Why the fine structure appears on the spectra from only some of the unstable crystals remains unexplained. That the structure should be due to a spin–orbit splitting of the $^2B_2 \rightarrow {}^2E$ transition[2] seems unlikely to us, since the number of bands and the order of magnitude to be expected for a spin–orbit splitting are not comparable to our observations.

As to the "charge-transfer spectrum" setting in for both polarizations at 30,000 cm^{-1} we must expect such bands to be due to a transfer of an electron localized on the metal to the equatorial ligands. Since the vector from the vanadium metal to an equatorial ligand is not perpendicular to the V=O bond, the transition moment will have both perpendicular and parallel components. Such a strongly allowed transition is therefore expected to be seen in both polarizations.

In conclusion, the spectral behavior of vanadyl sulfate observed in the new measurements seems best explained on the basis of the original Ballhausen–Gray level scheme. On the other hand, we are not of course suggesting that this level scheme is valid for all vanadyl complexes.

Acknowledgments. One of us (B. F. D.) extends his thanks to the Cultural Exchange Programme between Denmark and U.S.S.R., which made possible his most enjoyable stay at the H. C. Ørsted Institute of the University of Copenhagen. A discussion with Professor Harry B. Gray is gratefully acknowledged.

Complete Neglect of Differential Overlap Calculations on Second-Row Molecules

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Received December 20, 1967

Abstract: The CNDO parameters necessary for calculations on molecules containing second-row atoms have been estimated, by comparison with reference calculations, for the atoms Si, P, S, and Cl. It was found that this method of deriving the parameters, as opposed to the method which makes some use of spectral data, is subject to certain restrictions. The parameters have been used to calculate the bond angles and dipole moments of a selection of chemically interesting molecules containing a second-row atom. Both of these properties were found to be reliably within reasonable agreement of the experimental values. Finally, the importance of 3d orbitals to the bonding in these molecules is discussed.

The simplification of Roothaan's[2] self-consistent field equations through the adoption of semiempirical schemes has permitted the calculation of properties and charge distributions of large chemically interesting molecules.[3] One of the more successful approximations to be investigated is the complete neglect of differential overlap (CNDO) method.[4,5] This method is based on the neglect of all overlap charge distributions and the empirical calculation of all one-electron matrix elements. An important feature of the method is that these matrix elements are constructed from atomic parameters which are obtained from atomic spectral data and by comparison of CNDO calculations with more detailed calculations on simple molecules. These parameters have been estimated for all first-row atoms (Li → F) and hydrogen,[5,6] and calculations based on them have proved very successful.[7]

In the case of second-row atoms (Na → Cl) the estimation of the atomic parameters, necessary for CNDO calculations, has been hampered by the paucity of detailed calculations on second-row molecules. However, CNDO calculations, based on assumed atomic parameters, have been carried out[8] for a series of second-row molecules and suggest that the CNDO method should be very useful as a means of interpreting the properties of these molecules. Although the bond angles and the general trends of the dipole moment, calculated by the CNDO method, were very good, the poor dipole moments of certain of the molecules suggested that the theory needs to be carefully parametrized. In the present paper the atomic parameters for Si, S, P, and Cl are estimated by comparison with detailed calculations (based on Gaussian orbitals) on simple molecules. As the estimation of the diagonal elements from atomic spectral data presents serious difficulties in the case of second-row atoms,[8] these too were estimated by comparison with the reference calculations.

Theory

Molecular orbital theory approximates the N-electron wave function for a molecule by an antisymmetrized product of doubly occupied molecular orbitals (one-electron functions). The molecular orbitals ϕ_i are expressed as a linear combination of atomic orbitals

$$\phi_i = \sum_{\mu} \chi_\mu C_{\mu i} \qquad (1)$$

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[1] Address inquiries to Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.

[2] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[3] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[4] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

[5] J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

[6] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[7] D. Breen, M.Sc. Thesis, University of Virginia.

[8] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

where χ_μ is the μth atomic orbital in the basis set. The molecular orbital coefficients are obtained as the solutions to Roothaan's matrix equations[1]

$$FC = SCE \tag{2}$$

where E is the diagonal matrix of orbital energies, S the overlap matrix with elements

$$S_{\mu\nu} = \int \chi_\mu \chi_\nu \, \mathrm{d}\tau \tag{3}$$

C is the matrix of orbital coefficients $C_{\mu i}$, and F is the Fock matrix

$$F_{\mu\nu} = H_{\mu\nu} + \sum_\sigma \sum_\lambda P_{\sigma\lambda} \{ \langle \mu\nu | \sigma\lambda \rangle - 0.5 \, \langle \mu\lambda | \sigma\nu \rangle \} \tag{4}$$

where the one-electron term H is given by

$$H_{\mu\nu} = \int \chi_\mu \left\{ -{}^1/_2 \nabla^2 - \sum_A \frac{Z_A}{R_{A1}} \right\} \chi_\nu \, \mathrm{d}\tau \tag{5}$$

where Z_A is the effective nuclear charge of the Ath atom, and R_{A1} is the radius connecting the Ath nucleus and electron 1. The electron repulsion integrals are given by

$$\langle \mu\nu | \sigma\lambda \rangle = \int \chi_\mu(1) \chi_\nu(1) \frac{1}{r_{12}} \chi_\sigma(2) \chi_\lambda(2) \, \mathrm{d}\tau_1 \mathrm{d}\tau_2 \tag{6}$$

The CNDO approximation[4,5] provides a method for greatly simplifying the above equations while still retaining the essential features of the treatment of the electron repulsion. The first approximation is to set $S_{\mu\nu} = 0$ unless $\mu = \nu$, in which case $S_{\mu\mu} = 1$. The second approximation is to neglect all exchange integrals, and to replace the remaining Coulomb integrals by average values which are independent of the orbital species, and depend only on the participating atoms and their separation. In practice these integrals γ_{AB} are set equal to the s-orbital Coulomb integrals.[5] Finally, all the remaining one-electron terms are calculated empirically. The simplified equations are

$$FC = CE \tag{7}$$

where F is now given by (a) diagonal element for μ on atom A[5]

$$F_{\mu\mu} = {}^1/_2(A + I)_{\mu\mu} - {}^1/_2(P_{\mu\mu} - 1)\gamma_{AA} + \sum_B (P_B - Z_B)\gamma_{AB} \tag{8}$$

(b) off-diagonal element for μ on A and ν on B[4]

$$F_{\mu\nu} = {}^1/_2(\beta_A{}^0 + \beta_A{}^0)S_{\mu\nu} - {}^1/_2 P_{\mu\nu}\gamma_{AB} \tag{9}$$

where ${}^1/_2(A + I_{\mu\mu})$ is the mean of the electron affinity and ionization potential of orbital μ. These quantities are calculated from atomic spectral data. P_B is the total electron density on atom B

$$P_B = \sum_\mu P_{\mu\mu} \tag{10}$$

the summation being over all atomic orbitals on B. An important feature of the CNDO approximation is embodied in eq 9. Namely, the off-diagonal one-electron matrix elements are assumed to be proportional to the corresponding overlap integral. Further, the constant of proportionality is taken to be the mean of atomic parameters $\beta_A{}^0$ which are characteristic of the participating pair of atoms only.

The basis set for molecules which only contain protons or atoms from the first row of the periodic table is comprised of 1s orbitals (exponent = 1.2) centered on each proton and 2s and 2p Slater atomic orbitals centered on each of the first-row atoms. The necessary electron affinities and ionization potentials have been obtained from atomic spectra for all first-row atoms. The remaining atomic parameters $\beta_A{}^0$ have been estimated by calibrating CNDO calculations against more detailed computations. The parameters were chosen so that the CNDO molecular orbitals corresponded as closely as possible to the reference molecular orbitals.

Little modification is required to include second-row atoms in the theory. The basis set is expanded to include 3s, 3p, and 3d atomic orbitals on each second-row atom. Slater values are used for the exponents of the 3s and 3p atomic orbitals. There is some doubt as to the proper 3d exponent to use in these calculations, but at the present level of approximation it is probably reasonable to set it equal to the 3s and 3p exponent.

The diagonal Fock-matrix elements are calculated for 3s, 3p, and 3d orbitals from eq 8. A detailed discussion of this is given in ref 8. Preliminary calculations suggested that it would be profitable to depart slightly from the CNDO method when calculating certain off-diagonal elements involving second-row atoms. These changes are (i) the Hamiltonian-matrix element H (a) if either μ *or* ν are 3d orbitals (centered on A)

$$H_{\mu\nu} = \beta_A{}^{\mathrm{d}} S_{\mu\nu} \tag{11}$$

(b) if both μ and ν are 3d orbitals (on A and B)

$$H_{\mu\nu} = {}^1/_2(\beta_A{}^{\mathrm{d}} + \beta_B{}^{\mathrm{d}})S_{\mu\nu} \tag{12}$$

where $\beta_A{}^{\mathrm{d}}$ is a parameter specifically for the 3d functions of A. (ii) Some improvement in the theoretical dipole moments can be achieved by decreasing the Fock-matrix element connecting (second-row) atomic orbitals on the same center. This can be justified by noting that the inclusion of one-center exchange integrals, as in a more elaborate theory, would have just this effect. In the present calculations the Fock-matrix element between atomic orbitals, of principal quantum number 3, on the same center is given by

$$F_{\mu\nu} = -({}^1/_4)P_{\mu\nu}\gamma_{AA} \tag{13}$$

where γ_{AA} is the one-center 3s Coulomb integral for atom A.

Dipole Moments. The dipole moment in the CNDO approximation[5] may be expressed as the sum of two contributions: (1) the polarization contribution from the net charge densities

$$= -2.5413 \sum_A (P_A - Z_A)R_A \tag{14}$$

(2) the local atomic polarization μ^{a} for (a) first-row atoms

$$\mu_z{}^{\mathrm{a}} = -2.5413 \sum_A \frac{5}{\sqrt{3}} P^A{}_{s,z} \frac{1}{\alpha_A}$$

and (b) second-row atoms

$$\mu_x{}^{\mathrm{a}} = -2.5413\sum_A\left(\frac{7}{\sqrt{3}}P^A{}_{s,x} + \frac{7}{\sqrt{5}}P^A{}_{xz,z} + \frac{7}{\sqrt{5}}P^A{}_{xy,y} + \frac{7}{\sqrt{5}}P^A{}_{x^2-y^2,x} - \frac{7}{\sqrt{15}}P^A{}_{z^2,x}\right)\frac{1}{\alpha_A}$$

$$\mu_y{}^{\mathrm{a}} = -2.5413\sum_A\left(\frac{7}{\sqrt{3}}P^A{}_{s,y} + \frac{7}{\sqrt{5}}P^A{}_{yz,z} + \frac{7}{\sqrt{5}}P^A{}_{yx,x} + \frac{7}{\sqrt{5}}P^A{}_{x^2-y^2,x} - \frac{7}{\sqrt{15}}P^A{}_{z^2,x}\right)\frac{1}{\alpha_A}$$

$$\mu_z{}^{\mathrm{a}} = -2.5413\sum_A\left(\frac{7}{\sqrt{3}}P^A{}_{s,z} + \frac{14}{\sqrt{15}}P^A{}_{z,z^2} + \frac{7}{\sqrt{5}}P^A{}_{x,xz} + \frac{7}{\sqrt{5}}P^A{}_{y,yz}\right)\frac{1}{\alpha_A}$$

where α_A is the Slater exponent for atom A, and $P^A{}_{s,z}$ is the bond order between the x and pz atomic orbitals centered on A.

Gaussian Calculations and the Atomic Parameters. The diagonal atomic parameters $^1/_2(I + A)_{\mu\mu}$ and the off-diagonal scaling factors are obtained, for the 3s and 3p atomic orbitals, by comparison of CNDO molecular orbitals with those obtained from more detailed SCF calculations. These reference molecular orbitals were obtained from calculations based on Gaussian functions.

In the reference calculation all electrons were explicitly included. The basis set thus comprised of 1s orbitals (exponent = 1.2) centered on each proton, 1s, 2s, and 2p Slater orbitals centered on each first-row atom, and 1s, 2s, 2p, 3s, and 3p orbitals centered on each second-row atom. The calculation was performed by representing each of these Slater orbitals as a linear combination of four or five Gaussian functions. The calculations were carried out using a POLYATOM-type computer program.[9]

The calibration of the CNDO program was carried out by first transforming the reference molecular orbitals, expressed as coefficients of Slater orbitals, to a basis of orthogonalized orbitals. The necessary transformation, which permits a direct comparison between the reference and CNDO molecular orbitals, is[5]

$$C_{\mathrm{ref}}' = S^{1/2}C_{\mathrm{ref}}$$

where the C_{ref}'s are the reference molecular orbitals and $S^{1/2}$ is the square root of the overlap matrix. The values of the atomic parameters, for a given element, were chosen by comparing the CNDO orbitals for the hydride molecule, calculated for several values of the parameters, with C_{ref}. No special fitting method was used; the orbitals were simply compared on an element by element basis. The degree to which it was possible to match the CNDO orbitals with C_{ref} is illustrated by Tables I–IV. The final values of the atomic parameters are listed in Table V.

The CNDO calculations were found to be somewhat more sensitive to the difference between the diagonal elements for 3s and 3p orbitals than to their actual values. That is, the CNDO calculations are most sensitive to two variables, the difference between $^1/_2(I + A)$ for 3s and 3p atomic orbitals, and the ratio of $\beta_A{}^0$ and the average value of the diagonal $^1/_2(I + A)$ elements for 3s and 3p orbitals. For this reason it is difficult to assign very accurate values *simultaneously* to both $^1/_2(I + A)$ and $\beta_A{}^0$ by this method. However, the calculation did show that the diagonal elements suggested by Santry and Segal[8] are somewhat too large in magnitude. The values which were chosen for the

Table I. Reference Molecular Orbitals for PH_3[a]

	Molecular				
Atomic	$1a_1$	1e	$2a_1$	2e	$3a_1$
H_1	−0.3601	0.5786	0.1436	0.5761	0.4272
H_2	−0.3601	−0.2893	0.1436	−0.2881	0.4272
H_3	−0.3601	−0.2893	0.1436	−0.2881	0.4272
3s	−0.7396	0	−0.4548	0	0.4775
$2p_x$	0	0.6980	0	−0.7010	
$2p_y$	0	0	0	0	0
$2p_z$	0.2165	0	−0.8452	0	0.4665

[a] Note that the sum of the squares of the orbital coefficients is not exactly unity because the (small) contributions from inner-shell orbitals are not shown.

Table II. CNDO Molecular Orbitals for PH_3 Calculated at the Equilibrium Geometry

	Molecular				
Atomic	$1a_1$	1e	$2a_1$	$3a_1$	2e
H_1	0.3753	0.5939	0.1796	0.4003	−0.5603
H_2	0.3753	−0.2970	0.1796	0.4003	0.2801
H_3	0.3753	−0.2970	0.1796	0.4003	0.2801
3s	0.7110	0	−0.5710	−0.4104	0
$3p_x$	0	0.6862	0	0	0.7274
$3p_y$	0	0	0	0	0
$3p_z$	−0.2683	0	−0.7597	0.5923	0

Table III. Reference Molecular Orbitals for H_2S

	Molecular					
Atomic	$1a_1$	$1b_2$	$2a_1$	$1b_1$	$2b_2$	$3a_1$
H_1	0.4222	0.4924	0.2191	0	0.5074	−0.5227
H_2	0.4222	−0.4924	0.2191	0	−0.5074	−0.5227
3s	0.7392	0	−0.4953	0	0	0.3978
$3p_x$	0	0	0	0.9887	0	0
$3p_y$	0	0.7090	0	0	−0.6874	0
$3p_z$	0.2442	0	0.7964	0	0	0.5305

Table IV. CNDO Molecular Orbitals for H_2S

	Molecular					
Atomic	$1a_1$	$1b_2$	$2a_1$	$1b_1$	$2b_2$	$3a_1$
H_1	0.4144	0.4983	0.2770	0	0.5015	0.5017
H_2	0.4144	−0.4983	0.2770	0	0.5015	−0.5017
3s	0.7661	0	−0.5530	0	−0.3276	0
$3p_x$	0	0	0	1.0	0	0
$3p_y$	0	0.7095	0	0	0	−0.7048
$3p_z$	0.2639	0	0.7353	0	−0.6242	0

Table V. Atomic Parameters (volts) for CNDO Calculations[a]

Atom	$\beta_A{}^0$	$^1/_2(I + A)_s$	$^1/_2(I + A)_p$
Si	−8.5	−9.0	−4.5
P	−10.0	−11.2	−5.2
S	−11.5	−13.0	−6.4
Cl	−12.2	−16.0	−7.0

[a] The proposed approximation is completed by setting a $^1/_2(I + A)_d = 0$ and $\beta_d = -6$ for all atoms.

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(9) M. D. Robin and N. A. Kuebler, *J. Chem. Phys.*, 47, 1201 (1967). K. O-ohota, H. Tanaka, and S. Huzinga, *J. Phys. Soc. Japan*, 21, 2306 (1966).

Table VI. Experimental Molecular Geometries and Dipole Moments (Debyes)

Molecule	Bond length, Å	Bond length, Å	Bond angle, deg	Bond angle, deg	Dipole
CS	1.535[a]	...	...	...	1.97[a]
COS	CO, 1.161[b]	CS, 1.561	Linear	...	0.72[k]
SO_2	1.4321[c]	...	119.5	...	1.59[l]
H_2S	1.334[d]	...	93.3	...	1.02[m]
PH_3	1.4206[e]	...	93.5	...	0.578[n]
PF_3	1.535[f]	...	100	...	1.025[o]
POF_3	PO, 1.45[g]	PF, 1.52	102.5 ± 2	...	1.77[p]
PSF_3	PS, 1.86[g]	PF, 1.53	100	...	0.633[q]
SOF_2	SF, 1.585[h]	SO, 1.412	FSF, 92.8	OSF, 106.8	1.618[h]
SO_2F_2	SF, 1.57[i]	SO, 1.37	FSF, 92.8	OSO, 129.6	1.110[i]
SF_4	SF, 1.545[j]	SF^1, 1.646	FSF, 101.5	F^1SF^1, 187	0.632[j]

[a] R. C. Mockler and R. G. Bird, *Phys. Rev.*, **98**, 1837 (1955). [b] T. W. Dakins, W. E. Good, and D. K. Coles, *ibid.*, **71**, 640 (1947). [c] D. Kivelson, *J. Chem. Phys.*, **22**, 904 (1954). [d] G. R. Bird and C. H. Townes, *Phys. Rev.*, **78**, 421 (1950). [e] C. A. Burrus, A. Jacke, and W. Gordy, *ibid.*, **95**, 700 (1954). [f] Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952). [g] N. J. Hawkins, V. W. Cohen, and W. S. Koski, *ibid.*, **20**, 528 (1952). [h] R. C. Ferguson, *J. Am. Chem. Soc.*, **76**, 850 (1954). [i] R. M. Fristrom, *J. Chem. Phys.*, **20**, 1 (1952). [j] W. M. Tolles and W. D. Gwinn, *ibid.*, **36**, 1119 (1962). [k] R. G. Shulman and C. H. Townes, *Phys. Rev.*, **77**, 421 (1950). [l] G. F. Crable and W. V. Smith, *J. Chem. Phys.*, **19**, 502 (1951). [m] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955. [n] C. A. Burrus, *J. Chem. Phys.*, **28**, 427 (1958). [o] R. G. Shulman, B. P. Dailey, and C. H. Townes, *Phys. Rev.*, **78**, 421 (1950). [p] S. N. Ghosh, R. Trambarulo, and W. Gordy, *ibid.*, **87**, 172 (1952). [q] N. J. Hawkins, V. W. Cohen, and W. S. Koski, *J. Chem. Phys.*, **20**, 528 (1952).

3s and 3p atomic parameters from these calculations on hydride molecules are listed in Table V. These parameters may be taken to be accurate to about 1 eV in the following sense. If the diagonal elements for the 3s and 3p orbitals were to be simultaneously changed by up to 1 eV, it would be possible to make a compensating change in $\beta_A{}^0$ so that the CNDO molecular orbitals would not have noticeably deteriorated.

Finally, it only remains to discuss the 3d parameters in order to complete the specification of the method. The diagonal, $^1/_2(A + I)$, terms are assumed to be zero for the 3d orbitals. Previous workers[8] assigned values ranging from -0.150 for sodium to -0.997 V for chlorine. However, as the molecular parameters are only accurate to 1 V, and in any case the calculations based on these numbers suggest that they are too large (in magnitude), the above provides a reasonable approximation. The off-diagonal scaling factors $\beta_A{}^d$ were given the same value of -6 V for all elements (Si → Cl). This value was suggested by the previous calculations on second-row molecules.

Application of the Method to Several Second-Row Molecules

The theory outlined above has been applied to the calculation of the bond angles and dipole moments of several chemically interesting molecules containing a second-row atom.

The theoretical dipole moments are consistently in reasonable agreement with the experimental values, usually to within 0.5 D. In agreement with the previous CNDO calculations on second-row molecules,[8] the 3d orbitals are found to make a substantial contribution to dipole moments. This contribution is, however, rather sensitive to the value chosen for the 3d orbital exponent, and so until more definite values are assigned to these parameters it will be difficult to devise a more reliable calculation. The calculation of dipole moments would also be complicated further if the 3d exponents are as sensitive to molecular environment as has been suggested.[10]

One of the notable successes of CNDO theory has been the calculation of the bond angles for a large range of first-row molecules, usually to within a few degrees of the observed values. These calculations strongly suggest that the forces which are responsible for the gross shape of first-row molecules are reasonably well represented by the parametrization of the CNDO theory. Turning to the calculations on second-row molecules, we find that they are almost, but not quite, as satisfactory in this respect. This, at least in part, is due to the fact that the range of shapes for relatively simple molecules is greater in the second row.

Many of the interesting features of the geometries of the molecules listed in Table VI are represented in the theoretical results of Table VII. For example, the magnitude and sense of the small deviation from linearity of the F′SF′ fragment observed in SF_4 is represented in the theoretical geometry, as are the small changes in the bond angles in going from SO_2F to SO_2F_2 and from PF_3 to POF_3 or PSF_3.

Table VII. Theoretical Bond Angles and Dipole Moments

Molecule	Bond angle, deg	Bond angle, deg	Dipole moment, D
CS	...	...	2.0
COS	Linear	...	1.2
SO_2	120	...	−1.7
H_2S	99	...	−1.4
PH_3	99	...	−0.7
PF_3	98	...	0.6
POF_3	102	...	2.3
PSF_3	101	...	1.3
SOF_2	FSF, 96	OSF, 112	2.1
SO_2F_2	FSF, 94	OSO, 123	0.6
SF_4	FSF, 116	F′SF′, 191	−0.6

The participation of 3d orbitals in the bonding of second-row atoms was first proposed in order to explain the shapes of molecules such as PF_5, and later to explain the shapes of molecules such as ClF_3 and SF_4. It is therefore interesting to note that, according to the CNDO approximation, it is possible to calculate the bond angles of these molecules using a basis of s and p orbitals alone.[8] There is some evidence that this result holds for other approximations, in that Manne[11] has

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(10) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

(11) R. Manne, *Theor. Chim. Acta*, **6**, 312 (1966).

also successfully calculated the bond angles in ClF_3 using a basis set of s and p orbitals only. Thus it appears, according to empirical molecular orbital theories, that the role of the 3d orbitals is to stabilize the second-row molecule,[8] rather than to be an essential factor in determining the molecular shape (which appears to be largely determined by the s and p orbitals).

Conclusions

The original method proposed for the derivation of the atomic parameters $^1/_2(I + A)$ in the CNDO theory was based on atomic spectral data.[5] An attempt was made to follow this method when the theory was extended to include second-row atoms,[8] but the paucity of data resulted in many uncertainties in the parameters which were obtained. In principle there is no reason why these parameters should not be obtained independently of spectral data, as are the off-diagonal parameters, by a comparison of the CNDO molecular orbitals with some reference calculation. This procedure has been investigated in the present paper.

Although the calibration method proposed above is in principle as good as any other, the present calculations suggest that it leaves something to be desired. This is because the molecular orbitals were found to be more sensitive to changes in the ratio of the diagonal to the off-diagonal parameters than to individual changes in these quantities. Nevertheless, some improvement in the second-row parameters has been obtained.

The calculations based on the revised parameters give reliably better dipole moments than the original calculations,[8] but there is a slight deterioration in the theoretical bond angles. However, qualitatively the two calculations are very similar and lead to the same general conclusions concerning the importance of 3d orbitals to the bonding of second-row atoms.

Attempts to generalize the method further to include atoms in other rows of the periodic table will face even more serious difficulties as regards the availability of atomic spectral data. As we have found that it is not completely satisfactory to base the parametrization solely on a comparison with a reference calculation, the most fruitful approach will probably be to make use of experimental data, such as dipole moments.

Solvation of Ions. XIII.[1] Solvent Activity Coefficients of Ions in Protic and Dipolar Aprotic Solvents. A Comparison of Extrathermodynamic Assumptions

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Abstract: Some extrathermodynamic assumptions for estimating single-ion solvent activity coefficients in water, formamide, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, acetonitrile, hexamethylphosphoramide, nitromethane, N-methyl-2-pyrrolidone, and 80% v/v DMSO–methanol at 25° and sulfolane at 30° are compared. We estimate that values of log ${}^{M}\gamma^{S}_{Ag^+}$ for transfer of silver cation from methanol to other solvents, S, are −0.8 (H_2O), −3.7 ($HCONH_2$), −5.1 (DMF), −6.6 (DMAC), −8.2 (DMSO), −6.3 (CH_3CN), −10 (HMPT), 1.7 (CH_3NO_2), −2 (sulfolane), −6.8 (NMePy), −7.4 (DMSO-M). Liquid junction potentials between $Ag|AgNO_3$ half-cells linked by a bridge of saturated tetraethylammonium picrate in these solvents have been evaluated. The iodine–triiodide assumption is, in our opinion, one of the easiest of the acceptable extrathermodynamic assumptions to apply to new solvent systems.

The question of single-ion solvent activity coefficients ${}^{0}\gamma^{S}_{A^+}$ and ${}^{0}\gamma^{S}_{B^-}$ for transfer of cations, A^+, or of anions, B^-, from a reference solvent (superscript 0) to another solvent (superscript S) and the extrathermodynamic assumptions needed to split ${}^{0}\gamma^{S}_{A^+}$ and ${}^{0}\gamma^{S}_{B^-}$ are topics of great importance and current interest.[1,3–18] There is even greater interest for us when one of the solvents is protic and the other is dipolar aprotic.[12,15,18] We will never know if an assumption is valid,[3] but the greater the number of independent assumptions, leading to similar values, the greater our confidence in those values. For this reason, a noncritical comparison of

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(1) Part XII: R. Alexander and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 5549 (1967).

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