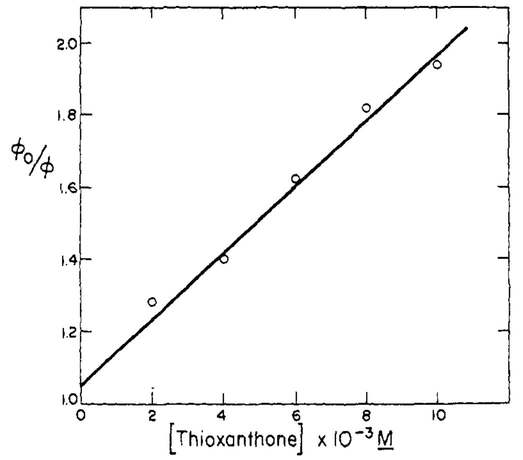

Figure 2. Quenching of 5×10^{-3} *M* stilbene isomerization by thioxanthone.

trolled.[9] Our results further imply that the rate of the thioxanthone self-quenching reaction (eq 3) is also less than diffusion controlled.

In order to establish the actual rate of the self-quenching reaction for thioxanthone, the following experiments were carried out. Solutions of 5×10^{-3} *M trans*-stilbene in degassed benzene with various concentrations of thioxanthone were irradiated at 365 nm. Quenching was observed, as shown in Figure 2. From the known rate of energy transfer from thioxanthone triplets to stilbene,[10] the rate of the self-quenching reaction can be calculated to be $2.3 \pm 0.5 \times 10^9$ l./(mol sec).

$$\text{thioxanthone}^3 + \text{thioxanthone} \xrightarrow{k_q} \text{complex*} \longrightarrow \text{products} \quad (3)$$

$$\text{thioxanthone}^3 + \text{stilbene} \xrightarrow{k_{et}} \text{stilbene}^3 \longrightarrow \text{products} \quad (4)$$

$$\phi_0/\phi = 1 + k_q[\text{thioxanthone}]/k_{et}[\text{stilbene}] \quad (5)$$

We conclude (1) that thioxanthone is a practical triplet-state sensitizer provided that energy transfer is much faster than $2 \times 10^9 \times$ [thioxanthone] sec^{-1} and (2) that the triplet states of simple enones such as cyclopentenone and cyclohexenone are higher than that of thioxanthone (65 kcal/mol).

Acknowledgment. The authors thank Mr. John Mead for valuable technical assistance.

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[10] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).
[11] Alfred P. Sloan Fellow.

C. D. DeBoer*
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

R. H. Schlessinger[11]
Department of Chemistry, University of Rochester
Rochester, New York 14627

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A New, General Approach to Ligand Field Calculations. The Effective Perturbation Method

Sir:

Crystal or ligand field theory, introduced by Bethe[1] over 40 years ago, has played a central role in the development of coordination chemistry. Even in its simplest form, involving the point charge model, electrostatic perturbation theory (EPT) has been remarkably successful in accounting for spectral, magnetic, and even some thermodynamic properties for transition metal complexes.[2] It is now generally realized that the physical models involved in EPT calculations are unrealistic. The semiquantitative or even qualitative agreement of experiment with *ab initio* point charge or point dipole calculations of this type is fortuitous.[3] When viewed as a phenomenological theory such objections vanish. For complexes of cubic symmetry (O_h or T_d), a single parameter (Δ or $10Dq$) is involved and the success of EPT may be regarded as a manifestation of group theoretical principles. For point groups of inferior symmetry the situation is less satisfactory. In addition to the fourth power radial integral $\langle r^4 \rangle$ (subsumed in Dq), one has a $\langle r^2 \rangle$ term. While for a given form of the d orbital wave functions these radial integrals may be calculated,[4] their use presumes the validity of a fallacious model and they are better treated as phenomenological parameters. This latter procedure of course destroys any predictive ability of EPT. The power of EPT lies in its ability to retain the *many electron* character of the free ion wave functions in the weak field formulation. On the other hand, *one electron* molecular orbital (MO) theory, which provides a more or less realistic description of bonding in transition metal complexes, ignores interelectronic interactions, nor can it account successfully for properties dependent on orbital angular momentum. EPT with its more limited pure d orbital basis can handle such subtleties.

In outline, a weak field EPT calculation for a d^n configuration proceeds as follows. Matrix elements $\langle m_l | V_{el} | m_l' \rangle$ of the electrostatic potential V_{el} between the complex one electron d orbital functions $|m_l\rangle$ are computed on the basis of a model. Diagonalization of the resulting 5×5 matrix yields the eigenfunctions and eigenvalues of the problem in the one electron d orbital basis as in eq 1 where **C** is the matrix of column eigen-

$$\mathbf{V}_{el}\mathbf{C} = \mathbf{CE} \quad (1)$$

vectors and **E** is the diagonal matrix of the energies. Next, the *many electron* wave functions, $|L,M_L,S,M_S\rangle$, for the free ion states to be included in the calculation are expressed as Slater determinantal wave functions involving the d orbital basis. Matrix elements of the type $\langle L,M_L | V_{el} | L',M_L' \rangle$ are easily evaluated in terms of the $\langle m_l | V_{el} | m_l' \rangle$ matrix elements. For an adequate description of magnetic properties, matrix elements of the spin-orbit coupling perturbation $\lambda\mathbf{L}\cdot\mathbf{S}$ must also be included. Diagonalization of the many electron matrix yields the desired energies and wave functions. The key feature of the above method is that the *many electron* properties depend ultimately upon the *one electron* matrix elements $\langle m_l | V_{el} | m_l' \rangle$ of V_{el}.

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[1] H. A. Bethe, *Ann. Phys.* (*Leipzig*), **3**, 133 (1929).

[2] Among the standard texts on the subject are H. L. Schläfer and G. Gliemann, "Ligand Field Theory," Wiley-Interscience, New York, N. Y., 1969; C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962; J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, U. K., 1961.

[3] See, for instance, R. E. Watson and A. J. Freeman, *Phys. Rev.*, **134**, A1526 (1964); S. Sugano and R. G. Shulman, *ibid.*, **130**, 517 (1963); W. H. Kleiner, *J. Chem. Phys.*, **20**, 1784 (1952); P. O'D. Offenhartz, *J. Amer. Chem. Soc.*, **91**, 5699 (1969), and references therein.

[4] (a) C. J. Ballhausen and E. M. Ancmon, *Mat. Fys. Medd. Dansk, Wid. Selsk.*, **31**, 1 (1958); (b) F. E. Ilse and H. Hartmann, *Z. Phys. Chem.*, **197**, 239 (1951).

It is the purpose of the present communication to enunciate a general method by which matrix elements analogous to $\langle m_1 | V_{el} | m_1' \rangle$ may be calculated starting from a one electron MO basis, eschewing EPT entirely. The 5×5 matrix so obtained will be referred to as the effective perturbation matrix, $\mathbf{V}_{eff}$.

A number of one electron MO theories have been proposed at the semiempirical level to explain the bonding and properties of transition metal complexes.[5] Such theories yield MO energies and wave functions of the type

$$\Psi_j = \sum_{i=1}^{5} a_{ij}\chi_i + \sum_{i=6}^{n} a_{ij}\varphi_i \tag{2}$$

where the χ_i's represent the set of d orbitals on the metal and the φ_i's are the other metal and ligand functions involved in the basis set. It is the set of five MO's which are "mainly d" in character which are the MO counterparts of the pure d orbitals of EPT. We desire to find that counterpart of eq 1, namely

$$\mathbf{V}_{eff}\mathbf{C} = \mathbf{CE} \tag{3}$$

where $\mathbf{E}$ is the diagonal matrix of energies of the mainly d MO's and $\mathbf{C}$ is the *orthonormal* matrix of column eigenvectors which *most nearly resembles* the MO eigenfunctions. It is clear that if $\mathbf{C}$ and $\mathbf{E}$ are in hand, $\mathbf{V}_{eff}$ can be readily calculated *via* eq 4.

$$\mathbf{V}_{eff} = \mathbf{CE\tilde{C}} \tag{4}$$

A reasonable procedure by which to obtain $\mathbf{C}$ is to truncate the five mainly d MO's, Ψ_j, to eliminate all but the d orbital part. Normalization yields the five functions β_j

$$\beta_j = \sum_{i=1}^{5} b_{ij}\chi_i \tag{5}$$

where $b_{ij} = a_{ij}(\Sigma_{i=1}{}^{5}a_{ij}{}^{2})^{-1/2}$, which will in general be nonorthogonal. The desired orthonormal matrix $\mathbf{C}$ may be obtained from the matrix $\mathbf{B}$, whose elements are the b_{ij}'s, using Löwdin's symmetric orthogonalization procedure[6] as follows. By definition $\mathbf{\tilde{C}C} = \mathbf{1}$ and $\mathbf{\tilde{B}B} = \mathbf{S}$, where $\mathbf{1}$ and $\mathbf{S}$ are the unit diagonal and overlap matrices, respectively. If one defines the real symmetric matrix $\mathbf{S}^{1/2}$ so that $\mathbf{S}^{1/2}\mathbf{S}^{1/2} = \mathbf{S}$, it follows that

$$\mathbf{C} = \mathbf{BS}^{-1/2} \tag{6}$$

The required $\mathbf{S}^{-1/2}$ matrix may be readily obtained. Suppose $\mathbf{U}$ is a matrix which diagonalizes $\mathbf{S}$ such that $\mathbf{\tilde{U}SU} = \mathbf{D}$, where $\mathbf{D}$ is a diagonal matrix. $\mathbf{D}^{-1/2}$ is defined such that its elements $\mathbf{D}_i{}^{-1/2} \equiv (\mathbf{D}_i)^{-1/2}$. Since $\mathbf{\tilde{U}S}^{-1}\mathbf{U} = \mathbf{D}^{-1}$, it is easily shown that

$$\mathbf{S}^{-1/2} = \mathbf{UD}^{-1/2}\mathbf{\tilde{U}} \tag{7}$$

We are assured[7] that the matrix $\mathbf{C}$, so obtained, most nearly resembles $\mathbf{B}$ in a least-squares sense and therefore the five orthonormal functions Γ_j of eq 8

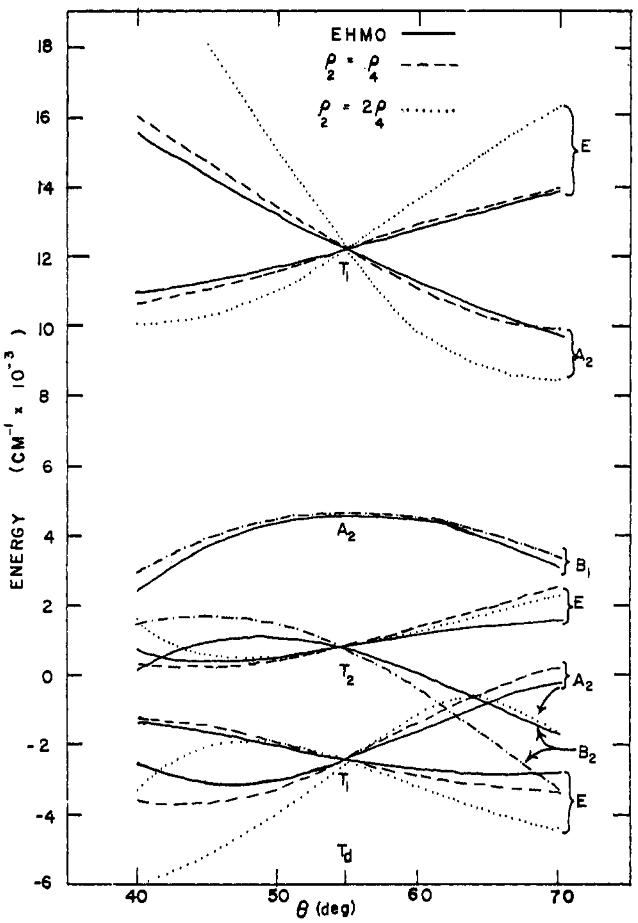

Figure 1. Variation of the many electron states arising from the ^{3}F and ^{3}P terms of $NiCl_4{}^{2-}$ as a function of angular distortion θ; calculated using $\rho_4 = 5175$ and the Racah parameter $B = 800\ \text{cm}^{-1}$.

$$\Gamma_j = \sum_{i=1}^{5} c_{ij}\chi_i \tag{8}$$

are the ones which most resemble the MO eigenfunctions Ψ_j of eq 2. The c_{ij}'s are the elements of matrix $\mathbf{C}$.

With the E_j's and matrix $\mathbf{C}$, derived as described above, $\mathbf{V}_{eff}$ may be obtained *via* eq 4. This represents a general method for applying the results of *one electron* MO theory to *many electron* ligand field calculations.[8]

As an illustrative example, extended Hückel (EHMO) and electrostatic point charge calculations were carried out on $NiCl_4{}^{2-}$ as a function of tetragonal angular distortion about the S_4 axis. The results for the many electron term states are shown in Figure 1. The solid curves represent the results of the application[9] of the

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(5) See, for instance, F. A. Cotton, *Rev. Pure Appl. Chem.*, **16**, 175 (1966); F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 6, 369, 376, 924 (1967); H. Basche, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966); R. F. Fenske and D. D. Radke, *Inorg. Chem.*, 7, 479 (1968); D. A. Copeland and C. J. Ballhausen, *Theor. Chim. Acta*, **20**, 317 (1971); G. C. Allen and D. W. Clack, *J. Chem. Soc. A*, 2668 (1970), and references therein.

(6) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950); *Advan. Phys.*, **5**, 1 (1956).

(7) B. C. Carlson and J. M. Keller, *Phys. Rev.*, **105**, 102 (1958).

(8) A referee suggested the possibility of using a slightly different procedure, namely that of symmetrically orthonormalizing the unnormalized 5×5 $\mathbf{A}$ matrix, whose elements are the a_{ij}'s taken directly from the MO calculation. In a practical sense the results of the two procedures are virtually identical. For the examples tested, the referee's method yielded $\mathbf{C}$ and $\mathbf{V}_{eff}$ matrices whose elements were identical to the extent of at least three significant figures with those obtained by the method outlined in this communication. The present method may be slightly preferable in that it retains the *relative* proportions of the various d orbital contributions to a particular MO *before* orthogonalization, while the alternative does not.

(9) Since the EHMO calculation employed a real d orbital basis, a unitary transformation was applied to the $\mathbf{V}_{eff}$ matrix obtained from it to yield $\mathbf{V}_{eff}$ in the complex d orbital basis. In addition, a constant term was added algebraically to the diagonal elements to cause the trace to vanish in accord with the usual result of degenerate perturbation theory.

effective perturbation method to the EHMO results. The broken curves give the results derived from the point charge calculations for two different choices of the radial parameter[10] ρ_2. The quantitative agreement between the two theories is gratifying and suggests that the present method represents a viable alternative to electrostatic crystal or ligand field theory. Furthermore it provides a practical means of testing semiempirical MO theories against many electron spectral and magnetic properties in complexes.

Acknowledgment. I thank Drs. O. Crawford, J. P. Lowe, and T. J. Moulson for helpful discussions and Mr. E. S. Greenberg for computational assistance.

(10) $\rho_2 = \langle r^2 \rangle / R^3$; $\rho_4 = \langle r^4 \rangle / R^5$, where R is the metal to point charge distance.

William DeW. Horrocks, Jr.
Whitmore and Chandlee Laboratories, Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

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Cuprous *tert*-Butoxide. A New and Useful Metalation Reagent

Sir:

This communication reports the interesting properties and metalation reactivity of cuprous *tert*-butoxide (**1**) which differs very much from cuprous alkoxides reported. Among the very few cuprous alkoxides studied, cuprous methoxide is known to be quite insoluble in organic solvents and unstable.[1] It decomposes at room temperature, sometimes explosively, into formaldehyde, methanol, and metallic copper.[1] On the contrary, **1** is soluble in organic solvents including nonpolar solvents like benzene and cyclohexane, and **1** is stable to be isolable by sublimation at *ca.* 170° under a reduced nitrogen pressure. Very interestingly, **1** proves to be a powerful metalation reagent. Thus, **1** reacts with hydrocarbons with an acidic hydrogen to produce smoothly the corresponding organocopper compounds.

The equimolar reaction of anhydrous CuCl with *tert*-BuOLi in tetrahydrofuran at an ambient temperature under nitrogen gave a yellow solution containing a pale yellow precipitate. On sublimation of the residue at *ca.* 170° (1 mm) after the removal of tetrahydrofuran, a pale yellow sublimate was obtained in a yield of 80%, which was identified as **1** by the following analyses. The copper content of the sublimate was found by iodometry to be 45.9% (calcd for **1**, 46.5%); the ir spectrum (Nujol) showed absorptions due to the skeletal vibration of the *tert*-butyl group at 1240 and 1180 $\mathrm{cm^{-1}}$ and absorptions of *tert*-butyl–O stretching at 940 and 920 $\mathrm{cm^{-1}}$ (doublet). The nmr spectrum in benzene showed only one sharp singlet at τ 8.74. The chemical shift of the *tert*-butyl protons was quite similar to that of *tert*-butyl alcohol. The diamagnetism of **1** was confirmed by the absence of esr signal. The *tert*-butoxy group content in **1** was 99%, determined from *tert*-butyl alcohol liberation by an instantaneous acidolysis with acetic acid which gave rise to cuprous acetate quantitatively.

Treatment of **1** with di-*tert*-butyl peroxide gave cupric di-*tert*-butoxide (**2**). The reaction of **1** with an excess of di-*tert*-butyl peroxide in benzene gave a dark green precipitate at 90°. After filtration, washing with benzene, and drying at a reduced pressure, **2** was obtained quantitatively as a yellow green solid. The copper content by iodometry was 30.5% (calcd 30.3%). The ir absorptions of 1240, 1180 and 915, 905 $\mathrm{cm^{-1}}$ were compatible with **2**. The methanolysis of **2** gave *tert*-butyl alcohol quantitatively with concomitant formation of cupric dimethoxide.

The thermal stability of **1** was higher than that of **2**. Heating of **2** at about 150° under a reduced nitrogen pressure caused the decomposition and gave a sublimate of **1**. The ir spectrum of the sublimate was identical with that of **1** prepared from CuCl and *tert*-BuOLi. This finding has offered an alternative way of preparation of **1** from $\mathrm{CuCl_2}$ and *tert*-BuOLi; *i.e.*, the sublimation of the reaction mixture of anhydrous $\mathrm{CuCl_2}$ with *tert*-BuOLi after the removal of the solvent of tetrahydrofuran gave a sublimate of **1** in a yield of 45%. This unusual high thermal stability of **1** may be ascribed to the absence of the β-hydrogen atom to copper, taking into account the decomposition products of thermally unstable cuprous methoxide described previously.[1]

In the metalation reaction using copper salts, copper alkoxide must be a useful reagent because of having a basic alkoxide group to abstract effectively an active hydrogen atom and liberate an alcohol. Thus, there is no need using a basic or buffered condition[2] to avoid inhibition of the reaction by developing acidity. The reaction of **1** with a large excess of phenylacetylene without any additive at room temperature produced immediately a bright yellow solid of cuprous phenylacetylide. The accompanying liberation of *tert*-butyl alcohol was analyzed by glpc and was shown to be almost quantitative.

$$\begin{array}{cccc} \mathrm{PhC{\equiv}CH} + & \textit{tert}\text{-}\mathrm{BuOCu} \longrightarrow & \mathrm{PhC{\equiv}CCu} + & \textit{tert}\text{-}\mathrm{BuOH} \\ 80\ \text{mmol} & 4.0\ \text{mmol} & 97\% & 97\% \end{array}$$

The metalation of phenylacetylene by **2** proceeded slowly at room temperature. The analysis of products has led to the following equation

$$\begin{array}{cc} 4\mathrm{PhC{\equiv}CH} + & 2(\textit{tert}\text{-}\mathrm{BuO})_2\mathrm{Cu} \longrightarrow \\ 102\ \text{mmol} & 2.55\ \text{mmol} \end{array}$$

$$\begin{array}{ccc} 2\mathrm{PhC{\equiv}CCu} + & \mathrm{PhC{\equiv}CC{\equiv}CPh} + & 4\textit{tert}\text{-}\mathrm{BuOH} \\ 96\% & 82\% & 96\% \end{array}$$

where the yield of diphenyldiacetylene was based on the isolated amount by recrystallization from aqueous ethanol.

Cyclopentadiene also reacted readily with **1**. Mixing of **1** with cyclopentadiene at 0° produced in several minutes metallic copper (yield 99%, purity 96%) and *tert*-butyl alcohol (yield 98%). Cyclopentadienylcopper was assumed as the essential intermediate, which was actually isolated as a phosphine complex when the reaction of cyclopentadiene with **1** was carried out in the presence of triethylphosphine. The addition of cyclopentadiene to a petroleum ether solution of **1** and triethylphosphine at −70° gave immediately a white precipitate of $h^5\text{-}\mathrm{C_5H_5CuPEt_3}$.[3] The reaction temperature of −70° is taken as being indicative of the remarkable metalation reactivity of **1**, which becomes

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(1) G. Costa, A. Camus, and N. Marsich, *J. Inorg. Nucl. Chem.*, 27, 281 (1965).

(2) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

(3) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956).