

Molecular Orbitals for Large Molecules. VI. Parameterized Self-Consistent-Field Theory for Transition Metal Compounds

J. A. Tossell and W. N. Lipscomb*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received June 21, 1971

Abstract: A new method is presented for nonempirical SCF-LCAO-MO calculations on molecules containing third-row atoms. Diagonal Fock Hamiltonian (F) matrix elements (α 's) are calculated from accurate one-electron integrals, and from two-electron integrals which are calculated accurately or are obtained from the Ruedenberg approximation. Finite overlap off-diagonal F -matrix elements are calculated using parameters obtained from model SCF calculations on chemically similar small molecules, and a new algorithm is presented for zero-overlap elements. α 's for core orbitals are approximated by a simple formula requiring only one-center integrals, all electrons are included, and the self-consistent-field equations are solved. Results are compared with those from *ab initio* SCF calculations, among which are those reported here for a series of diatomic hydrides, oxides, and fluorides of the elements from Co to Ge. A molecular orbital calculation on the ground state of the hypothetical square-planar ion CuF_4^{2-} ($^2B_{1g}$) employing the above approximate method is presented and compared with previous calculations and with experimental results on related compounds.

The Hartree-Fock approximation has given reasonable results for transition metal atoms¹ and molecules.²⁻⁴ In the LCAO-MO form, its application is restricted to small molecules, using small basis sets. The extended Hückel (EH) method,^{5a} when used with care,^{5b} has given good results for large molecules. The principal restriction on LCAO-MO calculations is the amount of time required to calculate the two-electron integrals. The approximation of Slater-type orbitals as linear combinations of Gaussians⁶ has reduced this difficulty for small molecules, but since the number of integrals increases as the fourth power of the size of the basis set, SCF calculations on large molecules are still prohibitively expensive. Molecules containing transition metal atoms are particularly difficult because of the large number of orbitals needed to describe the transition metal itself.

An examination of the logical foundation of the EH theory has yielded nonempirical molecular orbital (NEMO I and II) methods in which diagonal matrix elements of the Fock Hamiltonian are transferred directly from SCF calculations on small model compounds to larger molecules, and off-diagonal elements are calculated using parameters from these same model calculations.⁷ Self-consistency was not explicitly required. Three differences are immediately apparent between the transition elements compounds of interest in this study and the compounds treated by these earlier theories:⁷ (1) the former frequently contain highly charged atoms, (2) the compounds themselves

are often charged, and (3) their ground and excited states are often open shells.

An earlier analysis of several third-row metal hydride, oxide, and fluoride SCF calculations showed substantially transferability of constants (K) in the NEMO formalisms.³ However, serious difficulties appeared in the diagonal and zero-overlap off-diagonal elements. Also, earlier NEMO results on C_3H_4 (*i.e.*, CH_3CCH) suggested that although the method gave good energy eigenvalues, charge distributions were poorly reproduced,³ due in part to the failure of the formalism to allow fine adjustments in the α 's when transferred from one molecule to another. Even those self-consistent methods which give poorer energy eigenvalues might be expected to give better charge distributions than did the earlier NEMO theories, because self-consistent adjustment of the α 's of orbitals on various atoms was allowed. This expectation should be particularly relevant to highly charged transition element complexes. The addition or removal of electrons from a neutral complex might be expected to change the α 's quite drastically, as exemplified by a comparison of α values for TiH_3^+ and TiH_3F .⁴ Finally, the earlier NEMO methods have not been readily applicable to the open shells present in many transition metal compounds.⁹ Indeed, a method of at least the complexity of Pople's INDO¹⁰ theory is required if one wishes to consider open shells, since CNDO-level theories¹¹ ignore important one-center exchange integrals which are necessary to give the separation of different states arising from the same electronic configuration. These features are included below in a self-consistent theory which is designated as NEMO III.

Proposed Method

Summary. The method may be summarized as follows. The two-center nuclear attraction, two-center Coulomb, and two-center exchange integrals, and those

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one-center integrals which contribute to the diagonal elements, are calculated accurately. All other integrals are obtained by the Ruedenberg approximation¹² and the α 's are constructed directly from the integrals and the molecular density matrix. The finite-overlap off-diagonal elements of the potential energy are obtained from a modified Mulliken relation (eq 4), and the kinetic energy elements are calculated accurately. The core α 's are approximated simply, and changes in the core orbital elements of the density matrix are ignored in the self-consistent process.

Matrix Elements. In the SCF-LCAO-MO theory, the MO's are expressed as

$$\langle m | = \sum_i \langle i | C_{mi}$$

where i is a Slater-type orbital (STO) and the C_{mi} 's are the coefficients of the molecular orbitals. Minimization of the molecular energy with respect to the variation of the C_{mi} 's yields the matrix equation

$$FC_i = \epsilon_i SC_i \quad (1)$$

where F is the Fock matrix and S the overlap matrix. The matrix elements of the Fock operator are $F_{ij} = \langle i | T + V + R | j \rangle$ where T , V , and R are the kinetic energy, nuclear attraction, and electron repulsion operators, respectively. Explicitly, the Fock matrix elements for closed shells are

$$F_{ij} = T_{ij} + \sum_A (ij | Z_A r_A^{-1}) + \sum_{k,l} \{ (ij | kl) - 0.5(ik | jl) \} \rho_{kl} \quad (2)$$

The diagonal elements involve one- and two-center nuclear attraction integrals and one-, two-, and three-center electron repulsion integrals. The two- and three-center integrals are difficult to calculate; moreover, large numbers of them are required. We have chosen to calculate only some of them accurately and to approximate the rest with a formula due to Ruedenberg. We shall show that in order to obtain results quantitatively similar to *ab initio* SCF results we must calculate anisotropically and accurately the two-center Coulomb and exchange integrals $(i_A i_A | j_B j_B)$ and $(i_A j_B | i_A j_B)$, where i_A includes all of the components of a degenerate orbital i on atom A. Approximate two- and three-center integrals are obtained from the Ruedenberg formula

$$(ii | kl) = 0.5 \sum_{\alpha} \sum_{\beta} [(ii | l_{\alpha} l_{\beta}) S(k_{\alpha}, l_{\beta}) + (ii | k_{\alpha} k_{\beta}) S(k_{\alpha}, l_{\beta})] \quad (3)$$

where α and β range over all components of an orbital having a given n and l . This formula is essentially a generalization of Mulliken's formula, $(ii | kl) = 0.5 S_{ki} \cdot \{ (ii | kk) + (ii | ll) \}$. Such a generalization is required in order to preserve rotational invariance. Since the summations go only over the components of an orbital with a given n and l , the method is not invariant to hybridization.

Off-diagonal potential energy (UMATRIX) elements for which S_{ij} is nonzero are not calculated explicitly from the integrals but are obtained from the diagonal elements using a modified⁵ Mulliken relation

$$U_{ij} = k_{ij} S_{ij} (\bar{U}_{ii} + \bar{U}_{jj}) / 2 \quad (4)$$

(12) K. Ruedenberg, *J. Chem. Phys.*, **19**, 1433 (1951).

where each \bar{U}_{ii} is averaged over its components and all T_{ij} 's are calculated accurately.

Off-diagonal elements between orbitals whose overlap S_{ij} is zero cannot be obtained from (4). These zero-overlap (ZO) FMATRIX elements were calculated from the complicated formula

$$F_{i_A j_A} = \sum_k \sum_l \{ (i_A j_A | k_A l_A) - 0.5(i_A k_A | j_A l_A) \rho_{k_A l_A} \} - 0.5 \{ \sum_k (i_A i_A | j_A k_B) \rho_{i_A k_B} - \sum (j_A j_A | i_A l_B) \rho_{j_A l_B} \} + \sum_{B \neq A} (i_A j_A | r_B^{-1}) \{ Z_B' - \sum_{\text{monB}} P_m C_m \} \quad (5)$$

which is discussed in Appendix A.

Two further simplifications have been made in our calculations. First, between those atoms which are not nearest neighbors, two-center exchange integrals have been ignored, and Coulomb integrals have been averaged over components. Second, a simple method has been used for obtaining core α 's. Previous methods have ignored changes in the diagonal elements for core orbitals but since these changes are quite large,⁴ accurate reaction energies could not be obtained. Also, these α 's are dependent upon the molecular charge distribution and so must be obtained from the charge distribution at each iteration. The formula which we used was developed by Manne¹³

$$F_{i_A i_A} = F^0_{i_A i_A} + \sum \{ (ii | jj) - 0.5(jj | ij) \} \times \Delta P_j + \sum_{B \neq A} \frac{Q_B}{R_{AB}} \quad (6)$$

Here P_{j_A} is the gross atomic orbital population (GAOP) of orbital j_A , Q_B is the Mulliken charge of atom B, and $F^0_{i_A i_A}$ is the free-atom α . A neighboring neutral atom gives no contribution. Thus, this formula ignores what is often called the neutral penetration term, which is related to the difference between $(i_A i_A | r_B^{-1})$ and $(i_A i_A | j_B j_B) - 0.5(i_A j_B | i_A j_B)$. We find that for the inner shells of the first transition metals this error is not too large and is nearly constant for the various core orbitals. For hydrocarbons, the error is considerably more serious and produces errors as large as 0.15 au. In addition to allowing the calculation of reaction energies, we hope that accurate inner-shell eigenvalues will be useful for comparison with photoelectron spectroscopic results.¹⁴

Since core electrons are not included explicitly in the calculation of valence α 's, we must correct the two-center nuclear attraction terms for their presence. All density matrix elements between the core and valence orbitals are ignored, so the nuclear charge is corrected to

$$Z_B' = Z_B - \sum_{a_B} P_{a_B} - \sum_{a_B, i_B} \rho(a_B, i_B) S(a_B, i_B)$$

where a is a core orbital on B, i is a valence orbital, and P_{a_B} starts at the free-atom GAOP of a_B but is re-evaluated at each iteration.

The above equations are used to calculate the various FMATRIX elements at each iteration from the molecular density matrix. The complete Hamiltonian is diagonalized at each step because the diagonalization of only the valence-valence block (even when trans-

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(14) (a) L. N. Kramer and M. P. Klein, *Chem. Phys. Lett.*, **8**, 183 (1971); (b) R. Manne, *J. Chem. Phys.*, **46**, 4695 (1967).

formed to Hartree-Fock AO's) leads to substantial error.¹⁵ Self-consistency is considered to be obtained when the average variation in α from one cycle to the next is 0.002 au.

Molecular Energies. Both the one-electron and two-electron parts of the computed FMATRIX contain approximations. However, computational advances have made it possible to calculate the complete VMATRIX from accurate values of integrals, including all three-center integrals. The total electronic energy can then be evaluated explicitly as $\frac{1}{2}\sum\eta_i(\epsilon_i + H_i)$, where η_i is the occupation number of orbital i . Thus advances in computational technique for multicentered integrals have improved earlier methods⁷ for approximating total energies, binding energies, and virial ratios.

Transformed Integrals over Molecular Orbitals and Open Shells. The difference in energies of various electronic configurations of molecules can be expressed by combinations of eigenvalue differences and Coulomb and exchange integrals over MO's. The accurate calculation of the two-center Coulomb and exchange integrals over AO's permits us to obtain both Coulomb and exchange integrals over MO's to reasonable accuracy, and thus to distinguish between states of different multiplicity. The approximate formula we shall employ is

$$D(m, n) = \sum_{i,j} P(m, i)(ii|jj)P(n, j) \equiv (mm|nn)$$

$$X(m, n) = \sum_{i,j} P(m, i)(ij|ij)P(n, j) \equiv (mn|mn)$$

where $P(m, i)$ is the Mulliken population of AO i in MO m . This simple formula will give rotationally invariant results if the (ii, jj) and $(ij|ij)$ are averaged over components having the same n and l . The two-electron integrals can then be used to calculate term energy differences and in the calculation of second-order magnetic properties by Hartree-Fock perturbation theory.

At present we employ a version of Nesbet's symmetry and equivalence restrictions for open shells.¹⁶ The diagonal elements F_{ii} are corrected for the presence of unpaired spin by subtracting $-\frac{1}{2}\sum_j(ij|ij)P_j^\beta$, where P_j^β is the GAOP in orbital j of unpaired β spin. This procedure is rotationally invariant if the two-center exchange integrals are averaged. This formula then gives the correct interactions of the open-shell electron with itself, and thus probably the best energy.¹⁶ The open-shell Hartree-Fock energy is obtained by adding certain MO exchange integrals to the zero-order energy. When corrected by the appropriate MO exchange integrals, the results of different averaging methods in a symmetry and equivalence restricted calculation^{2a} on the open σ shell molecule ScO produced almost identical eigenvectors and energies (equal to within 10^{-5} au). Thus we hope that different methods of averaging the FMATRIX interactions will produce only small differences for our approximate calculations. Recent calculations by Moskowitz, *et al.*, have suggested that restricted Hartree-Fock methods may give results similar in accuracy to those of the unrestricted method, even for some spin-dependent properties.¹⁷

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(17) J. W. Moskowitz, C. Hollister, C. J. Hornback, and H. Basch, *J. Chem. Phys.*, **53**, 2570 (1970).

Discussion of Method

Discussion of Approximations for Diagonal Elements. In this section we shall test various approximations for two-center integrals by calculating diagonal FMATRIX elements (α 's) directly from *ab initio* SCF density matrices. The results will suggest how the present method (NEMO III) was obtained.

Many workers have shown the correspondence of the use of the symmetrical Mulliken approximation of two-electron integrals to the various NDO methods within a Löwdin OAO basis.¹⁸ We have attempted to reproduce *ab initio* SCF results using methods similar to the INDO and NDDO methods.^{10,11} In Table I we pre-

Table I. Simulation of SCF Results on C_3H_4 and TiH_3F Using Different Treatments of Two-Center Integrals

	F_{ii}				IV (NEMO III)
	SCF	I	II	III	
C_3H_4					
1C 2s	-1.44	-1.556	-1.556	-1.559	-1.489
1C 2p $_{\sigma}$	-0.733	-0.511	-1.113	-0.740	-0.735
1C 2p $_{\pi}$	-0.157	-0.475	-0.175	-0.364	-0.158
2C 2s	-1.490	-1.490	-1.478	-1.485	-1.532
2C 2p $_{\sigma}$	-0.824	-0.472	-1.252	-0.718	-0.819
2C 2p $_{\pi}$	-0.180	-0.453	-0.063	-0.336	-0.178
3C 2s	-0.503	-1.503	-1.564	-1.563	-1.558
3C 2p $_{\sigma}$	-0.461	-0.295	-0.555	-0.327	-0.398
3C 2p $_{\pi}$	-0.400	-0.336	-0.206	-0.325	-0.347
H $_4$	-0.553	-0.553	-0.555	-0.558	-0.547
H $_{5,6,7}$	-0.523	-0.523	-0.525	-0.528	-0.514
	SCF	III	NEMO		
q(1C)	-0.229	-0.634	-0.206		
q(2C)	-0.034	-0.361	-0.058		
q(3C)	-0.405	-0.164	-0.342		
q(H $_4$)	0.180	0.170	0.156		
q(H $_{5,6,7}$)	0.163	0.089	0.117		
TiH_3F					
Ti 3d $_{z^2}$	0.020	0.034	0.069	0.028	0.018
Ti 3d $_{zz}$	0.019	0.091	0.067	0.089	0.092
Ti 3d $_{x^2-y^2}$	0.067	0.069	0.143	0.068	0.066
Ti 4s	-0.476	-0.508	-0.510	-0.511	-0.510
Ti 4p $_z$	-0.206	-0.193	-0.513	-0.169	-0.217
Ti 4p $_x$	-0.142	-0.225	-0.065	-0.150	-0.139
F 2s	-3.004	-2.987	-2.987	-2.998	-3.000
F 2p $_z$	-0.433	-0.359	-0.480	-0.469	-0.469
F 2p $_x$	-0.435	-0.521	-0.460	-0.471	-0.470

sent α 's for C_3H_4 and TiH_3F calculated (I) by averaging two-center Coulomb integrals, nuclear attraction integrals, and exchange integrals; (II) by averaging two-center Coulomb and exchange integrals and retaining nuclear attraction integral anisotropies; (III) by retaining anisotropies in nuclear attraction and two-center Coulomb integrals and averaging exchange integrals; and (IV) by retaining anisotropies in all three types of two-center integrals (proposed method above). Methods I and III correspond closely to the INDO and NDDO methods. The first three methods produce substantial errors in the anisotropies of the α 's. The INDO approach gives good results for GaH_3 (not reported here), where Coulomb integral anisotropies balance exchange integral anisotropies. In molecules

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Table II. F_{ij} by Various Approximations

	SCF	I (K) ^b	II (K_R/K_V)	III (direct)
GaH ₃ ^a				
1H 1s, 2H 1s	-0.078	-0.078	-0.080	-0.158
1H 1s, 3d _{z²}	0.048	0.046	0.048	0.030
1H 1s, 4s	-0.405	-0.407	-0.425	-0.474
1H 1s, 4p _z	-0.374	-0.372	-0.441	-0.315
1H 1s, 3d _{x²-y²}	-0.079	-0.081	-0.084	-0.068
TiH ₃ F				
1H 1s, 2H 1s	-0.080	-0.080		-0.095
1H 1s, 3d _{z²}	0.074	0.079		0.030
1H 1s, 4s	-0.321	-0.323		-0.304
1H, 1s, 4p _z	-0.257	-0.250		-0.281
F 2s, 4s	-0.586	-0.586		-0.785
F sp _z , 4s	0.119	0.119		0.260

^a GaH₃ and TiH₃F results are from ref 3 and 4. ^b 1H 1s, 2H 1s K from GaH₃ and TiH₃F, otherwise K 's and K_R/K_V 's are taken from GaH, TiH, and TiF results.

cannot be obtained for certain diatomics, for example, nitrides and carbides of transition metals. Hopefully, further SCF calculations will be carried out on small polyatomics, using either Slater orbital basis sets or STO-KG methods,⁸ which approximate STO's by linear combinations of Gaussians. Until that time we must employ two-center K 's from the most closely related molecules available.

A second possible approximation for the off-diagonal elements would have been to calculate accurately the kinetic and nuclear attraction integrals and use a Mulliken-type relationship only on the two-electron part of the potential. The equation which would be used is

$$U_{ij} = V_{ij} + K_{ijR}(\bar{R}_{ii} + \bar{R}_{jj})/2$$

where $K_{ijR} = 2R_{ij}/(\bar{R}_{ii} + \bar{R}_{jj})$ in the model compound, and the R 's are the electron repulsion matrix elements.

Table III. K 's for GaH, TiH, and TiF Bonds

One Center										
	1s, 2s	1s, 3s	1s, 4s	2s, 3s	2s, 4s	3s, 3s	2p, 3p	2p, 4p	3p, 4p	3p, 4p
GaH	0.72	0.47	0.27	0.80	0.48	0.63	0.77	0.48	0.60	0.60
GaH ₃	0.72	0.47	0.27	0.80	0.48	0.63	0.77	0.48	0.61	0.61
Ga	0.72	0.47	0.27	0.80	0.48	0.63	0.77	0.48	0.63	0.63
Two Center										
		H 1s, 3s	H 1s, 4s	H 1s, 3p	H 1s, 4p	H 1s, 3d				
	GaH	1.121	1.105	0.724	1.135	0.612				
	GaH ₃	1.12	1.11	0.73	1.08	0.60				
One Center										
	1s, 2s	1s, 3s	1s, 4s	2s, 3s	4s, 4s	3s, 4s	2p, 3p	2p, 4p	3p, 4p	1s, 2s
TiH	0.71	0.46	0.24	0.79	0.49	0.70	0.75	0.45	σ 0.662	0.66
									π 0.681	
TiF	0.71	0.46	0.24	0.79	0.49	0.70	0.75	0.44	σ 0.667	0.658
									π 0.677	
TiH ₃ F	0.71	0.46	0.24	0.79	0.49	0.71	0.76	0.46	0.69	0.69
Two Center										
		H 1s, 3s	H 1s, 4s	H 1s, 3p	H 1s, 4p	H 1s, 3d				
	TiH	1.048	1.104	0.766	1.135	0.905				
	TiH ₃ F	1.05	1.06	0.77	1.09	0.92				
	F 2s, 4s	F 2s, 4p	F 2s, 3d	F 2p, 4s	F 2p, 4p	F 2p, 3d				
TiF	1.104	1.163	0.713	1.047	σ 2.910	σ 0.797				
					π 0.925	π 0.714				
					Wt av 1.225	0.765				
TiH ₃ F	1.10	1.16	0.71	1.08	1.22	0.79				

containing second-row atoms, where p_σ - p_σ and p_π - p_π interactions are possible, INDO averaging gives poor results. The α 's of the 3d orbitals are less affected by the averaging procedures than those of the 4s and 4p. Anisotropies in metal 3d ligand two-center Coulomb integrals are small, and exchange integrals are often so small that they may be neglected completely. The 3d α 's are dependent on the outer orbital densities, however, and 4s and 4p (and ligand 2s and 2p) anisotropies must be retained in order to give these densities to a reasonably good approximation.

Approximations for Off-Diagonal Elements. The K_{ij} 's for eq 4 are obtained from model SCF calculations, principally from calculations on diatomic molecules. The K 's for various types of interactions are found to be quite insensitive to the internuclear distance and to the particular molecule from which they are obtained. One-center K 's can also be obtained easily and directly from atomic SCF calculations. Difficulty arises when convergent SCF calculations

Elements of the UMATRIX obtained in this way for GaH₃ are given in Table II. In such an approach, lack of cancellation between the two large terms V_{ij} and R_{ij} causes serious error.

The integrals are available to calculate the two-center off-diagonal elements directly, using the formula

$$U_{iA jB} = V_{iA jB} + \sum_k (\phi_{iA} \phi_{jB} | \phi_k \phi_k) - 0.5(\phi_{iA} \phi_k | \phi_k \phi_{jB}) P_k \quad (7)$$

The errors in these off-diagonal terms are expected to be proportionally larger than those in the diagonal terms, since none of the necessary two-electron integrals is calculated exactly, and the approximate two-center integrals are multiplied by the large, usually positive, orbital populations. Hence, there is little cancellation of errors. Only if the two-center hybrid integrals were calculated accurately, e.g., by expansion of the Slater orbitals as limited sets of Gaussians,¹⁹ would this

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Table IV.

(A) Variation of Two-Center K 's with Distance and Exponent in GaH for $\zeta_{\text{H}1s} = 1.0$

	R		
	2.630	2.931	3.156
K (H 1s, 3s)	1.1281	1.1216	1.1175
K_R (H 1s, 3s)	1.2385	1.2568	1.2691
K_V (H 1s, 3s)	1.2100	1.2216	1.2294
K (H 1s, 4s)	1.1094	1.1150	1.1135
K_R (H 1s, 4s)	1.0332	1.0274	1.0200
K_V (H 1s, 4s)	1.0340	1.0340	1.0269
K (3p, H 1s)	0.7362	0.7246	0.7172
K_R (3p, H 1s)	1.0675	1.0808	1.0900
K_V (3p, H 1s)	0.9870	0.9936	0.9981
K (4p, H 1s)	1.1110	1.1351	1.1504
K_R (4p, H 1s)	1.0018	0.9884	0.9807
K_V (4p, H 1s)	1.0031	0.9990	0.9928

(B) Variation of K 's with $\zeta_{\text{H}1s}$; GaH, $R = 2.931$

	$\zeta_{\text{H}1s}$		
	1.2	1.0	0.8
	P_{ii}		
H 1s	1.157	1.375	1.517
H 4s	1.808	1.776	1.760
H 4p _z	1.127	0.964	0.846
H 3d _z ²	1.913	1.891	1.885
	$K_{i,\text{H}1s}$		
H 1s, 4s	1.115	1.105	1.106
H 1s, 4p	1.135	1.115	1.112
H 1s, 3d _z ²	0.612	0.578	0.537
H 1s, 3s	1.121	1.157	1.185

Table V. NEMO I, II, and III Results for GaH₃

i	SCF	NEMO I ^a	NEMO II ^b	NEMO III		
				Ga 1s, 2s, 2p, 3s Core	1s, 2s, 2p, 3s, 3p Core	No core
			F_{ii}			
3d _z ²	-0.413	-0.346	-0.322	-0.417	-0.424	-0.407
3d _{xx}	-0.461	-0.342	-0.322	-0.449	-0.457	-0.442
3d _z ² - y^2	-0.421	-0.290	-0.323	-0.420	-0.427	-0.408
4s	-0.648	-0.571	-0.601	-0.667	-0.665	-0.680
4p _z	-0.037	-0.011	-0.026	-0.037	-0.032	-0.025
4p _x	-0.351	-0.280	-0.279	-0.355	-0.355	-0.340
H 1s	-0.407	-0.405	-0.389	-0.396	-0.375	-0.406
1s	-378.960	-378.808	-378.775	-378.984	-378.942	-378.923
2s	-84.226	-84.077	-84.107	-84.249	-84.208	-84.199
3s	-14.161	-14.042	-14.059	-14.167	-14.138	-14.155
			P_{ii}			
3d _z ²	1.945	1.980	1.957	1.945	1.947	1.938
3d _{xx}	2.0	2.0	2.0	2.0	2.0	2.0
3d _z ² - y^2	1.930	1.972	1.958	1.938	1.938	1.939
4s	1.142	1.052	0.883	1.206	1.243	1.217
4p _z	0.013	0.011	0.011	0.010	0.010	0.010
4p _x	0.910	0.738	0.906	0.925	0.982	0.892
H 1s	1.076	1.189	1.149	1.046	0.994	1.066
ϵ (HFMO) ^c	-0.394	-0.266	-0.288	-0.386	-0.386	-0.380
ϵ (LEMO) ^c	0.090	0.090	0.075	0.072	0.069	0.076

^a α 's taken directly from GaH with the same internuclear distance and exponents. ^b C_{pq} parameters and average α 's from GaH. ^c HFMO = highest filled MO, LEMO = lowest empty MO.

method be expected to give good results. Preliminary results using our accurate integrals suggest that this is indeed so. In Table II we give a comparison of off-diagonal elements in GaH₃ and TiH₃F calculated from diatomic parameters and directly from the integrals.

The use of K 's from model compounds will give good results, provided that K 's describing various AO interactions do not change appreciably within a series of closely related molecules. It would also be very desirable if the K 's varied slowly with exponent and internuclear distance. In Table III we compare the mole-

cules TiH₃F and GaH₃ and their various fragments. Although the α 's vary substantially, we see that K 's are indeed remarkably constant.

In order to test the stability of the K 's under changes in bond length, we carried out SCF calculations on GaH at three different internuclear distances using the same basis set ($\zeta_{\text{H}1s} = 1.0$). Results are given in Table IVA. The various K 's are quite similar for all three distances. Also, a comparison given in Table IVB of calculations performed at $R = 2.931$ with $\zeta_{\text{H}1s} = 1.2$ and $\zeta_{\text{H}1s} = 0.8$ shows that K varies little with orbital exponent provided that the exponent change does not drastically change the wave function.

In Appendix B we give K 's for *ab initio* SCF calculations on CuF using two basis sets having slightly different exponents. The K 's differ little between the two calculations.

Comparison with *Ab Initio* SCF Results

Nemo III results are compared with the *ab initio* SCF and NEMO I and II results for some small molecules in Appendix C. In the NEMO I method α 's are taken without modification from SCF calculations for model compounds. In NEMO II α 's are obtained as

$$\alpha_i = C_{ii} \sum \alpha_{ik} F_{kk} \Delta_{jk}$$

so that the overlap of i with orbitals on adjacent atoms

was allowed to modify the diagonal element. Results are given in Tables V and VI, where we compare NEMO I,^{3a} II,^{5b} and III calculations with SCF results for GaH₃ and TiH₃F. Although the NEMO I and SCF results are similar, the failure to allow for changes in α 's and the need for averaging underestimate the electron populations on the central atoms and also reproduce their anisotropy poorly. The NEMO II calculation gives good α 's for 4s and 4p orbitals but poor results for 3d's and also for the H 1s and the core orbitals of the metal. Although the NEMO II method may give good

Table VI

(A) TiH ₃ F Valence- and Core-Orbital α 's and Zero-Overlap FMATRIX Elements			
	SCF	NEMO	
Valence-Orbital α 's			
			TiH, TiF
Ti 3p _z	-3.672	-3.643	-3.615, -3.614
3p _{x,y}	-3.671	-3.643	-3.611, -3.608
3d _z ²	0.020	0.036	0.054, 0.065
3d _{xy, yz}	0.091	0.110	0.221, 0.206
3d _{x²-y², xy}	0.067	0.084	-0.467, -0.463
4s	-0.476	-0.496	-0.375, -0.418
4p _z	-0.206	-0.209	-0.125, -0.193
4p _{x,y}	-0.142	-0.143	-0.017, -0.034
H 1s	-0.435	-0.420	-0.427
F 2s	-3.004	-2.980	-2.975
2p _z	-0.433	-0.432	-0.412
2p _{x,y}	-0.435	-0.433	-0.404
Core-Orbital α 's			
			Free atoms
Ti 1s	-183.655	-183.640	-183.223
2s	-37.938	-37.902	-35.495
2p _z	-18.036	-18.004	-17.592
2p _{x,y}	-18.037	-18.005	-17.592
3s	-6.302	-6.267	-5.957
F 1s	-26.103	-25.945	-26.133
FMATRIX Elements			
4p _z , 4s	-0.053	-0.047	
3d _{xy} , 4s	0.010	0.016	
3d _z ² , 4p _z	-0.061	-0.039	
3d _{x²-y²} , 4p _x	0.090	0.091	
3d _{xy} , 3d _{x²-y²}	0.085	0.079	
(B) Orbital Populations, Eigenvalues, and Energies			
	P_{ii}		
	SCF	NEMO	NEMO $F^{ZO} = 0.0$
H 1s	1.30	1.28	
Ti 3d _z ²	0.37	0.37	
3d _{xy, yz}	0.22	0.22	
3d _{x²-y², xy}	0.28	0.27	
4s	0.70	0.77	
4p _z	0.09	0.11	
4p _{x,y}	0.33	0.35	
F 2s	1.94	1.94	
2p _z	1.68	1.69	
2p _{x,y}	1.83	1.82	
q(H)	-0.30	-0.28	-0.40
q(Ti)	1.18	1.11	1.37
q(F)	-0.28	-0.27	-0.17
(HFMO)	-0.444	-0.421	-0.408
(LEMO)	0.075	0.075	0.009
Kinetic energy	947.299	947.109	
Total energy	-947.464	-946.830	

results for valence orbital populations, and fair anisotropies, the α 's of 3d orbitals cannot be obtained accurately. On the other hand, the NEMO III results are very close to the SCF results: for example, average values and anisotropies of all valence orbitals are given well. In both GaH₃ and TiH₃F we note that the ligand α 's are very similar for the diatomics and corresponding polyatomics. However, the self-consistent procedure would be destroyed by any attempt to maintain ligand α 's constant, since the ligand α 's could not reflect the self-consistent conditions.

Table VI contains α 's calculated from the SCF density matrix for TiH₃F in the NEMO III approximation. The largest errors among the valence orbitals are for F 2s and F 2p. The α 's of the Ti core are all too positive by about 0.03 au, probably as a result of the neglect

of the neutral penetration term. Only the α of the F 1s is seriously in error. The eigenvalues and charge distribution are quite close to the SCF values.

In TiH₃F we see that all zero-overlap elements, including those between different components of the 3d orbital are given reasonably well by formula 5. However, although the formulas for the diagonal and zero-overlap off-diagonal elements are separately rotationally invariant, when they are used together the results are not rotationally invariant (see ref 7b). Therefore, our results do depend upon the coordinate system chosen. No provision is made in the programming for including all zero-overlap elements automatically. Moreover, the algorithm for generating them is the least accurate of the formulas employed, and this formula requires parameterization from *ab initio* SCF results. Therefore, the NEMO III method is restricted at present to molecules of high symmetry. A rotationally invariant alternative for zero-overlap elements has been given previously,^{7b} but the results are less accurate.

The results of a NEMO III calculation on CuF, using two different core-valence divisions, are given in Table VII (see Appendix B for the basis set). Diagonal FMATRIX elements, eigenvalues, and orbital populations are all fairly good, as are zero-overlap FMATRIX elements. We note that an expansion of the d-orbital basis to two Slater orbitals causes no difficulty in the method, regardless of whether or not the inner Slater orbital is included in the core. In our NEMO III calculations, errors in total energies, given in Tables VIB and XVII, are small on a percentage basis ($\pm 0.05\%$) but are large compared with dissociation energies. Hence, the calculations can be expected to give at best only trends in reaction energies.

The above results show that α 's may be calculated accurately by our method and that K 's may be transferred within a series of molecules. Therefore, we can, for example, calculate an accurate wave function for TiH₃F using only the basic equations and parameters from TiH and TiF.

Molecular Orbital Results for CuF₄²⁻

The above method has been applied to the calculation of the ²B_{1g} ground state of the hypothetical square-planar ion CuF₄²⁻. This ion was chosen because off-diagonal parameters (K 's) were available from the SCF calculation for CuF. The diatomic distance and the exponents for the free-atom basis set were employed (see Appendix B). The calculation also allows us to test the NEMO III theory for open shells. Two-center K 's for the F-F interactions were not available from our polyatomic SCF calculations. Hence, we employed parameters taken from calculations on F₂ at the appropriate distances. Results are compared with both simpler and more rigorous theories on related molecules, even though no results exist for CuF₄²⁻ itself.

Ros and Schuit⁹ carried out Wolfsberg-Helmholtz type calculations for CuCl₄²⁻; they used an approximate semiempirical formula for generating α 's and required charge consistency. Demynuck and Veillard²⁰ performed an *ab initio* SCF calculation on CuCl₄²⁻ using a small Gaussian orbital basis set and Roothaan's open-shell formalism. The Cu charge was 1.28 and the d orbital ordering was d_{x²-y²} >

(20) J. Demynuck and A. Veillard, *Chem. Phys. Lett.*, 6, 204 (1970).

Table VII. Comparison of NEMO and SCF Results for CuF

<i>i</i>	F_{ii}				P_{ii}		
	SCF	NEMO III ^a			SCF	NEMO III	
		A	B			A	B
Cu 3s	-11.768	-11.752	-11.572	Cu 3d _{z²'}	1.168	1.200	1.208
3p _z	-7.129	-7.170	-7.111	3d _{xz}	1.237	1.245	1.241
3d _{z²}	1.133	1.074	1.107	3d _{x²-y²}	1.241	1.248	1.245
3d _{xz}	1.043	0.988	1.031	4s	0.839	0.860	0.893
3d _{x²-y²}	1.053	1.000	1.040	4p _z	0.130	0.130	0.135
3d _{z²'}	0.248	0.206	0.231	4p _{x,y}	0.115	0.107	0.114
3d _{xz} '	0.239	0.194	0.245	F 2s	1.982	1.988	1.989
3d _{x²-y²'}	0.246	0.200	0.250	2p _z	1.310	1.229	1.233
4s	-0.250	-0.259	-0.235	2p _{x,y}	1.996	1.994	1.994
4p _z	-1.048	-1.091	-1.055				
4p _{x,y}	-1.025	-1.068	-1.022				
F 1s	-26.083	-26.052	-26.038				
2s	-2.818	-2.816	-2.801				
2p _z	-0.176	-0.169	-0.152				
2p _{x,y}	-0.370	-0.362	-0.350				
q(F)	-0.205	-0.284	-0.216				
<i>i, j</i>	F_{ij}^{ZO}						
4p _z , 4s	-0.049	-0.068	-0.068	(HFMO σ)	-0.249	-0.249	-0.221
4s, 3d _{z²'}	0.007	0.004	-0.016	(LEMO σ)	0.144	0.123	0.139
4p _z , 3d _{x_y'}	0.020	0.014	-0.011	(HFMO π)	-0.359	-0.335	-0.317
4p _x , 3d _{z²'}	-0.017	-0.016	-0.016	(HFMO δ)	-0.495	-0.502	-0.457
F 2p _z , F 2s	-0.043	-0.048	-0.049				

^a NEMO A is general method with 1s, 2s, 2p, 3s, core. NEMO B is general method with 1s, 2s, 2p, 3s, 3p, 3d core.

$d_{z^2} > d_{xz,yz} > d_{xy}$. However, the "uncorrected" eigenvalues of the unfilled orbital were lower than those of some filled d orbitals. The open-shell MO for the best basis set employed had 89% Cu 3d_{x²-y²} character. The highest energy filled MO's were predominantly Cl 3p orbitals, with the filled 3d orbitals at lower energy.

Recently Basch, Hollister, and Moskowitz²¹ performed an *ab initio* SCF calculation on NiF₄²⁻, using a large number of fixed linear combinations of Gaussian orbitals, called Gaussian-type functions (GTF's). A double ζ representation was used for the F 2p orbitals and the Ni 3d orbitals. The results showed 17 "core" orbitals, followed by 4 predominantly 3d orbitals with the order 3d_{z²} < 3d_{xz,yz} < 3d_{xy}. The next 12 orbitals were predominantly F 2p orbitals. The first unoccupied orbitals are Ni 4s, followed by Ni 3d_{x²-y²} and finally Ni 4p. Populations and charges were: Ni-(core)¹⁸3d^{8.13}4s^{0.020}4p^{0.49}F(core)^{3.96}2p^{5.34}, q(Ni) = 1.12. They found that transition energies, calculated as ${}^1E(i \rightarrow j) = \epsilon_i - \epsilon_j - J_{ij} + 2K_{ij}$, were not always proportional to eigenvalue differences because of large differences in the values of the two-electron integrals over MO's.

We present two sets of NEMO III results using different methods of averaging within the symmetry and equivalence restrictions. In the first (A), the electron in the half-filled 6b_{1g} orbital is allowed to repel itself as if a closed shell were present. Thus, the orbital eigenvalue requires a zero-order correction. In the second method (B), the 6b_{1g} interaction with itself is correct but its interactions with the filled orbitals are not, and hence their eigenvalues require zero-order corrections.

These are the two extreme methods of averaging within the symmetry and equivalence restrictions for this system. We find that results for these two methods

(21) H. Basch, C. Hollister, and J. W. Moskowitz, "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 449.

Table VIII

	CuF ₄ ²⁻ α's	
	A	B
Cu 1s	-328.575	-328.531
Cu 2s	-71.580	-71.540
Cu 2p _z	-35.118	-35.077
Cu 3s	-11.223	-11.205
Cu 3p _z	-6.679	-6.656
Cu 3d _{z²}	1.546	1.567
xz, yz	1.460	1.484
x ² - y ² , xy	1.589, 1.446	1.403, 1.478
Cu 3d _{z²'}	0.731	0.471
xz, yz	0.711	0.721
x ² - y ² , xy	0.802, 0.726	0.741, 0.738
4s	-0.088	-0.085
4p _z	-0.576	-0.569
x, y	-0.629	-0.626
1F 1s	-25.339	-25.315
1F 2s	-2.222	-2.223
1F 2p _z	0.248	0.263
x	0.300	0.228
y	0.239	0.254
F (2p _σ , 2s)	-0.040	-0.040

are quite similar. As would be expected, the atomic orbitals constituting the open-shell MO (3d_{x²-y²} and F 2p) are stabilized in the second calculation (calculation B) and their populations increase slightly relative to the populations of calculation A. The resulting increase in the 3d_{x²-y²} population raises the α's of the other d orbitals slightly. The only qualitative difference between the two calculations is in the ordering of the 3b_{1g} (x² - y²) and 6a_{1g} (z²) MO's. Unless indicated, results discussed in the text below will be for calculation B.

Generally, our results show smaller charge separations (in terms of Mulliken charges) and greater covalency than do previous calculations. The charge on Cu is 0.44, with charge transfer (relative to the 3d¹⁰4s atom) out of both the 3d_{x²-y²} and the 4s orbitals and with increased charge in the 4p orbitals. The F orbi-

Table IX. CuF_4^{2-} Eigenvalues and Mulliken GAOP's in MO's for Calculation B

Orbital	ϵ			ϵ_{uncorr}
18	-0.064	(0.56 + 1.00) $3d_{xy}$ + 0.44F 2p	$1b_{2g}$	-0.068
19, 20	-0.019	(0.70 + 1.16) $3d_{xz}$ + 0.14F 2p	$1e_g$	-0.024
21	-0.008	(0.56 + 0.99) $3d_{z^2}$ + 0.05F 2s + 0.40F 2p	$6a_{1g}$	-0.030
22	0.007	(0.50 + 0.81) $3d_{x^2-y^2}$ + 0.09F 2s + 0.60F 2p	$3b_{1g}$	-0.099
23	0.142	(0.11 + 0.19) $3d_{z^2}$ + 0.494s + 0.12F 2s + 1.08F 2p	$7a_{1g}$	0.092
24, 25	0.247	0.07 4p + 1.93F 2p	$5e_u$	0.188
26	0.255	2.00F 2p	$3a_{2u}$	0.251
27	0.271	2.00F 2p	$1b_{2u}$	0.267
28, 29	0.292	(0.07 + 0.07) $3d_{xz}$ + 1.82F 2p _z	$2e_g$	0.287
30	0.292	(0.23 + 0.20) $3d_{xy}$ + 1.56F 2p	$2b_{2g}$	0.288
31	0.307	2.00F 2p	$1a_{2g}$	0.302
32, 33	0.308	0.014p + 1.99F 2p	$6e_u$	0.280
34	0.494	(0.19 + 0.12) $3d_{x^2-y^2}$ + 0.69 F 2p	$4b_{1g}$	0.494
35	1.053	(0.14 + 0.03) $3d_{z^2}$ + 1.254s + 0.12 F 2s + 0.44F 2p	$8a_{1g}$	1.053

Table X. CuF_4^{2-} Orbital Populations

	Mulliken GAOP's		Mulliken overlap populations	
	A	B	B	
$(3d + 3d')_z^2$	1.879	1.865	Cu $3d_{z^2}$, F 2s	0.008
xz	2.002	2.003	Cu $3d_{x^2-y^2}$, F 2s	0.023
$x^2 - y^2$	1.709	1.717	Cu 4s, F 2s	-0.026
xy	2.008	2.008	Cu 4s, F $2p_\sigma$	-0.069
4s	0.765	0.729	Cu 4p _σ , F 2s	0.014
4p _z	0.039	0.015	Cu 4p _σ , F $2p_\sigma$	0.064
4p _{x,y}	0.119	0.111	Cu $3'd_{xz}$, F $2p_{\pi v}$	-0.002
F 2s	1.960	1.955		
F 2p _z	1.995	1.995		
F 2p _σ	1.646	1.662		
F 2p _{π_h}	1.995	1.995		
q(Cu)	0.40	0.44		
$\sum \epsilon_i$	-1177.870 ^a	-1177.059 ^b		
One-electron energy	-3698.140	-3698.614		
Total energy	-2026.950	-2026.782		
Kinetic energy	2032.260	2032.475		
N	411.055	411.055		
	$\sum E^{\text{at}} = -2030.079 = E(\text{Cu}^{2+}) + rE(\text{F}^-)$			

^a Corrected by subtracting $0.5K(4b_{1g}, 4b_{1g})$. ^b Corrected by adding $0.5 \sum_{i=1}^{32'} (4b_{1g}, i)$ where the summation excludes the core MO's 1s, 2s, 2p, and 3s.

tals are filled except for the p orbital of σ symmetry with respect to the Cu-F bond, which has a GAOP of 1.67. The orbital populations are: $\text{Cu}(\text{core})^{18}3d^{9.60-4s^{0.73}4p^{0.24}}\text{F}(\text{core})^{2.0}2s^{1.95}2p^{5.65}$. The small atomic charges seem reasonable in view of the small charge separation in the model *ab initio* SCF calculation on CuF, but the failure of the NEMO III results for CuF to give an accurate F $2p_\sigma$ population may also be a factor leading to this small atomic charge.

The α 's, eigenvalues, and MO compositions are given in Tables VIII and IX. The orbital populations and energy quantities are given in Table X. The orbital structure is similar to that found by Basch, *et al.*, for NiF_4^{2-} and by Demuynck and Veillard for CuCl_5^{2-} . The lowest 17 orbitals are core orbitals. Orbitals 18 through 22 are predominantly Cu 3d orbitals in the order $xy < xz, yz < z^2 < x^2 - y^2$. The orbitals from 24 to 33 are predominantly F 2p. The half-filled $4b_{1g}$ orbital (no. 34) is about 30% $3d_{x^2-y^2}$. The lowest unoccupied MO is the $8a_{1g}$, composed primarily of 4s and F 2p. The eight highest orbitals are almost entirely the atomic virtual orbitals arising from the 3p, 4p and 3d, $3d'$ combinations.

One measure of agreement with experiment for transition metal halide calculations is the value of the transferred hyperfine coupling on the ligand. Previous ap-

proximate calculations have given good results for this quantity.^{22,23} Our results for the open shell, described as $\phi_{34} = 0.563d_{x^2-y^2} + 0.07X(s) + 0.44X(\sigma)$, where the X's are symmetry-adapted combinations of ligand s and p_σ orbitals, are $f_s = (0.07)^2 = 0.49\%$ and $f_\sigma = (0.44)^2 = 19.3\%$. The hyperfine constants for CuCl_4^{2-} are $f_s = 0.61\%$ and $f_\sigma = 11.9\%$,²⁵ and so the electron distribution in the $4b_{1g}$ orbital would seem to be at least qualitatively correct. The CuF distance used is the gas-phase value and is probably smaller than the appropriate solid-state distance. This would tend to increase the covalency and the f parameters.

Previous workers have considered the distortion of the 3d orbital in metal complexes to be a measure of covalency.²³ The spatial expansion of the 3d orbital in the complex can be compared with that in the free atom by taking the ratio of the Mulliken populations in the inner and outer 3d Slater orbitals for our double- ζ calculation. Such results are presented in Table XI. Along with the ligand coefficients in the metal MO's, these quantities can give a measure of the covalency. We find that filled xy and z^2 orbitals are slightly expanded and that antibonding and unfilled orbitals are

(22) H. Rinneberg, H. Haas, and H. Hartmann, *J. Chem. Phys.*, **50**, 3064 (1969).

(23) H. M. Gladney and A. Veillard, *Phys. Rev.*, **189**, 385 (1969).

Table XI. Ratio of Outer/Inner 3d-Orbital Populations^a

Orbital	Ratio
18	1.79
19	1.66
21	1.79
22	1.62
23	1.73
28	1.00
30	0.91
34	0.63

^a Free atom, 1.68. For calculation B.

Table XII. Transition Energies (au) of CuF₄²⁻

<i>i</i>	<i>j</i>	$\Delta\epsilon_{ij}$	J_{jj}	J_{ij}	K_{ij}	ΔE , au	ΔE , cm ⁻¹	
1b _{2g}	xy → x ² - y ²	4b _{1g}	0.558	0.446	0.500	0.007	0.507	112.2 × 10 ³
1e _g	xz, yz → x ² - y ²	4b _{1g}	0.513	0.446	0.516	0.011	0.448	98.3 × 10 ³
6a _{1g}	z ² → x ² - y ²	4b _{1g}	0.502	0.446	0.488	0.045	0.482	105.7 × 10 ³
6e _u	F 2p → x ² - y ²	4b _{1g}	0.186	0.446	0.356	0.056	0.304	66.7 × 10 ³
6e _u	F 2p → F s, F 2p, 8a _{1g}		0.745		0.305	0.029	0.398	87.3 × 10 ³

slightly contracted, as has been found in the *ab initio* SCF results. This is consistent with a recent interpretation of Racah parameter values in Mn²⁺ compounds.²⁴

From the eigenvalue differences and transformed integrals, we can calculate transition energies from filled orbitals to the half-filled and unfilled orbital (see Appendix D). These energies are listed in Table XII. Clearly, transition energies are strongly influenced by the *J* and *K* integrals. Although the *J* integrals over inner d orbitals are similar to the free-atom value of 1.03308 au, the *J* integrals of the half-filled 4b_{1g} orbital with the filled orbitals are much lower, because of covalency in the 4b_{1g}.

Our results show that the lowest charge-transfer transition is the 6e_u → 4b_{1g} (F 2p → Cu 3d_{x²-y²}) transition at 66,700 cm⁻¹. The charge-transfer transition to the predominantly 4s (8a_{1g}) orbital is at 88,700 cm⁻¹. The d-d transitions to the half-filled 4b_{1g} orbital fall at higher energy. As in the NiF₄²⁻ calculation of Basch, *et al.*, the relative energy of the z² → x² - y² transition is raised by the low relative value of *J*(6a_{1g}, 4b_{1g}) and the high value of *K*(6a_{1g}, 4b_{1g}). In our calculation, however, this effect is not large enough to give the 6a_{1g} → 4b_{1g} as the highest energy d-d transition.

This calculation required 1.5 min for the accurate two-electron integral computation, 1.3 min to approximate the many-center integrals and write a tape, 1 min to evaluate the one-electron integrals, and 12 min to calculate the self-consistent wave function (16 iterations) on the IBM 360/65.

Conclusions

The CuF₄²⁻ results indicate that our method is capable of reproducing semiquantitatively the relative energies of different ligand and metal orbitals and of giving correct metal orbital anisotropies. Our ability to calculate the two-center integrals over MO's, *J*_{*ij*} and *K*_{*ij*}, makes possible the calculation of transition energies and the consideration of open shells. Approximate total energies can also be obtained. Since the core orbitals are allowed to change in energy as a function of the charge distribution, the energies of the core MO's are given accurately.

(24) L. L. Lohr, Jr., *J. Chem. Phys.*, **55**, 27 (1971).

We expect that approximate calculations of this type can serve two purposes. First, they should give insight into the type of basis set required to accurately describe these compounds. The lack of low-energy virtual orbitals in our calculations makes clear the inadequacy of the present basis set. The presence of a 4s orbital is necessary to obtain reasonable covalency parameters,²³ and a diffuse 4p orbital may be necessary for the construction of virtual orbitals. Any expansion of the set must be done carefully, however, to avoid imbalance. For example, Carson and Moser² suggested

that the use of a double- ζ ligand 2p basis might unbalance the basis set because the ligand would be nearer than the metal to the Hartree-Fock limit. In the present basis, orbital energies differ from their Hartree-Fock limits^{1b} by +0.038 for 4s, +0.075 for 3d, and +0.730 for F 2p. The highly positive (+0.244) 2p eigenvalues of F using the present basis provide a partial explanation for the many positive values of ϵ among the filled orbitals.

Secondly, we expect that this method can give qualitatively correct results for charge distributions and energy trends in transition metal compounds. Our nonempirical framework prevents us from making prior assumptions about the ordering of energy levels, and we expect to obtain information about spectra and electron distribution which will be dependent only on the basis set employed. The use of double- ζ d-orbital basis allows us to evaluate the effect of covalency on the Racah parameters. Hyperfine coupling constants should also be given to fair accuracy. Explanations of chemical reactivity based upon semiempirical models can be checked. Perturbation theory can be applied to these wave functions in order to obtain values for second-order magnetic properties, such as chemical shifts.^{15,25}

Acknowledgments. We gratefully acknowledge support from the U. S. Office of Naval Research. J. A. T. is indebted to the National Science Foundation for a Predoctoral Fellowship. Substantial computational assistance was provided by R. M. Stevens and E. A. Laws. E. Switkes generously made available to us several unpublished SCF calculations.

Appendix A. Zero-Overlap Elements

These elements are particularly difficult to calculate since in different cases all three of the terms in eq 5 are sizable. The first term is a one-center term whose most important contribution is $\{1.5(ij|ij) - 0.5(ii|jj)\} \cdot \rho_{ij}$. The second comes from the exchange interaction of ρ_{iA} , j_A and the two-center charge distribution ρ_{iA} , k_B . The third arises from the at-

(25) Another new parameterized SCF method, requiring small computational time and capable of high accuracy, will appear: T. A. Halgren and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, in press.

Table XIII. Cu and Cr Energies with Different Basis Sets^a

		I	II (THF)	III (HF)	IV (MBS)
Cr	3d ⁴ 4s ²	-1041.7462	-1042.6073	-1043.3061	-1041.0062
Cr	3d ⁶ 4s	-1041.7468	-1042.6490		-1040.6664
		-0.0006	-0.0417		+0.3398
Cu	3d ⁹ 4s ²	-1636.5806	-1637.7987	-1638.9491	-1633.2393
Cu	3d ¹⁰ 4s	-1636.5183	-1637.7942	-1638.9614	-1632.3177
		+0.0523	+0.0045	-0.0123	-0.9216

^a I, present basis sets (4s, 2p, 2d); II, Claydon and Carlson's truncated Hartree-Fock (5s, 3p, 3d); III, Clementi's near-Hartree-Fock basis sets; IV, Clementi's optimized minimum basis set (4s, 2p, 1d).

traction of adjacent nuclei, shielded by their electrons. For GaH₃, only the first two terms are important, but for the 2s, 2p elements of first-row atoms all three terms are important, with the third predominating. Only the third term contains disposable parameters which may be obtained from the model SCF results by using the relation

$$C_{ij}^m = \{(i_A j_A | m_B m_B) - 0.5(i_A m_B | i_A m_B)\} / (i_A j_A | r_B^{-1})$$

Comparisons of SCF ZO FMATRIX elements and NEMO III results are given in the tables. The ZO elements are quite important in controlling the molecular charge distribution. In order to maintain rotational invariance in the formula, the C^m parameters must depend only on the n and l quantum numbers of m , not on the azimuthal quantum number. Equation 5 is applied only to one-center ZO elements; all two-center elements are neglected. The C_{ij}^m 's are also used to correct the F_{mm} 's for the presence of the density matrix element ρ_{ij} . We thus introduce a term

$$\Delta F_{m_B m_B} = \sum_{ij} C_{ij}^m \rho_{ij} (i_A j_A | r_B^{-1})$$

modifying the diagonal elements.

Appendix B. SCF Calculations on Atoms and Diatomics

We have performed several *ab initio* SCF calculations on transition metal atoms and diatomic molecules. Our purpose has been to provide parameters for our approximate calculations and to investigate the nature of the basis sets required for such calculations. The smallness of our basis sets prevents us from discussing the chemistries of the molecules studied in too much detail, but some general observations can be made.

Choice of Basis Sets. The first requirement of a basis set for transition metal calculations is that it give accurate atomic term separations. The relative energies of the 3dⁿ4s² and 3dⁿ⁺¹4s configurations of Cu and Cr are given in Table XIII for Clementi's best minimum basis set atom (BA MBS), the present basis set (MBS + double 3d), the truncated Hartree-Fock basis of Claydon and Carlson,^{1a} and Clementi's near-Hartree-Fock results.^{1b} Although for Cu the term separation for our basis set has the wrong sign, the size of the error is greatly reduced from its BA MBS value and is quite close to Claydon and Carlson's truncated Hartree-Fock value. We have chosen to add to the free-atom basis a 4p orbital chosen to minimize the ground-state atomic energy. Caution must therefore be exercised in discussing any "promotion" of electrons into this 4p orbital, since it does not have the spatial characteristics of an occupied 4p Hartree-Fock AO. Our basis set is then very similar to that used by Carlson and Moser in their later transition metal oxide calculations.^{2b}

The above type of basis set has been used for calculations on the diatomic hydrides from FeH to GeH. Experimental internuclear distances²⁶ were used for all molecules except for FeH, for which $R = 2.84$ was chosen. σ valence orbital exponents (e.g., 3d, 3d', 4s and 4p) have been optimized for CoH, CuH, and GaH (Table XIV). Stevenson³ has reported an optimized

Table XIV. Results of σ -Exponent Optimization for CoH, CuH, and GaH^a

		Free atom		Optimized molecular	
		ζ_i	$K(i, H 1s)$	ζ_i	$K(i, H 1s)$
CoH					
$R = 2.9132$	4s	1.484	1.138	1.519	1.433
${}^1\Sigma$	4p	5.235	0.909	5.025	0.898
$D^b = 3.69$	3d	6.370	1.174	6.600	1.130
	3d'	2.720	0.832	2.630	0.833
	H 1s	1.0		0.940	
	$E = -1379.9871$			$E = -1379.9943$	
CuH					
$R = 2.766$	4s	1.389	1.192	1.555	1.200
${}^1\Sigma$	4p	3.250	0.865	2.876	0.927
$D^b = 4.30$	3d	6.740	0.873	6.824	0.830
	3d'	2.710	0.703	2.774	0.686
	H 1s	1.0		0.936	
	$E = -1637.2607$			$E = -1637.2677$	
GaH					
$R = 3.156$	4s	1.871	1.116	1.929	1.117
${}^1\Sigma$	4p	1.625	1.141	1.720	1.142
$D^b = 0.72$	3d	7.885	0.762	7.735	0.746
	3d'	3.493	0.549	0.435	0.553
	H 1s	1.0		0.987	
	$E = -1921.2327$			$E = -1921.2336$	

^a For all three molecules, setting the π and δ exponents to the σ optimized value raised the energy. ^b D = dipole moment (debyes).

SCF wave function for CuH employing a single 3d and a single 4d function in the basis set. He found optimum exponent values of 0.934, 1.729, and 2.5 for the H 1s, Cu 4s, and Cu 4p orbitals, respectively.

CoH, CuH, and GaH Exponent Optimizations. In Table XIV we note first that the H 1s optimum exponent is less than 1.0 in all cases. Second, the 4s orbital is slightly expanded for CoH and CuH and contracted for GaH. The contraction of the 4s orbital is expected, since it is strongly bonding. The 4p orbitals in CoH and CuH expand, as expected, from their highly contracted free-atom form in order to participate more strongly in the bonding. This expansion, however, is small, showing that for CoH and CuH the role of the 4p in lowering the energy of the predominantly metal

(26) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

Table XV

	$P(3d_{\sigma,\pi,\delta}^{\text{tot}})$		$P(4s)$	A $P(4p_{\sigma,\pi})$	$P(L 2s)$	$P(L 2p_{\sigma,\pi})$	R			
	2s, 3s	2s, 4s	3s, 4s	3p, 4p	3d, 3d $_{\sigma,\pi,\delta}$	L 2s, 4s		L 2s, 4p	L 2s, 3d'	L 2p, 4s
GeO ^a	1.99, 4.00, 4.00	1.79	0.76, 1.14	1.94	1.53, 2.88	3.118				
GaF ^a	1.99, 4.00, 4.00	1.83	0.59, 0.35	1.96	1.64, 3.68	3.354				
ZnO ^a	1.98, 4.00, 4.00	1.80	-0.44, -0.88	2.00	0.22, 4.00	3.685				
CuF ^a	1.85, 4.00, 4.00	0.84	0.13, 0.23	1.98	1.31, 3.99	3.294				
CuF ^b	1.81, 4.00, 4.00	0.85	0.14, 0.22	1.97	1.32, 3.98					
NiF ^a	0.38, 4.00, 4.00	1.20	-0.39, -0.76	1.99	1.43, 4.00	3.781				
NiO ^a	0.022, 4.00, 4.00	1.70	-0.41, -0.81	2.00	0.28, 4.00	3.591				
CoF ^a	1.25, 4.00, 2.00	1.47	-0.39, -0.78	1.99	1.30, 4.00	3.572				

$P(3d^{\text{tot}}) = P_{3d} + P_{3d'}$

^a Free-atom exponent. ^b Optimized 4p $_{\sigma}$ and adjusted 4s, 3d, and 3d'.

3p MO's is much more important than its role in the bonding with H. In GaH the 4p contracts slightly and is strongly bonding. The changes in the 3d exponents are small and show no discernible pattern. The effect of the 3d optimization upon the molecular energy is also small (less than 0.0002 au for GaH). The optimized 3d and 3d' exponents for CuH are much closer to the optimum Cu 3d¹⁰ 4s value than they are to the Cu 3d⁹4s² ($\zeta_{3d} = 7.02$, $\zeta_{3d'} = 3.00$).

An SCF calculation on CuH, in which a H 2p orbital was added to the basis set and optimized, was performed to see if increased variational freedom on hydrogen would significantly change the results. The energy is -1637.27307 au, a lowering of 0.0054 au, and the virial ratio is 1.002. The orbital populations are 4s 0.261, 4p 0.007, 3d $_{\sigma}$ 1.880, H 1s 1.481, H 2p 0.045, and the dipole moment changes from 4.30 to 4.18 D. The optimized exponents are 1.407 and 1.325 for the σ and π components of the H 2p, respectively. The two-center K's for H 2p are quite high. All of the GAOP's in the MO's for the H 2p orbital are less than 0.03, and the largest contributions are in π orbitals, suggesting that electron density in the 3d and 4p π 's is attracted to the H 2p $_{\pi}$. An uncoupled Hartree-Fock perturbation theory calculation of the ¹H shielding in this molecule shows that the inclusion of H 2p is not critically important for this property.¹⁷ We shall therefore continue to use only the H 1s function, with a standard exponent of 1.0. The choice of extra functions on the metal was investigated by adding and attempting to optimize a second 4p orbital (4p') of low exponent. Contrary to our hope, the energy decreased continuously as the exponent of this orbital was increased. In CuH the 4p' participation in the bonding was in all cases very small compared to that found for 4p in GaH. In later polyatomic calculations, we hope to test a diffuse 4p function in the basis set, partly because of the importance attached to the 4p function in earlier EH calculations.²⁷

(27) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6669 (1968).

Our optimizations show that the exponents of the 3d, 3d', and 4s orbitals do not change greatly upon hydride formation, that low values for ζ H 1s are appropriate, and that the optimized 4p exponent, although lower than the free-atom value, is still quite high. The last result is consistent with Mulliken's assertion that excited orbitals should be "shrunken" in order to approximate the size of the occupied orbitals with which they mix.²⁸

We also found that the interpolation of optimized exponents for the hydrides of Ni, Zn, and Ge from the three optimized results produced significant energy lowerings, indicating consistency across the series. Results for these hydrides are given in ref 15.

SCF Calculations on Oxides and Fluorides. SCF calculations were performed for GeO, GaF, ZnO, CuF, NiO, CoF, and NiF. Distances were bond distances for the diatomic molecules where available¹⁶ and were taken from solid compounds in other cases, and are listed in Table XVA. GeO, GaF, GaN, ZnO, and CuF are closed shells and the electron configurations of NiF, NiO, and CoF were respectively 8 σ^2 4 π^4 δ^4 , 8 σ^2 4 σ^4 δ^4 , and 9 σ^2 4 π^4 δ^2 . Ligand exponents were given their BA MBS values^{1c} and metal basis sets were of the type listed in Table XIV. The Cu 4p $_{\sigma}$ exponent was optimized in CuF at a value of 2.74, similar to the free-atom value of 3.25 and quite close to the optimized value of 2.88 in CuH.

We shall discuss only the CuF, NiF, and GeO results in detail. In this discussion we shall add 3d and 3d' populations and call the combination "3d". Orbital populations and K's for all calculations are given in Table XVB. In CuF (9 σ^2 4 π^4 δ^4), orbitals 1-7 σ and 1-2 π are inner-shell orbitals, while 8 σ is 84% 3d and 14% F 2p and 9 σ is 40% 4s, 50% F 2p, and 7% 3d. The 3 π and 4 π orbitals are bonding and antibonding combinations of 3d and F 2p. The 10 σ orbital is the 4s, F 2p antibonding orbital, with about 8% 3d participation. Eigenvalues are 8 σ -0.477, 9 σ -0.299, 10 σ 0.144, 3 π -0.513, and 1 δ (3d $_{\delta}$) -0.495. We find

(28) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

Table XVI. NEMO III α 's for Hydrocarbons

	SCF	NEMO III	NEMO III-SCF		NEMO	SCF
C₂H₂						
C 1s	-11.294	-11.223	0.069	F 2p _z , 2s	-0.199	-0.184
C 2s	-1.460	-1.497	-0.037			
C 2p _z	-0.749	-0.741	0.008			
C 2p _{x,y}	-0.169	-0.157	0.012			
H 1s	-0.564	-0.552	0.012			
C₂H₄						
C 1s	-11.276	-11.124	0.132	F 2p _z , 2s	-0.018	-0.029
C 2s	-1.449	-1.513	-0.064			
C 2p _z	-0.385	-0.337	0.048			
C 2p _{x,y}	-0.354	-0.317	0.037			
H 1s	-0.501	-0.504	-0.003			
C₂H₄						
C 1s	-11.284	-11.138	0.146	F 2p _z , 2s	0.138	0.106
C 2s	-1.463	-1.511	-0.048			
C 2p _z	-0.549	-0.507	0.042			
C 2p _x	-0.411	-0.373	0.039			
C 2p _y	-0.146	-0.092	0.054			
H 1s	-0.537	-0.535	0.002			
H₂O Optimized MBS						
H 1s	-0.563	-0.598	+0.035	F 2p _z , 2s	-0.168	-0.130
O 1s	-20.552	-20.435	-0.117			
O 2s	-2.350	-2.356	+0.006			
O 2p _z	-0.377	-0.362	-0.015			
O 2p _x	-0.353	-0.330	-0.023			
O 2p _y	-0.402	-0.371	-0.031			
NH₃ Optimized MBS						
H 1s	-0.542	-0.572	+0.030	F sp _z , 2s	-0.158	-0.119
N 1s	-15.524	-15.373	-0.149			
N 2s	-1.874	-1.913	+0.039			
N 2p _z	-0.354	-0.325	-0.029			
N 2p _{x,y}	-0.331	-0.297	-0.034			

that the Mulliken charges are small ($q(\text{Cu}) = 0.284$), that the two highest σ and π orbitals are not centered on either nucleus, that the d levels are, highest to lowest, $\sigma > \delta > \pi$, and that the F 2s is almost completely filled and does not participate in the bonding.

Results for CuF, in which the Cu 4p_z exponent was optimized and the valence exponents were given the optimized CuH values, are very similar. The energy lowering was 0.0387 au. The dipole moment increased from 2.85 to 3.25 D and the virial ratio $-E/T$ changed from 1.0016 to 1.0010. Eigenvalues differed by less than 0.05 au except for the 10 σ orbital which became primarily 4p_z and was lowered from 1.4539 to 0.9676 au.

The orbital structure of the $8\sigma^2 4\pi^4 \delta^4$ configuration of NiF is somewhat different from that of CuF. The 8 σ orbital is now primarily 4s and F 2p, while the 9 σ half-filled orbital contains 35% 3d_{z²}, 46% 4s, and 19% F 2p. The LEMO (10 σ) has substantially more 3d_{z²} character. The 3d orbital populations are σ 0.46, π 3.92, δ 4.0 and the Ni atom has a Mulliken charge of +0.42. Eigenvalues are: 9 σ -0.205, 10 σ 0.233, 3 π (3d_{xy}) -0.482, and 1 δ (3d_{xy}) -0.410.

In both CuF and NiF we find the d-orbital ordering $\sigma > \delta > \pi$, with substantial stabilization of the 3d π by bonding with the F 2p π . In NiF the σ orbitals with large 3d contributions are half-filled or unfilled, while the 3d_{xy} orbital in CuF is only 0.018 au above the δ orbital and is completely filled. The 3d population for NiF is 8.38 and that for CuF is 9.85, little different from the atomic values.

The population analysis for GeO shows an oxygen charge of -0.346 electron, with a large 4p, F 2p overlap population and substantial charge transfer from Ge 4p

to F 2p. The HFMO (10 σ) is a bonding orbital involving the 4s, 4p and O 2p, while the highest occupied π orbital (4 π) is primarily F 2p_x, with about 25% 4p π character. Eight σ , 9 σ , 10 σ , and 4 π are not localized on either center (z_{Ge} 9 $\sigma = 1.6735$, 10 $\sigma = 0.3585$, 4 $\pi = 2.3345$, 8 $\sigma = 2.7231$, $R_e = 3.118$). The 7 σ ($\epsilon = -1.5698$), 3 π ($\epsilon = -1.5603$), and 1 δ ($\epsilon = -1.5646$) are the 3d σ , π , and δ orbitals. The charge on Ge is due to the loss of electrons from the 4s (0.21) and the 4p (0.13). The total energy is -2147.1959 au, giving a binding energy of 0.0312 au, $-E/T = 0.9993$, and a dipole moment of 0.8361 D. The 2C K 's for F 2s and F 2p_{x,y} interactions with the Ge 4s, 4p, and 3d' orbitals are quite similar. For the π and δ orbitals little symmetry separation is found for the K 's ($K_{3d',3d} \sigma$ 0.9600, π 0.9602, 0.9602). GeO shows substantial covalency and important contributions of 4s, 4p, and F 2p to bonding. F 2s participates little in the bonding and has only small overlap populations.

Table XV gives the orbital populations and K 's for all calculations. We see that the one-center K 's are essentially constant, except for those involving the 4p orbital, and that even here calculations employing similar exponents give similar results. Two-center K 's show somewhat more invariability, but K 's for the larger interactions are still remarkably consistent. The K 's involving the metal 4p orbital do seem to vary with exponent and orbital population. The K 's do not show any clear dependence on overlap, overlap population, or internuclear distance.

Appendix C. NEMO III Results for Small Molecules

Comparison with SCF Results. We present α 's calculated using the proposed method and *ab initio*

Table XVII. C₃H₄ Results for NEMO I, II, and III

	SCF	NEMO I	NEMO II	NEMO III ^a
$\frac{1}{2}\sum_i n_i \epsilon_i$	-39.10	-39.06	-38.95	-38.92
T	115.071	114.91	115.19	115.04
2e (HFMO)	-0.38	-0.36	-0.35	-0.39
1e	-0.59	-0.62	-0.58	-0.57
7a ₁	-0.60	-0.63	-0.55	-0.60
6a ₁	-0.70	-0.75	-9.71	-0.73
5a ₁	-0.94	-0.92	-0.91	-1.00
Q(C1)	-0.226	-0.57		-0.206
Q(C2)	-0.037	+0.22		-0.058
Q(C3)	-0.406	-0.04		-0.342
Q(H4)	0.180	+0.21		0.143
Q(H5, 6, 7)	0.163	+0.06		0.154
Total energy	-115.597			-115.248
-E/T	1.0044			1.0019

F_{ij}^{ZO}	SCF	NEMO	C _m 's			
			C 1s	C 2s	C 2p	CH
1C 2p _z , 1C 2s	-0.186	-0.210	0.95	0.22	0.50	0.22
2C 2p _z , 2C 2s	0.129	0.155	0.97	0.32	0.56	
3C 2p _z , 3C 2s	0.056	0.034	0.98	0.42	0.62	0.26

^a General method.

SCF density matrices and compare them with *ab initio* SCF results for C₂H₂, C₂H₆, and C₂H₄ in Table XVI. We find that α 's for H are given accurately, as are aniso-

tropies for C 2p α 's. Errors for CH₂ and CH₃ carbons are similar in this series of compounds. NEMO III eigenvalues and orbital populations for C₃H₄ are compared with SCF results and with NEMO I and II results in Table XVII. The zero-overlap algorithm gives reasonable results for all four compounds. We also wish to perform calculations in which the ligands of the metal atom are H₂O and NH₃, and have therefore calculated NEMO III α 's for H₂O and NH₃. The results (Table XVI) are similar to those for hydrocarbons.

Appendix D

The derivation of energy differences for transitions of filled and half-filled b_{1g} is as follows:

$$E(^2B_{1g}) = 2H_i + H(b_{1g}) + J_{ii} + 2J(i, b_{1g}) - K(i, b_{1g})$$

$$E(^2i) = H_i + 2H(b_{1g}) + J(b_{1g}, b_{1b}) + 2J(i, b_{1b}) - K(i, b_{1g})$$

$$\Delta E = H(b_{1g}) - H_i + J(b_{1b}, b_{1b}) - J_{ii}$$

$$\epsilon_{b_{1g}}^\alpha = H(b_{1g}) + 2J(i, b_{1g}) - K(i, b_{1g})$$

$$\epsilon_i^{av} = H_i + J_{ii} + J(i, b_{1g}) - 0.5K(i, b_{1g})$$

$$\Delta\epsilon = H(b_{1g}) - H_i - J_{ii} + J(i, b_{1g}) - 0.5K(i, b_{1g})$$

$$E = \Delta\epsilon + J(b_{1g}, b_{1g}) - J(i, b_{1g}) + 0.5K(i, b_{1g})$$

Arrhenius Preexponential Factors for Primary Hydrogen Kinetic Isotope Effects¹

Mary E. Schneider and Marvin J. Stern*

Contribution from the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033. Received June 30, 1971

Abstract: "Exact" model-reaction calculations are used to determine the lower limit to the Arrhenius preexponential factors, A_Q , for primary deuterium kinetic isotope effects in the harmonic approximation and in the absence of quantum mechanical tunneling. Attempts are made to force the A_Q values as low as possible solely through adjustments in the force constant changes, at the isotopic positions, between reactants and transition states. Values of A_Q lower than ~ 0.7 could not be achieved without making the models so mechanistically unreasonable as to render the results meaningless. A more conservative estimate of the lower limit, *viz.*, $A_Q \gtrsim 0.5$, is obtained by considering the lowest value found for the Arrhenius preexponential factor of the purely quantum mechanical contribution to a kinetic isotope effect to be the lower limit to the preexponential factor of the entire isotope effect. This conclusion is in excellent agreement with a prediction made by Bell on the basis of a less rigorous theoretical treatment and lends support to the common practice of interpreting experimental values of A_Q significantly lower than 0.5 as due to the operation of tunneling in the reactions.

The Arrhenius preexponential factors A_Q for primary hydrogen isotope effects, according to the equation

$$\ln(k_H/k_D) = \ln A_Q + B/T \quad (1)$$

have been used for the detection of quantum mechanical tunneling in reactions involving, primarily, proton or hydrogen-atom transfer.² Bell, using a very simple model for a hydrogen-transfer reaction, predicted that values of A_Q should, in the absence of tunneling, be restricted to the range $0.5 \leq A_Q \leq 2^{1/2}$ and usually close to

(1) Supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-3663.

(2) See the review by E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).

1.0.³ Experimental values⁴ of A_Q significantly lower than 0.5 for primary hydrogen kinetic isotope effects have been interpreted as due to the operation of quantum mechanical tunneling in the reactions.²

(3) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter XI.

(4) Most reported experimental values of A_Q were determined by taking the ratio of the individual Arrhenius preexponential factors for the protium and deuterium reactions, $A_Q = A_H/A_D$, whereas in this work we determine A_Q directly according to eq 1. If the data fit the Arrhenius equation exactly, the two methods yield identical results. However, for the room temperature region, even computer-generated kinetic isotope effect data are not fit exactly by eq 1. We have compared the two methods, using actual experimental data for several reactions, and have found differences in the resulting corresponding A_Q values of less than 0.05 unit.