Semiempirical Calculations on the Electronic Structure and Molecular Energy Levels of Complex Compounds

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Semiempirical CNDO calculations have been performed on several compounds containing either a transition-metal ion or atoms of the third row of the periodic table. The molecular energies obtained have been compared with those found using *ab initio* calculations, where available ($[\mathrm{NiF_6}]^{4-}$, $[\mathrm{CuCl_4}]^{2-}$, $[\mathrm{CuF_4}]^{2-}$, and $[\mathrm{NiF_4}]^{2-}$) or with already known photoelectron spectra.

A general qualitative agreement between semiempirical and *ab initio* or experimental results is found for both classes of compounds which encourages further investigation in this field.

THE possibility of obtaining an adequate description of the electronic structure of molecules containing a heavy atom is presently drastically limited by two factors: (i) computer time becomes prohibitive as *ab initio* calculations lead to reliable results, consequently these are limited to a restricted group of molecules and a generalisation of the results becomes difficult, (ii) the reliability of results from semiempirical procedures is dubious and they have to be constantly checked with experimental data or *ab initio* calculations.

As part of a programme concerned with the interpretation of the photoelectron (p.e.) spectra of complex compounds, we have investigated the possibility of using well-known semiempirical procedures to obtain information on the molecular energy levels of such complexes. A CNDO calculation has been performed on several compounds each containing a third-row atom or a transition metal, using a literature parameterisation method. For each compound a comparison is made with either an existing *ab initio* calculation or with experimental p.e. spectra.

The transition-metal complexes studied were $[\mathrm{NiF_6}]^{4-}$-(O_h), $[\mathrm{CuF_4}]^{2-}$(D_{4h}), $[\mathrm{CuCl_4}]^{2-}$(D_{4h} and T_d), and $[\mathrm{NiF_4}]^{2-}$-(D_{4h}), for which *ab initio* results have been reported, and $[\mathrm{VCl_4}]$ and $[\mathrm{TiCl_4}]$, where results may be compared with p.e. spectra. The calculations were performed using a program supplied by the Q.C.P.E. organisation modified for the inclusion of third-row atoms according to the method of ref. 1, and for one transition metal according to ref. 2, the only modification to these procedures being the use of Burn's exponent [3] for all the atoms involved. All calculations were carried out on the Univac 1108 computer of Rome University.†

RESULTS AND DISCUSSION

Molecules containing a Transition-metal Atom.—The results of the calculations on these molecules are deposited as Supplementary Publication No. 21244 (6 pp.).‡

Among the complexes listed, that allowing the most direct comparison with existing *ab initio* calculations is $[\mathrm{NiF_6}]^{4-}$ since the latter were carried out in the UHF scheme, the same adopted for all our open-shell calculations. This semi-empirical calculation is not only qualitatively similar to the results obtained from the *ab initio* calculation, which is the case for all the calculations reported here, but also reproduces both the energy range within which the *d*-orbitals fall and the energy differences between these orbitals and those of the ligands.

If we now take $[\mathrm{CuCl_4}]^{2+}$ as an example, the comparison may be extended to include a semi-empirical calculation of a modified INDO type, as well as the *ab initio* calculation. All three calculations give very similar results, although the INDO calculation carried out using the RHF method lends itself to a more direct comparison with the *ab initio* rather than with ours. Nevertheless, it may be noted that there are few differences between the CNDO and INDO results.

For all the calculations performed there are several important points of agreement with the *ab initio* calculations.

(i) The m.o.s of the metal which are predominantly *d* in character are at lower energy than the non-bonding and anti-bonding m.o.s of mainly ligand p_σ and p_π character.

(ii) The percentage *d*-participation is high (>90%) showing that the metal–ligand bond is only weakly covalent. (These two results are in disagreement with those obtained from the classical Wolfsberg–Helmholz semiempirical description,[4-6] which predicts a much higher covalence in the metal–ligand bond, with consequent increase in the energy of the mainly metal *d*-orbitals.)

(iii) The electronic ground-state described by the *ab initio* calculations $\{{}^2B_{1g}$ for $[\mathrm{CuF_4}]^{2-}$ and $[\mathrm{CuCl_4}]$, ${}^3A_{2g}$ for $[\mathrm{NiF_6}]^{4-}$, ${}^2T_2$ for $[\mathrm{CuCl_4}]^{2-}$ $(T_d)\}$, *i.e.* with the unpaired electrons on metal *d*-orbitals, is in agreement with our results, which give a spin density different from zero for practically the *d*-orbitals only.

On the negative side, we note that the energy interval

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† A single-molecule computation performed on the UNIVAC 1108 by means of our CNDO method needs *ca.* 30 s.; the time necessary for an *ab initio* minimal basis set calculation on the same molecules is not less than 1 h.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index Issue, for details.

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within which the *d*-orbitals fall is rather small, a defect intrinsic to the CNDO method which fails to discriminate clearly between the *d*-orbitals. In addition, the population analysis shows that the 4*s*- and 4*p*-orbitals of the central atom are too highly populated. Thus, for example, for $[NiF_6]^{4-}$, the *ab initio* calculation gives a population of 0·06 for the 4*p*-orbital and of 0·07 for the *s*-orbital, while the present CNDO calculations give 1·299 and 0·57, respectively. It is precisely this large mixing that causes some of the inversions between the non-bonding orbitals and the ligand anti-bonding orbitals.

For $[VCl_4]$ and $[TiCl_4]$, for which *ab initio* calculations are not available, the results have been compared with p.e. spectra reported in the literature.[7] These spectra are very similar to one another with the difference that in $[VCl_4]$ there is an extra band towards lower ionisation energy which has been attributed to the unpaired *d*-electron which occupies an antibonding molecular orbital of *e* symmetry. $[VCl_4]$ Also shows some splitting of the principal bands. Within the limits of application of Koopmans' theorem,[8] the CNDO calculations on $[VCl_4]$ give the same number of bands as found experimentally for the energy range investigated. For the first ionisation potential another comparison has been made by having performed a separate calculation on the ion $[VCl_4]^+$. A comparison of the calculation with that on the neutral molecule shows that the missing electron has been abstracted from a m.o. of predominantly metal *d*-character. According to this ΔSCF calculation the difference of the total energies for $[VCl_4]$ and $[VCl_4]^+$ improves the agreement with the experimental results, which leads us to conclude that the ionisation of m.o.s of metal *d*-character does not follow Koopmans' theorem, as has already been demonstrated by the *ab initio* and CNDO calculations of refs. 9—12.

TABLE

Experimental vertical ionisation potentials (eV), and values calculated from Koopmans' theorem.* The symmetry is in parenthesis

$[TiCl_4]$		$[VCl_4]$		$[GeCl_4]$		$[GeF_4]$		$[GeH_2Cl_2]$		$[GeH_2F_2]$	
Calc.	Expt.[7]	Calc.	Expt.[7]	Calc.	Expt.[13]	Calc.	Expt.[13]	Calc.	Expt.[14]	Calc.	Expt.[14]
14·13(t_1)	11·78(t_1)	23·68$^{\alpha}$ 12·34$^{\rho}$	9·41	13·21(t_2)	12·17(t_1)	17·74(t_2)	16·03(t_1)	13·19	11·42	15·1	13·0
15·11(t_2)	12·78(t_2)	14·21$^{\alpha}$ 14·06$^{\alpha,\beta}$	11·75	15·16(t_1)	12·64(t_2)	20·94(t_1)	16·56(t_2)	13·62	11·72	15·8	14·6
16·20(e)	13·23(e,t_2)	14·24$^{\alpha}$	12·7	16·59(e)	13·05(e)	21·40(e)	17·08(e)	13·84(a_2)	12·02	16·8(a_2)	16·3
17·01(t_2)		14·85$^{\alpha}$	12·88	19·95(t_2)	14·88(t_2)						
		15·18$^{\alpha,\beta}$	13·54			23·74(t_2)	18·54(t_2)	15·46	13·76		
17·01(a_1)	13·97(a_1)	16·78$^{\alpha,\beta}$	13·9	23·99(a_1)	18·38(a_1)						
		18·08$^{\alpha}$ 18·06$^{\alpha,\beta}$ 18·21$^{\alpha}$	14·4								
		18·67$^{\alpha,\beta}$	15·26								

$^{\rho}$ Calculated from ΔSCF method

$[GeH_3Cl]$		$[GeH_3F]$		$[GeH_3Br]$		$[SiH_3Br]$		$[CH_3Br]$		$[GeH_3SH]$	
Calc.	Expt.[14]	Calc.	Expt.[14]	Calc.	Expt.[14]	Calc.	Expt.[14]	Calc.	Expt.[14]	Calc.	Expt.[15]
13·45(e)	11·30(e)	14·9(e)	12·3(e)	11·98(a_1)	10·7(e)	11·71(a_1)	11·0(e)	14·3(a_1)	9·7(e)	12·42	9·69
14·96(a_1)	13·05(a_1)	16·0(a_1)	15·0(a_1)	13·78(e)	12·51(a_1)	12·80(e)	16·59(a_1)	14·8(e)	12·5(a_1)	13·51	11·39
17·70(e)	13·30(e)	20·5(e)	15·0(e)	16·87(e)	12·9(e)	17·06(e)	16·63(e)	22·9(e)	13·8(e)	14·14	12·50
										16·62	14·08

$[AsH_3]$		$[Se(CH_3)_2]$		$[(GeH_3)_2O]$		$[(GeH_3)_2S]$		$[SeH_2]$	
Calc.	Expt.[16]	Calc.	Expt.[15]	Calc.	Expt.[15]	Calc.	Expt.[15]	Calc.	Expt.[17]
15·52(a_1)	10·05(a_1)	12·5	8·4	10·3	10·4	12·22	9·25	14·87(b_1)	9·95(b_1)
15·52(e)	12·0(e)	13·4(a_1)	11·0(a_1)	13·7(a_1)	10·9(a_1)	12·76(a_1)	10·66(a_1)	16·59(a_1)	12·45(a_1)
		15·0(b_2)	12·0(b_2)	13·7(b_2)	12·2(b_2)	13·12(b_2)	11·30(b_2)	16·63(b_2)	13·10(b_2)
		19·9	14·0	15·0	13·5	14·95	12·30		

* Bond lengths and angles from ref. 18.

Molecules containing Third-row Atoms.—Several calculations have been performed on molecules of the type $[GeX_4]$, $[GeH_2X_2]$, $[GeH_3X]$ (X = F or Cl), $[GeH_3SH]$, $[AsH_3]$, $[SeH_2]$, $[(GeH_3)_2O]$, $[(GeH_3)_2S]$, and $[Se(CH_3)_2]$ (see Figure and Table).

For the molecules shown in the Figure there is substantial agreement between calculated eigenvalues and the experimental energy-level orders deduced from p.e. spectra (although the calculated values are systematically lower by *ca.* 10%) and the shift in I.P. found

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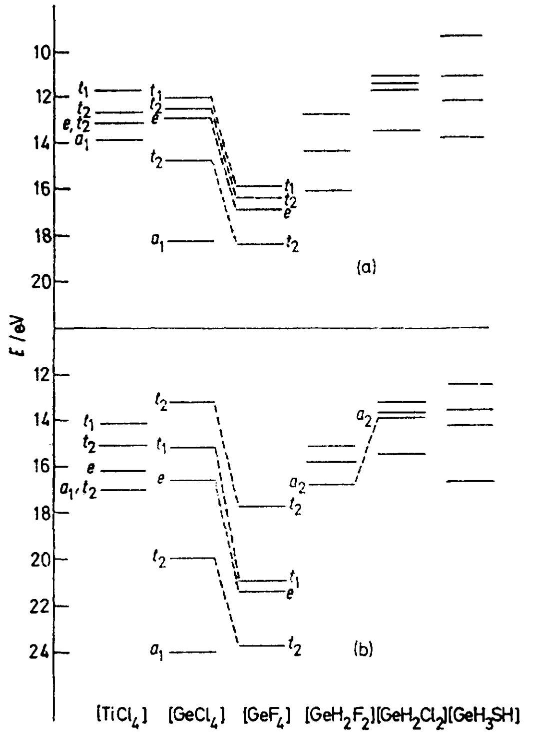
in the series is reproduced. We also note that some assignments of the p.e. spectra of the molecules in the Figure, accepted in the literature on the basis of purely empirical criteria and extrapolation from CNDO/2 calculations on similar carbon and silicon compounds, are in disagreement with the present results. Thus, whilst it was believed that the halogen lone-pair electrons (*i.e.* those m.o.s in which these lone pairs participate, which are strictly non-bonding by symmetry: t_1 for $[GeX_4]$ and a_2 for $[GeX_2H_2]$) always have the lowest I.P., this is not always the case from our calculations.



Experimental (a) and theoretical (b) ionisation energies for the listed molecules

Agreement between experiment and theory is rather less satisfactory for other molecules in the Table, and in particular for $[AsH_3]$, $[SeH_2]$, and CH_3Br which indicates that an improved parameterisation is necessary for As, Se, and Br atoms.

Conclusions.—It is evident that there is general qualitative agreement between our semiempirical results and the corresponding *ab initio* calculations or experimental p.e. spectra. At this point several caveats are necessary. First, this agreement is always only qualitative, and perhaps no more may be expected from such an approach. Nevertheless, we point out that this agreement is better for compounds containing a transition-metal atom surrounded by other first row atoms, the best agreement being found for $[NiF_6]^{4-}$. This seems to indicate that further studies on the parameterisation for second-row atoms are necessary, as also suggested by Clack.[19]

Turning to the results of calculations on open-shell systems, we point out that for those cases in which the m.o.s are doubly occupied and there is only a single unpaired electron, the results always agree with *ab initio* ones in the assignment of the *singly* occupied orbital. In addition, for $[VCl_4]$ the calculation on the ion and neutral molecule clearly show that Koopmans' theorem is not valid when *d*-electrons are involved in the ionisation. In this regard, it is interesting to quote a recent paper by Clack,[20] presenting a refined version of CNDO, in which the one-centre exchange integrals are retained. The results obtained in this paper indicate that adequate consideration of these terms can allow a good interpretation of properties directly connected with interaction of unpaired electrons, such as ionisation potentials and energies of electronic transitions.

In conclusion, we feel that the large number of calculations carried out on such a relatively wide range of systems and the differences between them add value to the qualitative agreement obtained and support further studies of semiempirical procedures for investigating the electronic structures of complex systems.

[4/1642 *Received, 5th August,* 1974]

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