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A Molecular Orbital Method for Inorganic Molecules: Application to Transition Metal Oxides

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Semiempirical approximations for the SCF–Hamiltonian matrix elements in the LCAO–MO framework, similar to those used in the SCCC–MO method, are developed from the appropriate Roothaan equation. The expression for the off-diagonal elements is found, by comparison with minimal basis set SCF–MO computations, to be semiquantitatively accurate. The equation for the diagonal elements is noteworthy because it includes a correction term to account for two-center interactions. A limited application is made to the transition metal diatomic oxides TiO and CuO, where the empirical parameters are derived by fitting the observed ground-state configuration for TiO. Other computed properties are then found to be in reasonable agreement with experiment, more rigorous computations, and intuitive chemical reasoning.

Introduction

The search for a reliable approximate computational procedure for electronic structure calculations, within the framework of SCF–LCAO–MO theory, is being pressed in many laboratories and on various levels.[1–11] The problem essentially reduces to that of computing the matrix elements of the SCF–Hamiltonian. The exact formalism being too difficult, ways are sought to introduce computational simplifications into the exact expression for the matrix elements. Two cases are then roughly distinguished. If the reduced expressions have been obtained by introducing simplifications in a systematic way, using well-defined approximations, we have, for example, the Pariser–Parr and Pople (PPP)[2,3] method. Alternatively, if there is no explicit listing of the approximations needed to arrive at the assumed computational procedure from the exact formalism, the result is, for example, the Wolfsberg–Helmholz[1] or SCCC–MO[11] method.

We have taken up the work begun by Richardson in 1956,[4] in an attempt to systematize and improve the SCCC–MO method. In the course of this analysis, approximations for the SCF–Hamiltonian matrix elements were obtained which are slightly different from those used in the conventional SCCC–MO method.[11] This modified semiempirical procedure and its application to the electronic structures of transition metal diatomic oxides are presented here.

Method

The SCF–Hamiltonian in the LCAO–MO approximation for a closed shell system can be written as[12,13]

$$F = -T - \sum_n Z_n/r_n + \sum_p \sum_r [\sum_j C_{jp}C_{jr}][2(p, /r,) - (p, / ,r)] \quad (1)$$

where

$$T = \frac{1}{2}\nabla^2 \quad (2)$$

$$\phi_j = \sum_p C_{jp}\chi_p \quad (3)$$

ϕ_j and χ_p are, respectively, the MO's and basis atomic orbitals. $(p, /r,)$ and $(p, / ,r)$ are the familiar Coulomb and exchange operators,[12] here defined over the basis orbitals. The matrix elements are then given by

$$F_{qs} = (q/F/s) \quad (4)$$

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(2) R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

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(12) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(13) R. K. Nesbet, *ibid.*, **35**, 552 (1963).

As shown by Richardson[4] and Berthier,[9] if the Mulliken approximation[14,15] is formally applied to (1), as shown in eq 5, it is found in the resulting expression for F that the double sum over p and r gives each two-electron term twice

$$(p,\ /r,\ ) = \frac{1}{2}S_{pr}[(p,\ /p,\ ) + (r,\ /r,\ )] \qquad (5a)$$

$$(p,\ /\ ,r) = \frac{1}{2}S_{pr}[(p,\ /\ ,p) + (r,\ /\ ,r)] \qquad (5b)$$

where S_{pr} is the overlap integral. Actually, it should be noted that only (5a) is correctly the Mulliken approximation and always integrates to correct magnitudes. In fact, for exchange integrals in which the two orbitals referred to a given electron are the same, eq 5b is a very poor approximation. However, these integrals are considered to be relatively small and are not as numerous as ones in which the two orbitals referred to a given electron are different. In the latter case eq 5b is also a reasonably good approximation.

The double sum in eq 1 can thus be reduced to a single sum and the total normalized population[16] of basis orbital p factored out as in (6). Equation 1 then reduces to[4,9]

$$f_p = \sum_j\sum_r C_{jp}C_{jr}S_{pr} \qquad (6)$$

$$F = -T - \sum_n Z_n/r_n + \sum_p f_p[2(p,\ /p,\ ) - (p,\ /\ ,p)] \qquad (7)$$

which is very similar to the form for F obtained in the PPP method with complete neglect of differential overlap (CNDO).[3] It is significant to the accuracy of (7) that its general form can be obtained both from CNDO and complete dependence on, and inclusion of, overlap; especially since the CNDO expression has recently been shown to be accurate to terms second order in the overlap integral.[17]

For a heteronuclear diatomic molecule, with nuclei a and b, (7) can be written as

$$F = F^{\mathrm{a}} + R^{\mathrm{b}} = F^{\mathrm{b}} + R^{\mathrm{a}} = -T + R^{\mathrm{a}} + R^{\mathrm{b}} \qquad (8)$$

$$R^{\mathrm{a}} = -Z_{\mathrm{a}}/r_{\mathrm{a}} + \sum_{p\mathrm{a}} f_{p\mathrm{a}}[2(p\mathrm{a},\ /p\mathrm{a},\ ) - (p\mathrm{a},\ /\ ,p\mathrm{a})] \qquad (9)$$

$$F^{\mathrm{a}} = -T + R^{\mathrm{a}} \qquad (10)$$

$$\sum_p = \sum_{p\mathrm{a}} + \sum_{p\mathrm{b}} \qquad (11)$$

The letters a and b have been added to the indices to label the nucleus on which that orbital is centered or to indicate that a given sum is over orbitals originating on that nucleus only. The corresponding expressions for R^{b} and F^{b} are derived from (9) and (11), respectively, by substituting b for a.

Defining

$$(q\mathrm{a}/F^{\mathrm{a}}/q\mathrm{a}) = -W_{q\mathrm{a}} \qquad (12)$$

and, analogously, using the Mayer–Sklar approximation[18,19]

$$(s\mathrm{b}/F^{\mathrm{a}}/q\mathrm{a}) = -W_{q\mathrm{a}}S_{q\mathrm{a}s\mathrm{b}} \qquad (13)$$

and taking one-half the sum of the first two alternative expressions for F in (8), yields[4]

$$F_{q\mathrm{a}s\mathrm{b}} = -\frac{1}{2}S_{q\mathrm{a}s\mathrm{b}}[W_{q\mathrm{a}} + W_{s\mathrm{b}}] + \frac{1}{2}(q\mathrm{a}/R^{\mathrm{a}} + R^{\mathrm{b}}/s\mathrm{b}) \qquad (14)$$

Finally, if from (8), $R^{\mathrm{a}} + R^{\mathrm{b}} = F + T$ is substituted into (14) we obtain for two-center off-diagonal elements

$$F_{q\mathrm{a}s\mathrm{b}} = -S_{q\mathrm{a}s\mathrm{b}}[W_{q\mathrm{a}} + W_{s\mathrm{b}}] + (q\mathrm{a}/T/s\mathrm{b}) \qquad (15)$$

Note that T is defined as the negative of the kinetic energy operator, which is of opposite sign to that used by Cusachs[8a] in the form suggested by Ruedenberg.[20] Note further that eq 15 is not appropriate for one-center off-diagonal elements.

The diagonal matrix elements, according to (7) and (12), are given by

$$F_{q\mathrm{a}q\mathrm{a}} = -W_{q\mathrm{a}} - Z_{\mathrm{b}}(q\mathrm{a},q\mathrm{a}/r_{\mathrm{b}}) + \sum_{p\mathrm{b}} f_{p\mathrm{b}}[2(p\mathrm{b},q\mathrm{a}/p\mathrm{b},q\mathrm{a}) - (p\mathrm{b},q\mathrm{a}/q\mathrm{a},p\mathrm{b})] \qquad (16)$$

Through a series of further reductions[21] it is possible to finally obtain

$$F_{q\mathrm{a}q\mathrm{a}} = -W_{q\mathrm{a}} - [Q_{\mathrm{b}} + k^{\lambda}](q\mathrm{a},\ q\mathrm{a}/r_{\mathrm{b}}) \qquad (17)$$

where Q_{b} is the formal charge on atom b, as defined in (18), and k^{λ} is an empirically determined constant (λ differentiates σ, π, and δ symmetries)

$$Q_{\mathrm{b}} = Z_{\mathrm{b}}^* - 2\sum_{p\mathrm{b}} f_{p\mathrm{b}} \qquad (18)$$

Z_{b}^* is the effective nuclear charge on b, Z_{b} minus the core electrons. Equations 15 and 17 are the basis of the method applied here. Although derived from the Roothaan equations for closed-shell systems, these expressions may, with equal validity, be applied to open-shell systems, within the framework of the spin-polarized treatment with restrictions,[22,23] by evaluating Q_{b} in (17) separately for α and β spins. Alternatively, the differences in the diagonal elements of the α and β spins can be ignored and Q_{b} computed from the total spin population. This latter procedure was followed in the diatomic oxide calculations.

For extension to polyatomic molecules it is easily shown that an additional term, $+\sum_{\mathrm{c}(\neq\mathrm{a,b})}(q\mathrm{a}/R^{\mathrm{c}}/s\mathrm{b})$, appears on the right-hand side of (15). This term is expected to be small and can probably be neglected. For the diagonal elements, eq 17 is replaced by

$$F^{\lambda}_{q\mathrm{a}q\mathrm{a}} = -W^{\lambda}_{q\mathrm{a}} - \sum_{\mathrm{b}(\neq\mathrm{a})}[Q_{\mathrm{b}} + k^{\lambda}](q\mathrm{a},q\mathrm{a}/r_{\mathrm{b}}) \qquad (19)$$

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(16) R. S. Mulliken, *ibid.*, **23**, 1833, 1841 (1955).

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(21) H. Basch, Ph.D. Thesis, Columbia University, 1966.

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The introduction of an empirical parameter k^λ in (17) is necessary mainly in order to compensate for the approximation of treating the nonvalence electrons as a nonpolarizable core (perfect screening). The consequence of invoking this latter approximation has been found[24] to be a need to correct for penetration effects which modify Z^*, eq 18, in the diagonal elements. Diagonal Hamiltonian matrix elements computed with neglect of inner orbitals cannot and should not be the same as those calculated from (1) in a full SCF–MO treatment, since the off-diagonal elements connecting valence and core orbitals are not necessarily zero, as can be seen from (15). The quantities which, essentially, eq 17 will be used to compute are "effective" diagonal elements which hopefully will reproduce the "correct" orbital energies and coefficients obtained from a full SCF–MO treatment. Thus k^λ values will be fixed in one case for each geometry and then applied to the calculation of other molecules of similar nature.

It remains to define W_{qa} in (17). In eq 12, F^a, being the collection of all terms referred exclusively to center a, should be similar to the atomic SCF operator for atom a with an electronic configuration given by the f_{pa} in (6). If F^a were rigorously the atomic SCF operator appropriate to atom a (for some specific electronic configuration) and qa the appropriate SCF orbital function, then W_{qa} would be exactly the negative of the orbital energy of atomic orbital qa in the free atom or ion, for that configuration. Thus W_{qa} can be taken either from atomic spectral data[25] or atomic SCF computations,[26] interpolated for nonintegral charge and configuration.

In eq 17 the term $-[Q_b + k^\lambda](qa,qa/r_b)$ represents the interaction of an electron in orbital qa with the electrons and nucleus of atom b and is called the interatomic-Coulomb correction.[27] Since k^λ is a correction for the penetration of orbital qa into the inner-orbital cloud of atom b, k^λ should have a positive value.[21] Thus, for small negative values of Q_b (-0.2 to -0.6), it is likely that the interatomic-Coulomb correction will be approximately zero and the (metal) diagonal element will equal the charge corrected ionization potential or orbital energy, W_{qa}. In the case of a ligand diagonal element, where adjustment for partial charge makes W_{qa} more positive relative to the neutral atom value, the interatomic-Coulomb correction will bring the matrix element back close to its *neutral atom value*. Thus, from this development there is some justification for choosing diagonal elements as prescribed[11] in the SCCC–MO method; the metal elements are charge corrected, whereas the ligand elements are *held constant* at values appropriate for the uncharged species.

The accuracy of (15) has been tested by the computation of off-diagonal SCF–Hamiltonian matrix elements for ClF, CO, and HF, using a minimal basis set of Slater-type orbital functions.[28] The W_{qa} values were taken as the appropriate Hartree–Fock ground-state free-atom orbital energies from the tabulation of Clementi.[26] Since corrections for partial positive and negative charge enter simultaneously in (15) but with opposite sign, it is expected that their sum will very nearly cancel. Therefore, the W_{qa} values were uncorrected for partial charge. The comparison of the SCF derived matrix elements and those obtained from (15) is shown in Table I. Agreement is seen to be semiquantitative.

TABLE I

COMPARISON OF EQUATIONS FOR OFF-DIAGONAL ELEMENTS (IN AU)

Matrix element	Approximate[a]	Exact[b]
	HF (0.92 A)	
1sH1sF	−1.496	−1.521
1sH2sF	−1.122	−1.200
1sH2pF	−0.605	−0.534
	CO (1.13 A)	
1sC1sO	−0.002	−0.003
1sC2sO	−0.592	−0.598
2sC1sO	−1.056	−1.079
1sC2pO	−0.982	−1.010
2pC1sO	−1.838	−1.870
2sC2sO	−0.936	−1.130
2sC2pO	−0.655	−0.761
2pC2sO	−1.158	−1.296
2pC2pO	−0.755	−0.488
2pC2pO[c]	−0.440	−0.441
	ClF[d] (1.63 A)	
1sCl2sF	−0.090	−0.092
1sCl2pF	−0.159	−0.164
3sCl1sF	−0.249	−0.260
3pCl1sF	−0.670	−0.699
2sCl2sF	−0.116	−0.130
2sCl2pF	−0.171	−0.226
2pCl2sF	−0.047	−0.062
2pCl2pF	−0.076	−0.099
3sCl2sF	−0.345	−0.395
3pCl2sF	−0.585	−0.685
3sCl2pF	−0.293	−0.367
3pCl2pF	−0.417	−0.452
2pCl2pF[c]	−0.012	−0.016
3pCl2pF[c]	−0.107	−0.120

[a] Equation 15. [b] Equation 4. [c] π symmetry; where not indicated the matrix elements are of σ symmetry. [d] Missing two-center elements are all less than 10^{-3} au.

Equations 15 and 17 represent no computational difficulty above that encountered in the simpler SCCC–MO method. The kinetic energy integrals can be expressed as linear combinations of overlap integrals,[8b] and the method of calculating the nuclear attraction integrals is identical with that used for the overlap integrals.[29] The inclusion of the interatomic-Coulomb term offers a conceptual advantage by realistically taking into account two-center interaction terms in the diagonal elements. Further, this computational pro-

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[24] H. A. Pohl, R. Rein, and K. Appel, *J. Chem. Phys.*, **41**, 3385 (1964).

[25] H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 458 (1965).

[26] E. Clementi, *IBM J. Res. Develop., Suppl.*, **9**, 2 (1965).

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[29] A. C. Wahl, P. E. Cade, and C. C. J. Roothaan, *J. Chem. Phys.*, **41**, 2578 (1964).

cedure is not presented in a completely *ad hoc* manner, but results from the introduction of familiar approximations in the Roothaan SCF–MO method.

Electronic Structures of Diatomic Transition Metal Oxides

According to crystal field theory,[30] the ordering of the d-orbital MO's in transition metal diatomic oxides, where the five degenerate d orbitals of the free metal atom split into three levels of molecular symmetries, δ, π, and σ, is predicted to be $\delta < \pi < \sigma$ in order of increasing energy. This ordering is, however, apparently inconsistent with the observed ground states of the oxides of at least the early transition metals. That is, the ground states of ScO, YO, and LaO are all $^2\Sigma$'s,[31,32] those of ZrO and HfO, $^1\Sigma$'s;[33] TiO has a $^3\Delta$ ground state,[33] TaO a $^2\Delta_r$;[34] CuO has either a $^2\pi_i$ or a $^2\Sigma$ ground state.[35] Assuming $^2\pi_i$ for CuO, the ground states of CuO and TiO are ambiguous with respect to the δ, σ ordering. Otherwise, these observed ground states require $\sigma < \delta < \pi$.

Further, limited basis set SCF–MO calculations on ScO[36] and TiO[37,38] are in agreement with this latter conclusion. A population analysis of the SCF wave function for TiO[38] (configuration σ^2, $^1\Sigma$) gives $Ti^{+0.55}$ $(3d^{1.25}4s^{1.72}4p^{0.53})$, with the valence σ MO predominantly of metal 4s character, as reflected in the population analysis. A low-lying σ MO of mainly 4s character had also been suggested earlier by Jørgensen.[39] Thus, the value of the crystal field theory in assigning ground states in the transition metal diatomics is hampered by the limitation of an exclusively d-orbital basis set.

With respect to the population analysis, the result of the SCF–MO calculations may not be conclusive. In the limit of going to large internuclear distances the SCF–MO wave function dissociates to the wrong ionic species; the inaccuracy being just that the 4s orbital is incorrectly substituted for the 3d in the ionic configuration. There are, however, qualitative reasons for accepting the large 4s character of the valence σ MO.

The 4s average of configuration ionization energy (called VOIP[25] for valence orbital ionization potential) of the first few neutral atom transition metals, from the configuration $d^{n-1}s$, is found to be greater than that of the 3d, with their energies not crossing (d becoming more stable) until vanadium, where they are about equal.[40] In going from the neutral atom to the charged species, however, any metal (+1) 3d VOIP is already larger than the corresponding 4s VOIP. Thus the character of the lower σ MO may vary from predominantly 4s to largely 3d in going from ScO to TiO, while possibly moving up to a position above the δ MO. We can also expect that the charges on the metals will not exceed +1, this latter value being appropriate for ScO, which is expected to be the most ionic of the diatomic oxides.

Semiempirical MO calculations were undertaken on TiO and CuO to test the validity of eq 15 and 17 as a basis for electronic structure calculations. A minimum requirement for any semiempirical method is that it correctly reproduce the ordering of the MO's necessary to give the observed ground state. The availability of the SCF–MO wave functions offers further possibilities for checking and comparison.

The computational procedure is similar to that outlined for the SCCC–MO method.[11] The W_q values (eq 15 and 17) are identified with the VOIP'S given previously,[11b,21,25] interpolated for partial charge and configuration according to the population analysis, the f_p's (eq 6). The kinetic energy, nuclear attraction, and overlap integrals were evaluated using Richardson's wave functions[41] for the metals and Clementi's[42] for oxygen; their values are given in Tables II and III. The f_p's were iterated to a self-consistence of ±0.01 or better.

TABLE II

CONTRIBUTIONS TO THE DIAGONAL ELEMENTS[a]

Symmetry	qa^b	(Self-consistent VOIP)[c] TiO	CuO	$(qa,qa/r_b)$ TiO[e]	CuO[f]	$(Q_b + k^\lambda)(qa,qa/r_b)^d$ TiO[e]	CuO[f]
σ	$3d_M$	−96.55	−162.96	80.74	76.26	2.95	0.32
	$4s_M$	−82.07	−120.61	58.75	66.84	2.12	0.28
	$4p_M$	−50.79	−68.69	46.95	56.56	1.72	0.24
	$2s_O$	−189.49	−193.59	71.65	72.55	−88.60	−87.40
	$2p_O$	−55.48	−59.33	77.20	78.28	−95.45	−95.95
π	$3d_M$	−96.55	−162.96	71.75	73.36	16.97	24.98
	$4p_M$	−50.79	−68.69	37.09	42.48	8.78	8.68
	$2p_O$	−55.48	−59.33	68.75	69.54	−71.26	−69.88
δ	$3d_M$	−96.55	−162.96	65.07	69.87	28.40	28.24

[a] Energies in 1000 cm^{-1}. [b] M = metal, O = oxygen orbital, configuration for TiO is $\sigma^1\delta^1$. [c] Ti (+0.666), Cu (+0.601). [d] $k^\sigma = 0.60$, $k^\pi = 0.40$, $k^\delta = 0.20$. [e] Bond distance of 1.62 A. [f] Bond distance of 1.60 A.

TABLE III

CONTRIBUTIONS TO THE OFF-DIAGONAL ELEMENTS[a]

λ	$qasb^b$	S_{qasb} TiO	S_{qasb} CuO	$(qa/T/sb)^c$ TiO	$(qa/T/sb)^c$ CuO	$S_{qasb}[VOIP_{qa} + VOIP_{sb}]^d$ TiO	$S_{qasb}[VOIP_{qa} + VOIP_{sb}]^d$ CuO
σ	3d2s	0.2876	0.1302	−33.45	−13.24	−82.87	−46.44
	3d2p	0.1504	0.1213	−46.22	−30.73	−22.87	−26.97
	4s2s	0.3159	0.3468	−11.07	−13.43	−85.79	−108.98
	4s2p	0.0639	0.1844	−3.02	−14.93	−8.78	−33.19
	4p2s	0.2704	0.3552	−8.06	−14.20	−64.98	−93.18
	4p2p	−0.0908	−0.0635	+4.59	+1.79	+9.64	+5.33
π	3d2p	0.2205	0.0990	−25.16	−10.07	−33.53	−22.00
	4p2p	0.1351	0.1771	−3.87	−6.86	−14.38	−15.16

[a] Energies in 1000 cm^{-1}. [b] Same-center off-diagonal elements are zero. [c] $T = {}^1/_2\nabla^2$. [d] See Table II.

It now remains to choose the k factors. For TiO (with one electron each in the σ and δ MO's) the values, $k^\sigma = 0.60$, $k^\pi = 0.40$, and $k^\delta = 0.20$ give the ordering

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[34] W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.*, **42**, 882 (1965).

[35] T. M. Dunn, private communication.

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[38] K. D. Carlson and R. K. Nesbet, *J. Chem. Phys.*, **41**, 1051 (1964).

[39] C. K. Jørgensen, *Mol. Phys.*, **7**, 417 (1964).

[40] C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin Co., New York, N. Y., 1964.

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TABLE IV

MOLECULAR ORBITAL DATA FOR TiO AND CuO

MO	ϵ, 1000 cm^{-1}	CO coefficients								
		$3d_\sigma$	$3d_\pi$	$3d_\delta$	4s	$4p_\sigma$	$4p_\pi$	2s	$2p_\sigma$	$2p_\pi$
					TiO($^3\Delta$)					
1σ	−284.54	0.1693	...	...	0.03076	−0.01395	...	0.9305	0.03063	...
2σ	−168.42	−0.3535	...	...	0.07735	0.03319	...	0.1778	−0.8779	...
1π	−139.65	...	0.3897	...	...	...	−0.005543	...	...	0.8396
3σ	−76.39	0.4256	...	...	−0.8583	0.1841	...	0.06388	−0.2311	...
1δ	−68.15	...	...	1.000	...	...	...	...	...	...
2π	−53.38	...	−0.8333	..	...	...	0.4509	...	...	0.4653
4σ	−44.80	−0.4480	...	...	−0.08451	0.8803	...	−0.002434	0.3547	...
3π	−36.30	...	0.4536	...	...	...	0.9034	...	...	−0.3873
5σ	45.99	0.7772	...	...	0.6245	0.5422	...	−0.6669	−0.2960	...
					CuO($^2\pi_i$)					
1σ	−288.13	0.1649	...	...	0.1210	0.02169	...	0.9087	0.02472	...
2σ	−187.30	−0.6574	...	...	0.03673	0.05762	...	0.1999	−0.6650	...
1π	−157.57	...	0.8291	...	...	...	0.008044	...	...	0.4819
1δ	−134.72	...	...	1.000	...	...	...	...	...	...
3σ	−131.72	0.6029	...	...	−0.5628	0.09038	...	0.08084	−0.5293	...
2π	−117.01	...	−0.5619	...	...	...	0.1314	...	...	0.8496
4σ	−75.53	−0.3395	...	...	−0.5912	0.6802	...	0.09255	0.5143	...
3π	−54.12	...	0.08480	...	...	...	1.008	...	...	−0.2980
5σ	24.39	0.3214	...	...	0.7271	0.8355	...	−0.6952	−0.2706	...

$\sigma < \delta < \pi$, with the δ–σ separation at 8200 cm^{-1}. If, however, the k's are brought closer, with $k^\sigma = 0.50$, $k^\pi = 0.40$, and $k^\delta = 0.30$, the reverse ordering, $\delta < \sigma < \pi$, is obtained. A population analysis of the former result (configuration σ^2 for comparison with the SCF–MO result) shows Ti$^{+0.72}$ ($3d^{1.70}4s^{1.50}4p^{0.08}$); the σ MO is predominantly of 4s character (73%) as predicted by the SCF–MO calculations and expected on the qualitative grounds outlined previously. The relevant MO energies and coefficients are set out in Table IV for both TiO and CuO.

Turning to CuO, again with $k^\sigma = 0.60$, $k^\pi = 0.40$, and $k^\delta = 0.20$, as seen in Table IV, the ordering of the valence MO levels is found to be $\delta < \sigma < \pi$. The character of the σ MO is roughly divided equally ($\sim ^1/_3$ each) between $3d_\sigma$ $4s_\sigma$ and $2p_\sigma$ (oxygen). Thus in the second half of the first transition series we can expect the σ MO to move above δ and increase in 3d character.

The ionization potential of TiO (presumably from δ) has been reported[37] to be within ±0.5 ev of the ground-state ionization potential of Ti, which is known[43] to be at 55,100 cm^{-1}. The orbital energy of the δ MO in TiO is calculated here at −68,100 cm^{-1}; this should roughly correspond to the negative of the first ionization potential of TiO. The agreement is reasonable.

In Table II the various contributions to the diagonal elements are listed for both TiO and CuO. Each element is the sum of the first and third columns of numbers for the diatomic molecule under consideration.

The off-diagonal elements in Table III are the sums of the second and third columns of numbers. One-center elements are arbitrarily set equal to zero. This is reasonable because for a one-center orthogonalized basis set they are usually small. One important result that is to be noted from this table is that the kinetic energy contribution to the off-diagonal elements can be large, especially for the important valence atomic orbitals.

In Figure 1 the MO diagram for TiO is presented, showing the splitting of the degenerate orbital VOIP'S by the interatomic-Coulomb term. Note that the oxygen p_σ diagonal element is significantly lower (more stable) than the p_π diagonal element. This is a completely general result for the method. It is obvious that the p_σ orbital on the oxygen is affected more by the metal nucleus than a corresponding p_π orbital. Therefore, the σ nuclear attraction integral will always be larger than that for the π orbital and the p_σ diagonal element correspondingly more negative than that of the p_π. The same relationship is obtained for the metal diagonal elements.

This result, lowering the ligand p_σ level relative to the p_π, has previously been used in the SCCC–MO method[11] to obtain levels in agreement with observed charge-transfer spectra. For example, the L→M charge-transfer spectra of the square-planar halide complexes of Pd(II) and Au(III)[44a] consist of two bands separated by approximately 10,000 cm^{-1}. These bands have been interpreted as due to electronic transitions from σ and π halide-based molecular orbitals to the empty b_{1g}-($x^2 - y^2$) metal-based molecular orbital.[44b] Calculations have shown that the approximately 10,000 cm^{-1} splitting of these two bands does not arise from differences in metal–ligand off-diagonal elements, but instead from the differences in ligand σ and π diagonal elements.[45]

The method's success in the limited application discussed here is very encouraging since, in fact, the diatomic metal oxides are a difficult case; the simple SCCC–MO method predicts the ordering $\delta < \sigma < \pi$ for all the diatomics. The splitting of the metal d-orbital diagonal elements, in the order $d_\sigma < d_\pi < d_\delta$,

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[43] C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, Vol. I, U. S. Government Printing Office, Washington, D. C., 1949.

[44] (a) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963); (b) H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965).

[45] H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

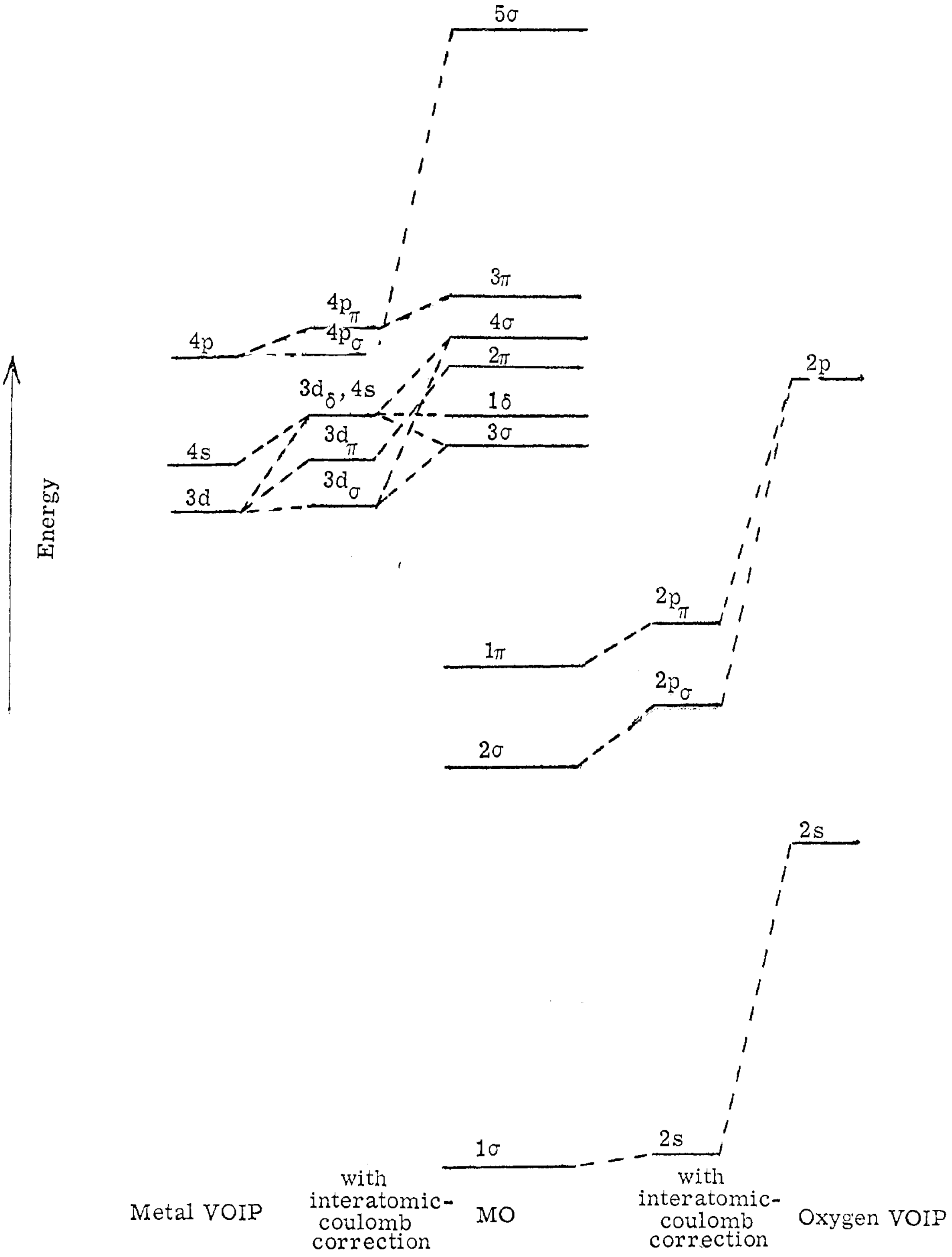

Figure 1.—Molecular orbital energy level diagram for diatomic metal oxides. Drawn to scale for TiO with the 1δ–3σ separation equal to 8200 cm^{-1}.

which is neglected in SCCC–MO, is crucial to obtaining the correct MO ordering in the diatomics containing early transition metals. The extremely sensitive position of the empirical parameter in the diagonal elements suggests that it might very well be possible to set a narrow range for the *k*'s which can be transferred from molecule to molecule. This remains to be seen from further applications of the method to polyatomic systems.

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