atoms, the interaction depending only on the interatomic distance. A simple bireciprocal equation was used to relate energy u to internuclear distance d: $u = d^{-x} - d^{-y}$. The total energy is then $U = \sum u$. A good fit with experimental structures was found for low values of x and y, typical values being $x = 2$ and $y = 1$. The simplicity of this model allows the rapid assessment of a large number of complex molecular polyhedra in which the geometric parameters are free to vary in order to reach a minimum energy and to map out more clearly the potential energy surfaces needed to understand the intramolecular rearrangements of these molecules.

Housecroft and Wade[2] have criticized this approach by raising four main arguments that are now discussed in turn. Then follows a short discussion on the inadequacy of the supposed structural analogy between the boron hydrides and other atom clusters that is the basis of "Wade's rules".

(1) The first criticism is that the variation of energy U with size of the $B_nH_n^{2-}$ cluster is misleading, and it was pointed out that U/n is a linear function of n. There are a number of minor errors in Housecroft and Wade's work that should be corrected before dealing with the substance of this criticism:

(a) The U values cited[2] for $B_8H_8^{2-}$ and $B_{12}H_{12}^{2-}$ are correct, but they have been incorrectly converted to U/n values.

(b) The U values cited[2] for $B_6H_6^{2-}$ and $B_{10}H_{10}^{2-}$ are incorrect, the correct values being −3.6928 and −10.6933, respectively.[3]

(c) Housecroft and Wade have quoted the slope of the U/n vs. n line as equal to $0.133n$, which is a miscalculation or misprint; from their figures the slope is $-0.113n$. (The sign of U/n given in their equations is also incorrect.) If the correct values for U are used for all values of n from 6 to 12,[1,3] the relationship becomes

$$U/n = -0.113n + 0.058$$

(d) This linear relation between U/n and n corresponds to a quadratic relation between U and n and does not lead to "the implication that all these closo anions $B_nH_n^{2-}$ use their skeletal electron pairs with precisely the same efficiency".[2]

However the important point is that we believe that it is a gross misuse of our approach to compare bonding energies for differently sized clusters. In spite of categorical statements in Housecroft and Wade's paper, we did not advocate this application. The simple bireciprocal energy expression $u = d^{-2} - d^{-1}$ is normalized neither with respect to energy units nor with respect to length units, and it was clearly stated[1] that both u and d are in arbitrary units. Normalization procedures, for example using the expression $u = a(d^{-2} - cd^{-1})$, lead to different values of the constants a (which normalizes with respect to energy) and c (which normalizes with respect to distance) for every cluster (see below).

(2) The second criticism is that the double-reciprocal potential does not lead to the correct size of the cluster. This comment arises from a misunderstanding of the properties of a bireciprocal expression and from a misreading of the original work. A simple bireciprocal potential $u = d^{-x} - d^{-y}$ cannot be used to predict the *size* of a molecule but can be used to predict its *shape*, the shape being defined either by the ratios of the bond lengths or by the angular coordinates plus the ratios of the radial coordinates. All distances are therefore in arbitrary units as clearly stated in the original work,[1] but these have been consistently misread as angstroms by Housecroft and Wade.

If desired, the calculated size of the cluster can be varied by modifying the potential to $u = d^{-2} - cd^{-1}$. The effect of decreasing c is to expand the u vs. d plot uniformly along the distance axis, leading to an increase in calculated size of the cluster but without change in shape. The known sizes of *closo*-$B_nH_n^{2-}$, where n = 6, 8, 9, 10, and 12, obtained from experimental crystal structures leads to

$$c \sim 1.30 - 0.033n$$

where the distances are now in angstroms.

(3) The third comment is the rather obvious observation that the relative number of cross-polyhedral terms increases as the number of atoms in the cluster increases.

In our approach it is the cross-polyhedral interactions that tend to make the cluster more spherical whereas the surface-polyhedral interactions tend to make the edge lengths of the polyhedron more equal. The experimental structures of $B_nH_n^{2-}$ molecules, with the exception of $B_6H_6^{2-}$ (see below), represent the balance between these two types of interaction and are best modeled by the particular bireciprocal potential we have chosen. The $B_6H_6^{2-}$ cluster is different from the other clusters as the octahedron is a regular polyhedron with all vertices equidistant from the polyhedron center and all edge lengths identical. There is therefore no conflict between the cross-polyhedral and surface-polyhedral interactions, and a regular octahedral structure is predicted for all values of x and y in the bireciprocal energy expression.

(4) The fourth comment concerns the partitioning of the total energy of $B_8H_8^{2-}$, $B_9H_9^{2-}$, and $B_{10}H_{10}^{2-}$ into the energy associated with the individual boron atoms. They find that the atoms with the highest coordination number are associated with the highest energy. Unfortunately the figures used to reach this conclusion are seriously in error. For example, they calculated that the five-coordinate atoms in $B_8H_8^{2-}$ are 36.6% more strongly bonding than the four-coordinate atoms, al-

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