$Mo_2O_4^{2+}$. On the other hand, the pyrophosphate complex has two coordination sites where water can coordinate; see Figure 9. The mechanism for cleavage of the oxo bridge of the molybdenum dimer is not clear, but an attractive possibility is that another pyrophosphate ligand could use these extra sites to make a transient complex, which could then break at the oxo bridges to form monomers.

Several papers report the dissociation of $Mo_2O_4^{2+}$ dimers.[4] Two classes of dissociation mechanism appear possible. For molybdenum(V) complexes with cysteine,[20,21] aminoethanethiol, and ethanedithiol,[20] the dissociation of molybdenum(V) dimers occurs in moderately basic solution and the participation of OH^- in the breaking of oxygen bridges to form a paramagnetic monomer is proposed. On the other hand, the monomer complex forms in acidic solution by the simultaneous dissociation of the dimeric complex with proton catalysis. Tartaric,[14] gluconic, and citric[4] acids give small amounts of monomer at or near pH 7.0. These ligands coordinate to molybdenum through oxygen atoms. Spence[4] pointed out that complexes with these ligands have low g values, reflecting a much smaller degree of electron delocalization onto the ligands as opposed to thio ligands. The pyrophosphate system belongs to the second class if we use the criteria of oxygen ligation, low g values, and dissociation at low pH. However, the superhyperfine splitting by phosphorus ligands clearly indicates some electron delocalization onto the ligands. It appears also that cleavage of the oxo bridge of the pyrophosphate dimer complex is not by OH^- as is the cleavage of the cysteine dimer complex.

The sensitivity of polyphosphate complexes of $Mo_2O_4^{2+}$ to oxidation, combined with the labilization of the dioxo-bridge bond reported here, suggests that further study would be useful to ascertain whether monomers of Mo(V) polyphosphates are reactive species in redox processes as well as to obtain more precise information on the several equilibria present.

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Nonempirical Valence-Electron Calculations on the Group 3B Monohalides

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The nonempirical valence-electron (NEVE) method for molecular orbital calculations on molecules containing heavy atoms has been extended to include fourth-row atoms in a minimum STO basis calculation. Unlike many MO methods in current use, the NEVE method allows comparisons down the periodic table. The present study illustrates this for the monohalides (F, Cl, Br, I) of the group 3B elements (B, Al, Ga, In). The results show trends in calculated properties which generally agree with the expectations of chemical intuition. The computational economy of the method, together with the good agreement with available all-electron ab initio results, indicates that the NEVE method should be of use in studies on a variety of inorganic systems.

Introduction

The development of valence-electron LCAO molecular orbital methods of reasonable economy and accuracy for use on molecules containing heavy atoms has not been rapid. The established semiempirical methods based on the EH and CNDO approximations have generally been unable satisfactorily to represent molecules containing atoms which differ markedly in characteristics such as atomic number or the number of valence electrons. This has meant that inorganic systems in particular have been poorly served by semiempirical calculations.

The need to account for core–valence interactions, both intra- and interatomic, is central in developments directed to these problems. Accurate model atomic potentials have recently been calculated by Bonifacic and Huzinaga[1] for use in molecular calculations. Klimenko and Dyatkina[2] have used a simple core pseudopotential and an orthogonalized AO basis in calculations on ClF. Horn and Murrell[3] have calculated effective atomic core charges as the basis of a simple model potential for valence-electron calculations on H_2S and SiH_4. Switalski and Schwartz[4] have used a simple valence-only atomic core potential model in calculations on polyatomic molecules containing first-row atoms. Ewig, Coffey, and Van Wazer[5] have used a similar method for calculations on the phosphorus halides, PF_3 to PI_3.

The NEVE Method

The nonempirical valence-electron (NEVE) method developed in this laboratory accounts for the core-valence interactions in a very simple manner. In earlier versions of the method,[6,7] this involved the addition of a core-correction energy

Table I. Atomic Valence Effective Core Charges of Groups 3B and 7B

Atom	Z^s_{eff}	Z^p_{eff}	Atom	Z^s_{eff}	Z^p_{eff}
B	3.2534	3.0269	F	7.2872	7.0379
Al	3.8034	3.7299	Cl	8.2349	7.6211
Ga	4.2214	3.8291	Br	9.3839	8.3153
In	4.5824	4.0989	I	10.1865	8.8299

to each diagonal F matrix element, with a minimum STO basis being used.

In the present version we have used the approach described by Horn and Murrell.[3] This involves the use of the simple core pseudopotential $Z_{\text{eff}}(r)/r$, where the effective atomic core charge Z_{eff}, for each valence atomic orbital, is determined from an atomic calculation. An all-electron atomic calculation using a chosen STO basis produces the Hartree–Fock (HF) valence orbitals with associated eigenvalues. The atomic integrals over the STO basis are then used to obtain the corresponding valence orbital integrals over the HF basis. For the condition that the valence orbital eigenvalues obtained in a valence-electron atomic calculation are identical with those in the all-electron calculation, the effective core charges Z_{eff} appearing in the core pseudopotential used in the valence-electron calculation are easily calculated.

The valence s and p effective core charges calculated in this way using best-atom exponents[8,9] for B, Al, Ga, In and F, Cl, Br, I are shown in Table I. As expected, these values are higher than the integral core charge in each case but necessarily less than the nuclear charge. For each atom $Z^s_{\text{eff}} > Z^p_{\text{eff}}$ since the angular functions of the p orbitals lessen their interaction with the spherical distribution of core electrons compared to the s orbitals. The trend of increasing Z_{eff} values down the periodic table reflects the increasing number of core electrons together with the expanding core electron distribution.

For the molecular calculations, the valence AO basis is then the HF valence AO's resulting from the atomic calculations together with the simple atomic core pseudopotential involving the effective core charges for each valence AO.

A reduction in the number of molecular integrals required in a calculation is achieved by including only integrals over one and two centers. Since the valence HF basis is nonorthogonal, these include the two-center hybrid and exchange integrals, the latter being the only integrals evaluated by approximation. The two-center one-electron integrals are calculated over the atomic HF basis, but the two-center two-electron integrals are calculated over the single-STO functions representing the outer parts of the atomic orbitals. This affords a considerable saving in computation time and gives integrals which differ only slightly from those calculated over the multi-STO HF functions.

In an earlier version of the NEVE method,[10] the two-center two-electron hybrid integrals were estimated by using a weighted form of the Ruedenberg approximation.[11] Here, the hybrid integrals are calculated exactly using the method described by Klimenko and Dyatkina.[12] The exchange integrals are then approximated by using the Ruedenberg approximation and the accurate hybrid integrals. The resulting formula, which is rotationally invariant, is

$$
\begin{aligned}
\langle \mu_A \lambda_B | \nu_A \sigma_B \rangle = {}^1\!/_4 \{ \sum_{\theta A}^{A} [S_{\theta_A \lambda_B} \langle \mu_A \theta_A | \nu_A \sigma_B \rangle \\
+ S_{\theta_A \nu_B} \langle \mu_A \lambda_B | \nu_A \theta_A \rangle] + \sum_{\phi B}^{B} [S_{\mu_A \phi_B} \langle \phi_B \lambda_B | \nu_A \sigma_B \rangle \\
+ S_{\nu_A \phi_B} \langle \mu_A \lambda_B | \phi_B \sigma_B \rangle] \}
\end{aligned}
$$

The role of the effective core charges in respect to the two-center core attraction integrals must be determined. Since

Table II. Atomic Total Energies and Core Self-Energies of Groups 3B and 7B (in Atomic Units)

Atom	All-electron calcn E	Valence-electron calcn E	Core self-energy, E_{core}
B	−24.3222	−2.3487	−21.9735
Al	−241.0154	−1.6886	−239.3268
Ga	−1916.3929	−1.6424	−1914.7505
In	−5728.9916	−1.4216	−5727.5700
F	−98.5711	−23.1021	−75.4690
Cl	−458.3151	−14.3790	−443.9361
Br	−2564.9433	−12.3950	−2552.5483
I	−6905.7994	−10.3743	−6895.4251

the effective core charges have been calculated for incorporation with the respective one-center attraction integrals, the question of what is the appropriate core charge for the two-center case arises. Our previous calculations[10] indicated that use of the integral rather than effective core charges in this situation gave better results. This is also the approach favored by Horn and Murrell.[3]

A measure of the effect of the approximations used in the NEVE method is given by the calculated total molecular energy. The valence-electron calculation produces a total valence electronic energy and a total core repulsion energy. Addition of the respective atomic core self-energies gives a total molecular energy which is comparable with the values derived in all-electron calculations and with the sum of the individual atomic ground-state energies.

The atomic core self-energies are determined as the difference in electronic energies for the simple atomic calculations described earlier, where the valence-electron calculation includes the calculated effective core charges. The values for the atoms involved in the present study are shown in Table II.

Results and Discussion

The group 3B monohalides offer a good test for the NEVE method in that each molecule involves dissimilar atoms in terms of the number of valence electrons and atomic and orbital sizes. As well, ab initio wave functions for some of the lighter molecules are available for comparative purposes.

The bond lengths used in the calculations are the available experimental values listed by Sutton,[13] together with estimated values for IF (2.11 Å), AlBr (2.29 Å), AlI (2.51 Å), and InF (1.98 Å).

Minimum STO basis all-electron ab initio calculations are available for BF[14] and GaF,[15] and data from these are compared with the NEVE results given in Table III for the monofluorides. There is good correspondence between the ab initio and NEVE results for both BF and GaF. The exclusion of the 3d electrons from the NEVE calculation on GaF has surprisingly little effect as indicated by the total energies. An examination of the ab initio wave function of Stevenson and Lipscomb[15] shows that the d-containing MO's are nearly pure d in character despite their eigenvalues being around −0.33 au in the valence region.

An extended STO basis ab initio (ai) calculation for BF[16] shows the expected lower eigenvalues than the NEVE calculation. The MO order 2σ, 1π, 3σ is the same and the eigenvalue differences are similar being 0.11 au (ai) compared with 0.12 au (NEVE) for $2\sigma - 1\pi$ and 0.34 au (ai) compared with 0.30 au (NEVE) for $1\pi - 3\sigma$.

A similar comparison is available with an extended STO basis ab initio calculation for AlF.[16] Again the ab initio eigenvalues are uniformly lower than the NEVE eigenvalues. The eigenvalue differences are similar being 0.06 au (ai) compared with 0.07 au (NEVE) for $2\sigma - 1\pi$ and 0.22 au (ai) compared with 0.18 au (NEVE) for $1\pi - 3\sigma$.

The NEVE dipole moments of the monofluorides each correspond to the polarity M^-F^+ though the atomic charges

Table III. Comparison of NEVE and Available Ab Initio Calculations for Group 3B Monofluorides (Energies in Atomic Units)

	BF (R = 1.265 Å)		AlF (R = 1.655 Å)	GaF (R = 1.775 Å)		InF (R = 1.980 Å)
	NEVE	Ab initio[a]	NEVE	NEVE	Ab initio[b]	NEVE
Molecular energy	−123.643	−123.604	−340.199	−2015.548	−2015.599	−5828.095
Fluorine charge	−0.080		−0.288	−0.266	−0.21	−0.309
Dipole moment,[c] D	−2.273	−1.96	−0.696	−0.780		−0.669
Eigenvalues MO[d]						
1σ	−1.691	−1.664	−1.457	−1.430	−1.415	−1.376
2σ	−0.776	−0.748	−0.526	−0.509	−0.495	−0.437
3σ	−0.359	−0.362	−0.272	−0.256	−0.253	−0.219
1π	−0.661	−0.639	−0.455	−0.438	−0.420	−0.389
Orbital populations M *n*s	1.724		1.815	1.814	1.82[e]	1.808
*n*pσ	0.693		0.517	0.578	0.58[e]	0.578
*n*pπ	0.503		0.380	0.342	0.40[e]	0.304
F 2s	1.949		1.933	1.947	1.95	1.951
2pσ	1.634		1.735	1.661	1.66	1.662
2pπ	3.497		3.620	3.658	3.61	3.696

[a] Reference 14. [b] Reference 15. [c] A positive dipole moment is of M$^+$F$^-$ polarity. [d] MO's are numbered within the valence shell. [e] Adjusted to give filled 3d subshell.

Table IV. NEVE Calculations for Group 3B Monochlorides (Energies in Atomic Units)

	BCl (R = 1.715 Å)	AlCl (R = 2.130 Å)	GaCl (R = 2.202 Å)	InCl (R = 2.401 Å)
Molecular energy	−483.181	−699.837	−2375.194	−6187.769
Total atomic energy[a]	−483.022	−699.677	−2375.040	−6187.622
Chlorine charge	0.124	−0.286	−0.261	−0.337
Dipole moment,[b] D	−2.839	0.840	0.429	0.995
Eigenvalues MO[c]				
1σ	−1.150	−1.010	−1.004	−0.969
2σ	−0.674	−0.503	−0.498	−0.447
3σ	−0.329	−0.283	−0.266	−0.235
1π	−0.519	−0.406	−0.405	−0.378
Orbital populations M *n*s	1.817	1.878	1.848	1.836
*n*pσ	0.975	0.582	0.647	0.614
*n*pπ	0.332	0.253	0.243	0.214
Cl 3s	1.972	1.951	1.962	1.961
3pσ	1.236	1.589	1.543	1.589
3pπ	3.668	3.747	3.757	3.786

[a] References 8 and 9. [b] A positive dipole moment is of M$^+$Cl$^-$ polarity. [c] MO's are numbered within the valence shell.

Table V. NEVE Calculations for Group 3B Monobromides (Energies in Atomic Units)

	BBr (R = 1.887 Å)	AlBr (R = 2.290 Å)	GaBr (R = 2.352 Å)	InBr (R = 2.543 Å)
Molecular energy	−2589.769	−2806.431	−4481.792	−8294.369
Total atomic energy[a]	−2589.612	−2806.267	−4481.630	−8294.212
Bromine charge	0.273	−0.153	−0.115	−0.193
Dipole moment,[b] D	−3.305	0.235	−0.221	0.300
Eigenvalues MO[c]				
1σ	−1.026	−0.913	−0.907	−0.879
2σ	−0.606	−0.472	−0.469	−0.424
3σ	−0.310	−0.267	−0.253	−0.225
1π	−0.443	−0.362	−0.362	−0.342
Orbital populations M *n*s	1.830	1.884	1.858	1.845
*n*pσ	1.070	0.685	0.744	0.708
*n*pπ	0.373	0.278	0.283	0.255
Br 4s	1.879	1.906	1.911	1.917
4pσ	1.221	1.525	1.487	1.530
4pπ	3.627	3.722	3.717	3.745

[a] References 8 and 9. [b] A positive dipole moment is of M$^+$Br$^-$ polarity. [c] MO's are numbered within the valence shell.

show that fluorine has attracted electron density in each case. The sign of the dipole moment is hence influenced by the monoatomic asymmetry (or lone pair) distribution of the group 3B atom which is large because its valence orbitals are more diffuse than the fluorine orbitals.

There are no minimum basis ab initio calculations with which to compare the NEVE results for the group 3B monochlorides which are outlined in Table IV. Extended basis ab initio calculations performed on AlCl and GaCl by Attermeyer, Das and Wahl have been quoted by Berkowitz and Dehmer.[17] The ab initio eigenvalues of the 2σ, 1π and 3σ valence MO's are consistently more negative that the NEVE values by around 0.06 au indicating that the NEVE results show the correct trends. In themselves the NEVE eigenvalues show the expected reduction in values in going from BCl to InCl corresponding to reduced electronegativity of the group 3B atom.

The calculated dipole moments show M$^+$Cl$^-$ polarity except for BCl where the more electronegative boron receives electron density from the chlorine with a resulting B$^-$Cl$^+$ dipole.

The NEVE calculations for the group 3B monobromides are given in Table V. These results show the expected electronegativity trends in eigenvalues, as well as relating similarly to the results for the monochlorides in Table IV. The calculations on the monoiodides of group 3B are described in Table VI. Again the expected trends are obtained. Similar to BCl, both BBr and BI show a negative charge on boron and a dipole moment with B$^-$X$^+$ polarity.

Table VI. NEVE Calculations for Group 3B Monoiodides (Energies in Atomic Units)

		BI (R = 2.110 Å)	AlI (R = 2.510 Å)	GaI (R = 2.575 Å)	InI (R = 2.754 Å)
Molecular energy		−6930.563	−7147.239	−8822.600	−12 635.183
Total atomic energy[a]		−6930.445	−7147.100	−8822.463	−12 635.045
Iodine charge		0.362	−0.089	−0.040	−0.112
Dipole moment,[b] D		−3.544	0.293	−0.292	0.171
Eigenvalues MO[c]					
	1σ	−0.855	−0.760	−0.752	−0.731
	2σ	−0.532	−0.432	−0.429	−0.391
	3σ	−0.287	−0.254	−0.242	−0.217
	1π	−0.373	−0.315	−0.316	−0.304
Orbital populations	M ns	1.861	1.904	1.874	1.859
	$np\sigma$	1.152	0.731	0.799	0.762
	$np\pi$	0.349	0.276	0.286	0.267
	I 5s	1.830	1.877	1.879	1.884
	5pσ	1.156	1.488	1.448	1.495
	5pπ	3.651	3.724	3.714	3.733

[a] References 8 and 9. [b] A positive dipole moment is of M^+I^- polarity. [c] MO's are numbered within the valence shell.

Table VII. NEVE and Experimental Ionization Potentials for InCl, InBr, and InI (in eV/molecule)

		$-\epsilon_i$[a]	Δ_i[b]	I_i[c]	
				Calcd	Exptl
InCl	3σ	6.40	0.38	6.02	9.75
	1π	10.28	1.86	8.42	10.85
	2σ	12.15	1.66	10.49	13.10
InBr	3σ	6.13	0.41	5.72	9.41
	1π	9.31	1.32	7.99	10.20
	2σ	11.55	1.29	10.26	12.74
InI	3σ	5.92	0.48	5.44	8.82
	1π	8.26	0.91	7.35	9.44[d]
	2σ	10.64	1.01	9.63	12.21

[a] NEVE eigenvalues. [b] Calculated Koopmans defect. [c] Ionization potentials. Experimental values from ref 17. [d] Average of $\pi_{3/2}$ and $\pi_{1/2}$ values.

The orbital populations given in Tables III–VI show trends related to the atomic s − p energy differences. The extent of s–p mixing is indicated by the valence s orbital populations. For the halogens this is close to 2 for the fluorides and chlorides but is slightly reduced for the bromides and iodides. The decreasing s–p energy difference from aluminum to indium correlates with the steady decrease in their s population in each halide series. However the boron 2s populations are out of line with these trends.

A useful experimental test of NEVE results is offered by the ionization potentials (IP's) measured by photoelectron spectroscopy. The available data for the molecules in the present study are for InCl, InBr, and InI. The He(I) spectra measured by Berkowitz and Dehmer[17] show three bands below 14 eV and corresponding to ionization from 3σ, 1π, and 2σ molecular orbitals, with the π band assigned partly by its higher intensity.

The simplest correlation of calculated eigenvalues with experimental IP's invokes the Koopmans approximation. Additionally, a determination of the Koopmans defect, such as by Cederbaum's formula,[18] accommodates the relaxation and correlation energies neglected in the Koopmans approximation. We have used the dominant-term formula for the defect Δ_i to correct the Koopmans value $-\epsilon_i$ to a calculated ionization potential I_i.

The results for the NEVE wave functions are compared in Table VII with the experimental vertical ionization potentials of InCl, InBr, and InI. For each molecule the orbital sequences are in agreement, though all of the calculated IP's are considerably lower than the experimental values. There are a number of reasons for this. A minimum STO basis always produces eigenvalues which are too positive and also Koopmans defects which are too large. Nevertheless the 2σ − 1π IP difference is accurately calculated while the 3σ IP is relatively low. The incorporation of the Koopmans defect does reduce the calculated 1π − 3σ IP difference since 3σ has a smaller defect. The photoelectron spectra suggest that the 3σ MO is of approximately nonbonding character whereas the NEVE calculations give reasonable antibonding character, in contrast to the 2σ and 1π MO's which are of bonding character. The NEVE result overestimates the antibonding character of the 3σ MO and this contributes to its relatively low calculated IP.

Conclusion

The NEVE method which is designed for valence-electron molecular orbital calculations on molecules containing heavy atoms gives sensible wave functions for the group 3B monohalides. The comparisons, where possible, of NEVE results with those of more rigorous all-electron ab initio calculations show generally good agreement and indicate that NEVE wave functions of larger inorganic molecules should be of useful accuracy.

The computational economy of the NEVE method is indicated by typical total computing times per molecule of 35 s (BF) to 60 s (InI) on a DEC-10 computer.

Registry No. BF, 13768-60-0; AlF, 13595-82-9; GaF, 13966-78-4; InF, 13966-95-5; BCl, 20583-55-5; AlCl, 13595-81-8; GaCl, 17108-85-9; InCl, 13465-10-6; BBr, 19961-29-6; AlBr, 22359-97-3; GaBr, 22655-59-0; InBr, 14280-53-6; BI, 13842-56-3; AlI, 29977-41-1; GaI, 15605-68-2; InI, 13966-94-4.

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