Ligand-field theory applied to diatomai metal molecules. Results for the $d_5^1d_{5}^{0}\sigma^2$ states of Ni$_2$, the $d_{Ni}^8d_{Cu}^{10}\sigma^2$ states of NiCu, and the $d_{Ni}^8(3F)d_{Cu}^{10}\sigma^2\sigma^*1$ excited states of NiCu

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A ligand-field theory has been developed for transition-metal diatomics having electronic configurations of $d_{Ni}^8d_{Cu}^{10}\sigma^2$, $d_{Ni}^4d_{Cu}^{10}\sigma^2$, and $d_{Ni}^8(3F)d_{Cu}^{10}\sigma^2\sigma^*1$. The theory treats each atom as a point charge and includes spin-orbit interactions. No contributions due to d-orbital chemical bonding are included. Since the d orbitals are quite small compared to the bond lengths in these molecules, the only inputs to the theory are the ligand charges ($Z_A$ and $Z_B$), the radial expectation values $\langle r^2 \rangle_{ab}$, and the atomic spin-orbit parameters $\xi_A$ and $\xi_B$ and the bond length, $R$. Calculations employing no adjustable parameters (setting $Z_{A,B} = +1.0$, and using radial expectation values and spin-orbit parameters from atomic tables) provide essentially quantitative agreement with $ab$ initio results on the $d_{Ni}^8d_{Cu}^{10}\sigma^2$ manifold of states in NiCu, and on the $d_{Ni}^4d_{Cu}^{10}\sigma^2$ manifold of states in Ni$_2$. This demonstrates that the ligand-field model has some validity for metal molecules containing nickel, primarily because of the compact nature of the 3d orbitals in this element. Similar calculations of the $d_{Ni}^4d_{Cu}^{10}\sigma^2$ manifold of states in Pt$_2$, and the $d_{Ni}^8d_{Pt}^{10}\sigma^2$ manifold of states in NiPt are presented for comparison to future $ab$ initio or experimental measurements, although the possibility of d-orbital contributions to the bonding in these species makes the ligand-field model less favorable in these examples. The $d_{Ni}^8(3F)d_{Cu}^{10}\sigma^2\sigma^*1$ excited electronic states of NiCu, which are well known from resonant two-photon ionization spectroscopy, are also investigated in the ligand-field model. As a final example, the $d_{Ni}^8(3F)^2\sigma^1$ excited electronic states of NiH are also examined using the same treatment as that employed for the $d_{Ni}^8(3F)d_{Cu}^{10}\sigma^2\sigma^*1$ excited manifold of NiCu.

1. INTRODUCTION

Achieving a detailed understanding of the electronic structure and chemical bonding in the diatomic transition-metal molecules, particularly in the 3d series, presents a formidable challenge to theoretical chemistry.

A major problem in this regard is the correlation of electronic motions in systems with partially filled d orbitals. In addition, the existence of low-lying excited states of the component atoms forces the theoretician to properly account for mixing of the various accessible separated atom asymptotes, which introduces further difficulties. Finally, proper treatment of the exchange interaction is needed to obtain quantitative results. Indeed, in the 3d series of transition-metal diatomics the ground state of the system often results from a delicate balance between exchange effects (which favor high-spin configurations) and chemical bonding (which favors low-spin configurations). As a result, minor errors in the treatment of electron correlation, exchange, or in the consideration of excited separated atom limits, can lead to results which are both quantitatively and qualitatively incorrect. Finally, and perhaps most troubling, even when such theoretical attempts are successful, one is often left with a complicated multiconfigurational wave function which may obscure the underlying physical effects which control the electronic structure of the molecule.

Despite the intrinsic difficulties in describing the electronic structure and chemical bonding in the transition-metal molecules, theoretical chemistry has provided great insight into the nature of the bonding in these species. For example, Bauschlicher and Langhoff have systematically elucidated the chemical bonding and electronic structure of ligated, unsaturated transition-metal molecules and 3d transition-metal dimers using $ab$ initio techniques employing high-level electron correlation and configuration-interaction methods. Balasubramanian has worked extensively with the 4d and 5d series transition-metal dimers by incorporating relativistic effects in his $ab$ initio calculations. The local-spin-density method has also been used to study the 3d and 4d homonuclear transition-metal dimers. All of these efforts are important and worthwhile, yielding qualitative and quantitative results that have provided insight into transition-metal chemical bonding. However, the computations are colossal and the results are often difficult to interpret in terms of simple, physically intuitive concepts. This situation could result because the bonding in these species is so complicated that simple concepts are insufficient; alternatively, we may have simply not yet found the simple concepts which can organize our thinking about these species.

Within the past decade, Field and others have developed a conceptually simple, computationally manageable theoretical approach to the study of the rare-earth oxides and halides, the transition-metal hydrides, and the calcium halides. In this approach ligand-field theory has been revived as a method to compute the electronic states of metal-containing diatomic molecules which possess
compact nonbonding orbitals that are electrostatically perturbed by a single fixed ligand. Unlike \textit{ab initio} methods, small basis sets and simple, physically intuitive, molecular Hamiltonians are sufficient for the analysis. Furthermore, the computations are trivial compared to \textit{ab initio} methods, since nothing more complicated than a matrix diagonalization routine combined with a program to evaluate angular momentum coupling coefficients is required. The application of this ligand-field method to the electronic states of the diatomic lanthanide oxides and halides has met with wonderful success. For example, Schall, Dulick, and Field successfully employed a zero-free parameter, multiconfigurational ligand-field approach to predict the experimentally observed low-lying electronic states of LaF. In this model, LaF is considered as a free atomic metal ion, La$^+$, perturbed by a nonpolarizable point $F^-$ ligand. Schall, Dulick, and Field, found that this zero-free parameter calculation was in agreement with the observed energy levels of LaF to within a few hundred wave numbers (cm$^{-1}$), provided several excited configurations of the La$^+$ ion were included. In the present work we extend these ideas to the diatomic transition-metal molecules, and demonstrate that simple ligand-field treatments of NiCu and Ni$_2$ provide predicted energy levels which differ only slightly from the results of previous \textit{ab initio} calculations.

Of course, ligand-field theory provides wave functions in addition to energy levels, and a more critical test of its validity is the extent to which properties calculated from the wave functions are in agreement with experimental measurements. Thus an important confirmation of the ligand-field treatment of the lanthanide oxides was obtained when the Zeeman and hyperfine parameters of CeO and PrO were accurately calculated. A correspondingly important test of the ligand-field calculation presented here is the prediction of the heterogeneous perturbation experimentally found between the $D[11.9]_2.5$ (primarily $^2$A$_{2g}$) and $C[11.9]_1.5$ (primarily $^2$II$_{1/2}$) excited states of NiCu, described in the preceding paper.

The success of ligand-field theory depends on its application to molecules in which the component atoms possess physically compact valence orbitals. For example, the successful application of ligand-field theory to the lanthanide oxides CeO and PrO resulted from the extremely compact $f$ orbitals of the rare-earth metal atom. Like the $4f$ orbitals of the lanthanides, the $3d$ orbitals of nickel are very tightly contracted and spatially inaccessible, in contrast to the outer $4s$ electron, which is readily available for chemical bonding. Field and co-workers have successfully applied ligand-field theory to the $\{\text{Ni}^+ 3d^8 2D\}$ supermultiplet of NiH, where they compare \textit{ab initio} predictions to the NiH deperturbed molecular constants rather than erroneously comparing them to effective molecular constants. They found that the \textit{ab initio} calculations were much better than originally thought, providing a synergism among \textit{ab initio} theory, ligand-field theory, and experiment. Based on this success, it is clear that nickel possesses the necessary characteristics for effective application of the ligand-field theory.

In this article, we present theoretical results using a ligand-field plus spin–orbit model for the low-lying electronic states of NiCu (d$^6$g$^2$ manifold) and Ni$_2$ (d$^6$g$^2$ manifold), where we can make comparisons to \textit{ab initio} results. In addition, we apply the model to the excited electronic states of NiCu (d$^6$g$^2$ manifold), where we can make a direct comparison to experimental results. The application of this simple physical concept based on \textit{atomic} parameters to successfully predict the electronic properties of molecular systems is both satisfying and useful. In Sec. II, the theoretical methodology for application of the ligand-field plus spin–orbit model is described. The theoretical results are presented, interpreted, and compared to experiment and \textit{ab initio} results in Sec. III. A summary of the work is then provided in Sec. IV.

II. THE LIGAND-FIELD MODEL FOR LATE TRANSITION-METAL DIATOMIC MOLECULES

Consider a diatomic molecule composed of two $d^8$ electrons separated by a internuclear distance, $r_e$, with physically contracted (closed or open) $d$ subshells, surrounded and chemically bound by a (relatively) diffuse $s$ orbitals containing the two electrons which leave the system uncharged. Provided the $d$ orbitals are sufficiently compact, no chemical bonding will occur between them, and the energetics of the system will be determined by simple electrostatic and spin–orbit effects. In essence, the known electronic states of the two $M^+$ ions may be considered to provide a set of Hund’s case (a) basis functions for the molecule, and the Hamiltonian matrix resulting from the electrostatic and spin–orbit interactions in the system may be evaluated to provide molecular energies and eigenfunctions. Hence, the term \textit{atomic-ion-in-molecule} is used to describe the ligand-field model.

A. The d$^8g^{10}e^2$ states of a heteronuclear transition-metal molecule

The most straightforward application of the ideas described above is to the case of a d$^8g^{10}e^2$ manifold of states, as presumably occurs in NiCu, NiAg, and NiAu. This manifold contains only 10 states, which are described in Hund’s case (a) as $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$. However, these are split by spin–orbit interactions into one $\Omega=5/2$, two $\Omega=3/2$, and two $\Omega=1/2$ states, all of which are doubly degenerate. To the extent that the $e^2$ electrons occupy orbitals which are diffuse and physically removed from the $d^8$ atom, or are roughly of spherical symmetry about this atom, their electrostatic effect on the $d^8$ core remains independent of the arrangement of the $d^8$ electrons, and does not influence the splittings between the states of the $d^8g^{10}e^2$ manifold. Accordingly, we treat the d$^{10}$ atom as providing a nonpolarizable +1 point charge, which exerts an electrostatic influence on the $d^8$ configuration of atom \textit{A}. For the purpose of evaluating the splitting of the states arising from the d$^8g^{10}e^2$ manifold, we ignore the neutralizing effect of the $e^2$ electrons. In addition, the spin–orbit energy of the open $d^8$ subshell must be included, since the electrostatic energy in the nickel-containing systems is comparable to the spin–orbit energies.
TABLE I. Basis wave functions for a heteronuclear $d^0d^{10} \sigma^2$ molecule.

<table>
<thead>
<tr>
<th>Molecular term</th>
<th>Configuration</th>
<th>Basis wave function $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Sigma^+$</td>
<td>$da$</td>
<td>$\hat{A}<em>1(d</em>{a}(\alpha))$</td>
</tr>
<tr>
<td>$^2\Pi_{1/2}$</td>
<td>$da$</td>
<td>$\hat{A}<em>1(d</em>{a}(\beta))$</td>
</tr>
<tr>
<td>$^2\Pi_{3/2}$</td>
<td>$da$</td>
<td>$\hat{A}<em>1(d</em>{a}(\gamma))$</td>
</tr>
<tr>
<td>$^2\Delta_{1/2}$</td>
<td>$da$</td>
<td>$\hat{A}<em>1(d</em>{a}(\delta))$</td>
</tr>
<tr>
<td>$^2\Delta_{5/2}$</td>
<td>$da$</td>
<td>$\hat{A}<em>1(d</em>{a}(\epsilon))$</td>
</tr>
</tbody>
</table>

$^a$The configuration is represented in terms of the $d$ hole on atom $A$.

$^b$The basis wave function is an antisymmetrized product of spin orbitals, equivalently written as a Slater determinant. In this case, one hole is present so $J_1 = -1$. The $m_I$ quantum number is given as 0, 1, or 2 as a subscript.

We begin by forming a basis set in Hund’s case (a), with electronic states constructed in the form $|\Lambda, S, \Sigma, \Omega\rangle$. For simplicity, this set of basis functions is obtained by treating the $d^0$ atom as possessing a single $d$ hole rather than a $d^4$ configuration of electrons. The five basis wave functions are listed in Table I, for the general case of any heteronuclear molecule with a $d^0d^{10} \sigma^2$ manifold of states.

The Hamiltonian for the $d^0d^{10} \sigma^2$ system is constructed following methods provided by Dulick. Since only one valence hole exists in the $d^0d^{10} \sigma^2$ system, there is no need to include electron-electron repulsions or exchange energy in the Hamiltonian. The total Hamiltonian is then simply

$$\hat{H}(d^0d^{10} \sigma^2) = \hat{H}_d + \hat{H}_{LF},$$

(2.1)

where $\hat{H}_d$ represents the internal Hamiltonian for the $d^0$ ion, and $\hat{H}_{LF}$ is the ligand-field Hamiltonian, which provides an electrostatic perturbation to the $d^0$ ion. In the present case of a $d^0$ ion, $\hat{H}_d$ contains only spin–orbit interactions,

$$\hat{H}_d = \hat{H}_d^{SO},$$

(2.2)

$\hat{H}_d^{SO}$ is a one-electron operator of the form

$$\hat{H}_d^{SO} = \sum \xi(r) \hat{S}_\alpha^\dagger \hat{S}_\alpha,$$

(2.3)

and the $H_d^{SO}$ matrix in our basis set is readily evaluated to be

$$H_d^{SO} = \begin{pmatrix}
2\Sigma_{1/2} & 2\Pi_{1/2} & 2\Pi_{3/2} & 2\Delta_{3/2} & 2\Delta_{5/2} \\
0 & -6^{1/2}\xi/2 & 0 & 0 & 0 \\
-6^{1/2}\xi/2 & \xi/2 & 0 & 0 & 0 \\
0 & 0 & -\xi/2 & -\xi & 0 \\
0 & 0 & -\xi & \xi/2 & 0 \\
0 & 0 & 0 & 0 & -\xi
\end{pmatrix},$$

(2.4)

where $\xi$ is the spin–orbit parameter for the $d^0$ ion. This is obtained by converting the spin–orbit operator [Eq. (2.3)] into an operator acting on holes, rather than electrons, which may be done quite generally by reversing the sign of the spin–orbit coupling parameter ($\xi$) wherever it appears.

The ligand-field Hamiltonian is given as

$$\hat{H}_{LF} = -\sum_i Z_L e^2/r_{Li},$$

(2.5)

where the summation is over all of the electrons of the $d^0$ ion, $Z_L$ is the ligand charge (taken as $+1$ in the present calculation), and $r_{Li}$ is the distance between the $ith$ electron and the point charge of the ligand. Alternatively, we may express this electrostatic interaction in terms of the repulsion of the single $d$ hole on the $d^0$ atom by the positive charge of the ligand by writing the ligand-field Hamiltonian as

$$\hat{H}_{LF} = Z_L e^2/r_{Li},$$

(2.6)

where $r_i$ now gives the distance between the hole and the ligand. With the standard definition of the $B^0_k$ radial integrals, given as

$$B_k^0 = Z_L e^2 \int_0^{\infty} R_m^2(r^k/r_{Li}^{k+1}) r^2 dr,$$

(2.7)

where $R_m(r)$ is the radial wavefunction of the hole, and $r_<$ and $r_>$ are the lesser and greater of $r$ (the distance of the hole from the nucleus of the $d^0$ atom) and $R$ (the distance between the $d^0$ atom and the $d^{10}$ ligand), respectively, the one-hole matrix elements may be evaluated to give

$$<3d_{m'}|\hat{H}_{LF}|3d_m> = \delta_{m, m'} \sum_k B_k^0 (-1)^{m_5} \begin{pmatrix} 2 & k & 2 \\ m & 0 & -m \end{pmatrix} \times \begin{pmatrix} 2 & k & 2 \\ 0 & 0 & 0 \end{pmatrix},$$

(2.8)

where $(2_m^0 0 0^-)$ and $(2_0^- 0 0^-)$ are $3j$ symbols which limit the contributing terms in the sum to $k = 0, 2, 4$.

The $B^0_k$ radial integrals may be broken up into the region from 0 to $R$ and from $R$ to $\infty$, giving

$$B_k^0 = Z_L e^2 \left[ \left( \int_0^R R_m^2(r^k/r_{Li}^{k+1}) dr \right)/R^{k+1} \right] + \left( \int_0^{\infty} R_m^2(r^k/r_{Li}^{k+1}) dr \right)/R^{k+1}.$$

(2.9)

It is sufficient for practical purposes to consider the second integral to be negligible, and to extend the range of the first integral to infinity, essentially assuming that the electrons of the $d^0$ system never extend out to the location of the ligand, allowing the $B_k^0$ integrals to be written as

$$B_k^0 = Z_L e^2 \left( \int_0^R R_m^2(r^k/r_{Li}^{k+1}) dr \right)/R^{k+1}.$$  

(2.10)

The $<r^k>$ moments required for the evaluation of Eq. (2.10) have been computed by Desclaux using numerical relativistic Dirac–Fock methods for all of the elements, and these values are used in Sec. III where specific molecules (such as NiCu) are considered. In our final $H_d^{LF}$ matrix we omit the constant $B^0_k$ term, since this shifts all of the levels from a given configuration by the same amount. When both regions of Eq. (2.9) ($r_< R$ and $r_> R$) make significant contributions, however, the $B^0_k$ term can have a
major impact on the relative energetics of different configurations, leading for example to a stabilization of $d^3s^1$ (or $f^3d^1$) configurations relative to the $d^{2+1}$ (or $f^{2+1}$) configurations in the transition-metal halides (or lanthanide halides). Since only a single configuration is considered in this manuscript, however, the constant $B_0$ term may be omitted. The final $H^{LF}$ matrix is then given after explicit evaluation of the 3-$j$ symbols as

$$
H^{LF} = \begin{pmatrix}
2/7B_0^2 + 2/7B_0^4 & 0 & 0 & 0 & 0 \\
0 & 1/7B_0^2 - 4/21B_0^4 & 0 & 0 & 0 \\
0 & 0 & 1/7B_0^2 - 4/21B_0^4 & 0 & 0 \\
0 & 0 & 0 & 1/7B_0^2 + 1/21B_0^4 & 0 \\
0 & 0 & 0 & 0 & 1/7B_0^2 + 1/21B_0^4
\end{pmatrix}
$$

The ligand-field Hamiltonian is diagonal in the Hund's case (a) basis of Table I, but the spin–orbit Hamiltonian mixes case (a) basis functions with the same value of $\Omega$. The total Hamiltonian, which is the sum of the spin–orbit and ligand-field Hamiltonian matrices, therefore block diagonalizes into one $1 \times 1$ and two $2 \times 2$ submatrices, which may be readily solved to obtain eigenvalues and eigenvectors. The block diagonalized total Hamiltonian matrices for the $\Omega = 1/2$, $3/2$, and $5/2$ blocks, are given in Table II for the $d_9d^{10}g^2$ states of a heteronuclear diatomic like NiCu, NiAg, NiAu, or PtCu, or a $d_9d^{10}p^2$ molecule like NiAl, NiGa, or NiIn, or a $d_9p^2$ molecule like NiH. Simple examination of the matrix elements shows that as long as $Z_L$ is taken as positive, the ground term is predicted to be $\Omega = 5/2$, which is a pure Hund's case (a) $2\Delta_{3/2}$ state. This has been experimentally determined to be the ground state for NiCu, NiAu, PtCu, NiAl, NiAl, and NiH.

### TABLE II. Hamiltonian matrix for a heteronuclear $d_9d^{10}g^2$ molecule.

<table>
<thead>
<tr>
<th>$\Omega = \frac{1}{2}$ block ($2 \times 2$):</th>
<th>$\Omega = \frac{3}{2}$ block ($2 \times 2$):</th>
<th>$\Omega = \frac{5}{2}$ block ($2 \times 2$):</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\Sigma_{1/2}^+$</td>
<td>$3\Pi_{1/2}$</td>
<td>$3\Pi_{3/2}$</td>
</tr>
<tr>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{1}{7}B_0^4}{\sqrt{3}}$</td>
<td>$-\frac{B_0^2 + \frac{1}{7}B_0^4}{\sqrt{3}}$</td>
</tr>
<tr>
<td>$-\frac{B_0^2 + \frac{1}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
</tr>
<tr>
<td>$\Omega = \frac{3}{2}$ block ($2 \times 2$):</td>
<td>$\frac{B_0^2 + \frac{1}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
</tr>
<tr>
<td>$\frac{B_0^2 + \frac{1}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
<td>$\frac{B_0^2 + \frac{3}{7}B_0^4}{\sqrt{3}}$</td>
</tr>
</tbody>
</table>

B. The $d_9d^{10}g^2$ states of a homonuclear transition-metal molecule

In going from a $d_9d^{10}g^2$ manifold of states in a heteronuclear molecule (such as NiCu) to the corresponding $d_9d^{10}g^2$ manifold in a homonuclear molecule (such as Cu$^+$), the basis wave functions are doubled into $g/u$ pairs due to inversion symmetry. The case (a) basis functions for this situation are listed in Table III. Although one might expect this to increase the complexity of the situation, it is straightforward to extend the treatment of the preceding subsection, since the total Hamiltonian may now be block diagonalized according to $\Omega$ and $g/u$ symmetry. The Hamiltonian must be generalized slightly to allow for spin–orbit interactions on each center, and for each ion core to be perturbed by the electrostatic field of the other. In the end, however, the Hamiltonian breaks up into blocks which are identical to those obtained in the heteronuclear case, with no distinction between the $g$ and $u$ blocks for a given $\Omega$ value. As a result, each calculated...
level is predicted to be quadruply degenerate, with a
degeneracy of 2 coming from the \(\pm \Omega\) degeneracy, and an-
other factor of 2 coming from the \(g/u\) degeneracy. As in
the heteronuclear case discussed above, the lowest elec-
tron wave state deriving from this manifold is predicted to be
\(2\Delta_{5/2}\) or \(2\Delta_{3/2}\) which are degenerate in this model. Any
splitting of the \(\mathcal{d}\) orbitals into bonding and antibonding
orbitals, however slight, will of course lift the \(g/u\) degener-
cy, leading to \(2\Delta_{5/2}\) predicted ground state. Owing to
the extremely poor overlap between the \(\delta_d\) and \(\delta_B\) atomic
degeneracy, however, the lifting of the \(g/u\) degeneracy is ex-
pected to be very minor, particularly in the \(3d\) series.

The \(\text{Cu}^2_+\) cation belongs in this category. Although the
ground term of this cation is undoubtedly \(\text{Cu}^2_+\sigma_0^0, 2\Sigma^+_u\),
the first manifold of states above the ground state derive
from the \(\text{Cu}^2_+\sigma_0^0, 2\Sigma^+_u\) configuration, and the predictions of this
model are relevant to them. All that is required to apply
this model to the \(\text{Cu}^2_+\sigma_0^0, 2\Sigma^+_u\) states of Cu\(^{2+}\) is an estimate
of the equilibrium bond length and values of \(r_{5d}^2\), \(r_{5d}^2\), and the appropriate spin–orbit parameter \(\xi_{\text{Cu}}(3d)\) for the
Cu\(^{2+}\) ion in its \(d^8\) state.

C. The \(d^8d^9\sigma^2\) states of a hetero- or homonuclear
transition-metal molecule

In the case of a \(d^8d^9\sigma^2\) manifold in a heteronuclear
molecule, one must explicitly consider a system with two
holes, properly account for the different spin–orbit inter-
actions on the two unlike atoms, and include the electro-
static perturbation of each ion core on the other. In per-
forming this calculation, probably the most difficult aspect
is that of selecting physically meaningful Hund’s case (a)
states wave functions in a manner which places one hole on
each atom. The basis set that we have used for both the
homonuclear and heteronuclear \(d^8d^9\sigma^2\) calculations is
available from the Physics Auxiliary Publication Service\(^{(1)}\)
(PAPS) of the American Institute of Physics or from one
of the authors (M.D.M.).

In forming the set of Hund’s case (a) basis functions
for the \(d^8d^9\sigma^2\) states of either like or unlike atoms \((2^D_{+2})\), we have chosen to work with functions that corre-
spond to \(\delta_d\), \(\delta_\sigma\), \(\delta_{\pi}\), \(\pi_{\sigma}\), \(\pi_\sigma\), or \(\sigma\sigma\) configurations of holes,
with one hole on each atom. This allows us to analyze the
final eigenfunctions in terms of their \(\delta\delta\), \(\delta\pi\), \(\pi\pi\), \(\sigma\sigma\), etc. character
quite readily. For like atoms, the \((2^D_{+2})\) separated atom
limit generates the following Hund’s case (a) states:
\[ \xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6, \xi_7, \xi_8, \xi_9 \]
where
\[ \xi = \sum_i r_i \xi^i, \]
for each atom to consist only of the spin–orbit Hamiltonian
for the electrons on that atom. Thus, for example,
\[ \hat{H} = \sum_i r_i V_{ij}, \]

where the summation is over all of the electrons on atom \(A\),
\[ \xi^i_{\alpha}(r_i) \]
represents the radially dependent spin–orbit parameter
for atom \(A\), and the orbital angular momentum \(l_i\) is
measured about the nucleus of atom \(A\). Again, this operator
may be converted into an operator acting on the holes
by reversing the sign of the spin–orbit parameter, \(\xi^i_{\beta}(nd)\).

The expression for \(\hat{H}_{\text{EF}}\) follows analogously. Matrix ele-
ments of \(\hat{H}_{\text{EF}}\) and \(\hat{H}_{\text{HF}}\) in the Hund’s case (a) basis are read-
ily evaluated in terms of atomic spin–orbit parameters
\(\xi_{\alpha}(nd)\) and \(\xi_{\beta}(nd)\) using the methods described by
Lefebvre-Brion and Field\(^{(2)}\).

The electrostatic portion of the Hamiltonian, given by
\[ \hat{H}_{\text{EF}} + \hat{H}_{\text{HF}}, \]
is evaluated in a similar manner as for the
\(d^8d^9\sigma^2\) system described above. The electrostatic pertur-

bation of the \(d^8_{\sigma}\) ion by the \(d^8_{\sigma}\) ion, for example, leads to

\[ \hat{H}_{\text{EF}} = - \sum_i Z_{i B} \frac{1}{r_{i B}}, \]

where \(Z_{i B}\) is the ligand charge of atom \(B\) (taken as +1 in the
present calculation), and \(r_{i B}\) is the distance between the \(i\)
electron and the point charge of ligand \(B\). The expression
for \(\hat{H}_{\text{EF}}\) follows similarly. The correspondence between ex-
pression (2.14) and Eq. (2.5) allows the derivations to
proceed similarly, giving simple one-electron matrix ele-
ments analogous to those given in Eqs. (2.8) and (2.10):

\[ \langle nd_{\alpha m} | \hat{H}_{\text{HF}} | nd_{\alpha m} \rangle = \delta_{m m'} \sum_k B_{00}^{k-1}(-1)^{m} \left( \begin{array}{ccc} 2 & k & 2 \\ m & 0 & -m \end{array} \right) \left( \begin{array}{ccc} 2 & k & 2 \\ 0 & 0 & 0 \end{array} \right), \]

where
\[ B_{01} = Z_{i B} \xi_{\alpha}(nd) \xi_{\beta}(nd) R^{k+1}. \]

Of course, entirely analogous expressions obtained for the
one-electron matrix elements of \(\hat{H}_{\text{HF}}\), and combinations of
TABLE IV. (Continued.)

\[ \langle \Phi(\sigma) | \hat{H} | \Phi(\sigma') \rangle = -\sqrt{\xi} \]

\[ \langle \Phi(\sigma) | \hat{H} | \Phi(\sigma') \rangle = -\xi \]

\[ \langle \Delta(\sigma) | \hat{H} | \Delta(\sigma') \rangle = B_{\sigma}^* + 6 - 3\xi \]

\[ \Omega = 4 \text{ block (4 x 4 for heteronuclear; 2 x 2 \& 2 x 2 for homonuclear)} \]

\[ \langle \Gamma(\delta) | \hat{H} | \Gamma(\delta') \rangle = -2 \]

\[ \langle \Phi(\delta) | \hat{H} | \Phi(\delta') \rangle = -B_{\sigma}^* + 6 - 3\xi \]

\[ \langle \Gamma(\delta) | \hat{H} | \Gamma(\delta') \rangle = -B_{\sigma}^* + 6 - 3\xi \]

\[ \langle \Phi(\delta) | \hat{H} | \Phi(\delta') \rangle = -B_{\sigma}^* + 6 - 3\xi \]

\[ \Omega = 5 \text{ block (1 x 1)} \]

\[ \langle \Gamma(\delta) | \hat{H} | \Gamma(\delta') \rangle = -2B_{\sigma}^* + 6 - 3\xi \]

where \( \xi = \xi_A = \xi_B \)

and \( B_{\sigma}^* = (Z_A^0)^{2} \sum_{n} \sum_{m} (-Z_B^0)^{2} \sum_{n} \sum_{m} \varepsilon_{n}^{2} / \xi_{\sigma}^{2} \)

D. The \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) states of a heteronuclear transition-metal molecule

As a final example of the application of ligand-field theory to diatomic transition-metal molecules, we consider the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) states of a heteronuclear molecule. This corresponds to the excited states of NiCu which were experimentally studied in the preceding paper.12 Again, we choose to work in a Hund’s case (a) basis, corresponding to the \( 4\Delta, 4\Pi, 4\Sigma^+, 2\Phi, 2\Delta, 2\Pi, \) and \( 2\Sigma^- \) states which derive from the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) configuration, with basis wave functions written as Slater determinants in terms of holes rather than electrons. These wave functions are generated in Appendix B and are available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics or from one of the authors (M.D.M.).

The Hamiltonian for the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) system is constructed as

\[ \hat{H}_A = \sum_{l} \varepsilon_{l} \sum_{a} r_{l} \hat{H}_{A}^{\sigma} \]

where \( \varepsilon_{l} \) is the spin-orbit parameter for the \( d_{\sigma}^0(3F) \) ion, and the sum runs over all electrons. Again, this is quite generally converted into a summation over holes by reversing the sign of the spin-orbit parameter, \( \varepsilon_{l} \).

The ligand-field Hamiltonian is again given as

\[ \hat{H}_A^L = - \sum_{l} Z_{B} e^{2} / r_{IB} \]

where the summation is over all of the electrons of the \( d_{\sigma}^0 \) ion, \( Z_{B} \) is the charge of the \( d_{\sigma}^0 \) ion, and \( r_{IB} \) is the distance between the \( l \)th electron and the point charge of the ligand.

Evaluation of the one-electron (or one-hole) matrix elements of \( \hat{H}_A^L \) proceeds exactly as in the previous cases, again yielding expressions (2.15) and (2.16) for the one-hole matrix elements \( \langle nd_{\sigma \alpha} | \hat{H}_A^L | nd_{\sigma \alpha} \rangle \). The complete evaluation of the matrix elements of \( \hat{H}_A^L \) in the Hund’s case (a) basis then leads to combinations of the one-electron matrix elements, as are given in the overall Hamiltonian matrices of Table V for the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) system.

Finally, the exchange between the \( 3F \) core and the \( 2\sigma^* \) electron is a significant factor in this molecule. For example, the corresponding interaction in the \( 3d_{\sigma}^0(3F)d_{\sigma}^{10}2s^* \) \( 2d^4 \) states of the Ni\(^{+}\) ion leads to a splitting of the \( 2F \) and \( 4F \) states of about 4800 cm\(^{-1}\). In a molecule like NiCu this should be reduced since the \( 2\sigma^* \) electron is not so localized on the \( d_{\sigma}^0 \) center, but it is nevertheless an important interaction which must be included in modeling the system. In the related treatment of the lanthanide oxides, for example, the analogous exchange parameter between the \( 4f \) and \( 6s \) electrons drops from 300 cm\(^{-1}\) in a free Ce\(^{3+}\) ion to 103 \( \pm 12 \) cm\(^{-1}\) in the ligand-field fit for the CeO molecule.5 In the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) system considered here this exchange effect is modeled in \( \hat{H}_{A-\sigma} \) by adding an exchange energy, \( G_{\sigma} \), to the diagonal matrix elements of the doublet terms and subtracting 2\( G_{\sigma} \) from the quartet terms, as given by Condon and Shortley26 for the analogous \( d_{\sigma}^0(3F)d_{\sigma}^{10}2s^* \) configuration. Table V presents the final block-diagonalized Hamiltonian matrices for the \( d_{\sigma}^0(3F)d_{\sigma}^{10}2\sigma^* \) system. In all cases, the use of Slater determinants to form the Hund’s case (a) basis functions facilitated the evaluation of the matrix elements. These were analytically evaluated using the Slater–Condon rules26 of one- and two-electron operators. The spin–orbit portions of these matrices were verified by setting the ligand-field portion to zero, diagonalizing the matrices, and making certain that the degeneracy pattern for \( 4F \) and \( 2F \) terms was correctly obtained.
TABLE V. Nonzero Hamiltonian matrix elements for a heteronuclear \( d^9(\ell F) d^0_{\ell 0} \sigma^* \) molecule.

\[
\begin{align*}
\langle \Delta \ell_1, \ell_1 | \hat{H} | \Delta \ell_2, \ell_2 \rangle &= -2G_2 + B_3 / 3 \\
\langle \ell_1, \ell_1 | \hat{H} | \ell_2, \ell_2 \rangle &= \xi / \sqrt{6} \\
\langle \Delta \ell_1, \ell_1 | \hat{H} | \ell_2, \ell_2 \rangle &= \xi / \sqrt{6} \\
\langle \ell_1, \ell_1 | \hat{H} | \Delta \ell_2, \ell_2 \rangle &= -2G_2 + B_3 / 3 \\
\langle \ell_1, \ell_1 | \hat{H} | \ell_2, \ell_2 \rangle &= \xi / \sqrt{6} \\
\end{align*}
\]

II. RESULTS AND DISCUSSION

A. The \( d^9(\ell F) d^0_{\ell 0} \sigma^* \) states of NiCu

Using the basis functions of Table I and the Hamiltonian matrices of Table II, a ligand-field calculation on the \( d^9(\ell F) d^0_{\ell 0} \sigma^* \) manifold of NiCu has been performed. In an initial calculation the parameters were fixed at the values \( \zeta(Ni,3d^8) = 603 \text{ cm}^{-1} \) and \( Z_{Cu} = +1 \), and the values of \( \langle r_{Ni}^2 \rangle = 0.3466 \text{ Å}^2 \) and \( \langle r_{Cu}^2 \rangle = 0.3204 \text{ Å}^4 \) were obtained by averaging the corresponding 3d_{Ni} and 3d_{Cu} values obtained in numerical Dirac–Fock calculations on the \( 3d^8 \) configuration of atomic nickel by Desclaux.\(^{17}\) Although the radial expectation values would be expected to change slightly upon moving to the \( 3d^9 \) configuration, these values are suitable for testing the validity of the ligand-field model. The results of this calculation are given in Table VI, where comparison is made to the only \textit{ab initio} calculation in existence on the NiCu molecule.\(^{25}\)

Shim's \textit{ab initio} calculation on the NiCu molecule utilized a Hartree–Fock procedure, followed by configuration interaction allowing full reorganization within the \( 3d \) and \( 4s \) subshells.\(^{26}\) The configuration-interaction calculation was performed separately on the \( ^2\Delta, ^2\Pi, \) and \( ^2\Sigma^+ \) states deriving from the \( d^9(\ell F) d^0_{\ell 0} \sigma^* \) configuration, using orbitals optimized in the Hartree–Fock calculation for each of these states. Following the configuration-interaction calculation, spin–orbit coupling was introduced to give the final set of states and their parentage in terms of the Hund's case (a) \( ^2\Delta, ^2\Pi, \) and \( ^2\Sigma^+ \) basis functions. The molecule was found to possess a \( ^2\Delta_{5/2} \) ground state, with \( r_\sigma = 2.41 \text{ Å}, D_e = 1.54 \text{ eV}, \) and \( \omega_e = 347 \text{ cm}^{-1}. \) These values differ considerably from the experimental values (\( r_\sigma = 2.235 \text{ Å}, D_e = 2.05 \pm 0.10 \text{ eV}, \) and \( \omega_e = 273 \text{ cm}^{-1}. \)) indicating that Shim's theoretical treatment is not quantitatively accurate; nevertheless, it is not clear that errors calculated in these properties necessarily imply errors in the calculated splittings between the states which make up the \( d^9(\ell F) d^0_{\ell 0} \sigma^* \) manifold.

Table VI demonstrates a nearly quantitative agreement...
between the results obtained in the present ligand-field calculation (with no adjustable parameters) and this \textit{ab initio} investigation. In addition, both calculations are in agreement with experiment in predicting a $^2 \Delta_J/2$ ground state.

To test the sensitivity of the model to the specific values of the parameters, the values of $\xi_{\text{Ni}(d^9)}$ and $Z_{\text{Cu}}$ were allowed to vary, and a least-squares fit to the energies obtained by Shim was also performed. This yielded the optimized values of $Z_{\text{Cu}}=+0.935$ and $\xi_{\text{Ni}(d^9)}=607.4$ cm$^{-1}$, very close to the ligand-field model parameters of $Z_{\text{Cu}}=+1$ and $\xi=603$ cm$^{-1}$, further supporting the ligand-field model for this system.

Although we would prefer to measure the validity of this calculation against experimental data for NiCu, the only experimental result for the $d^9Nid^9$ manifold is the identification of the ground state as $^2\Sigma^+$. However, there are experimental results for the low-lying ($d^9N^2$) electronic states of Ni$_3$, a diatomic molecule that is directly analogous to NiCu. These states have recently been treated by a ligand-field method which is similar to that presented here. In this calculation, the observed levels were fitted to a ligand-field plus spin-orbit Hamiltonian which included all of the effects above. In addition, however, configurational mixing between the $d^9N_2^2$, $^2\Sigma^+$ state and the $d^{10}N_2^+$, $^2\Sigma^+$ state was considered, and this was found to stabilize the $d^{10}N_2^+$, $^2\Sigma^+$ state and dilute its spin–orbit coupling to the $d^{10}N_2^+$, $^2\Pi_{1/2}$ state. Although one would also expect this effect to be important in NiCu as well, this cannot be demonstrated until further experimental data are available on the low-lying $d^{10}N^2 d^2$ states of the molecule.

Table VII and VIII present the results of the ligand-field calculation on Ni$_2$, along with a comparison to the \textit{ab initio} results of Shim. Unfortunately, our experimental knowledge of the $d^{10}N^2$ manifold of states in Ni$_2$ is rather limited. A previous gas-phase experimental study by Morse et al. \cite{33} established the ground state as possessing $\Omega''=4$, with a bond length of $r_0=2.200\pm0.007$ Å, based on the rotational resolution of a single vibronic band of jet-cooled Ni$_2$ near 11 430 cm$^{-1}$. Subsequently, Spain and Morse \cite{34} rotationally resolved a second $^5\Sigma^-$ band at 11 523.015 cm$^{-1}$ (this time with proper calibration based on the I$_2$ atlas), \cite{35} and again found the transition to originate from an $\Omega''=4$ electronic state, with a bond length of $r_0=2.199\pm0.005$ Å. These experimental results, which assign the ground state as possessing $\Omega''=4$, differ from the predictions of both \textit{ab initio} and ligand-field theory. At this time we do not fully understand this discrepancy between experiment and theory. Perhaps the Ni$_2$ molecules are not sufficiently cooled in the supersonic expansion, thereby allowing the lowest $\Omega=4$ state, predicted to be about 800 cm$^{-1}$ above the ground electronic state, to remain populated. This state might well be resistant to cooling, since the only states predicted to lie below it in energy are $^2\Sigma^+$, $^2\Pi^+$, and $^2\Sigma$. Deactivation of an $\Omega=4$ state to a $^2\Sigma^-$ or $^2\Pi^+$ state would require a reversal of the orbital angular momentum of one of the $\delta$ holes in the $d^9$ core of one of the nickel atoms. This $\Delta\Omega=4$ transition might well have a very low collision cross section. Likewise, deactivation of an $\Omega=4$ state to the $\Omega=5$ state might be improbable because the $d^9$ cores are well shielded from the outside world by the $\sigma^2$ framework, making the conversion from a “$g$” coupling of the cores to a “$u$” coupling improbable as well. Of course, it would be ridiculous to think that the ground

<table>
<thead>
<tr>
<th>State</th>
<th>$2\Delta_J/2$</th>
<th>$\Omega=3/2$</th>
<th>$\Omega=1/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{2}\Delta_J/2$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Omega=3/2$</td>
<td>719</td>
<td>798.5</td>
<td>703.6 (11.6)</td>
</tr>
<tr>
<td>$\Omega=1/2$</td>
<td>1602</td>
<td>1775.6</td>
<td>1669.7 (53.7)</td>
</tr>
</tbody>
</table>

**Table VI.** Comparison of \textit{ab initio} and ligand-field theory for the $d^9Nid^9$ states of NiCu.

A nonlinear least-squares fit in which $\xi_{\text{Ni}(d^9)}$ and $Z_{\text{Ni}}$ were varied, and the resulting energies fitted to Shim’s \textit{ab initio} results is presented in Tables VII and VIII as well. The converged values of $\xi_{\text{Ni}(d^9)}=623.9$ cm$^{-1}$ and $Z_{\text{Ni}}=+0.953$ which were obtained in the least-squares fit are close to the values $\xi_{\text{Ni}(d^9)}=603$ cm$^{-1}$ and $Z_{\text{Ni}}=+1.0$, lending further support to the ligand-field model. Moreover, the splitting pattern among the $d^9N_2^2$ set of states has been derived from a physical model based on atomic parameters which does not require huge basis sets and treatment of electron correlation for its application.

Again, we would prefer to test the ligand-field model for Ni$_2$ by comparison to experiment, rather than to \textit{ab initio} theory. Unfortunately, our experimental knowledge of the $d^9N^2$ manifold of states in Ni$_2$ is rather limited. A previous gas-phase experimental study by Morse et al. \cite{33} established the ground state as possessing $\Omega''=4$, with a bond length of $r_0=2.200\pm0.007$ Å, based on the rotational resolution of a single vibronic band of jet-cooled Ni$_2$ near 11 430 cm$^{-1}$. Subsequently, Spain and Morse \cite{34} rotationally resolved a second $^5\Sigma^-$ band at 11 523.015 cm$^{-1}$ (this time with proper calibration based on the I$_2$ atlas), \cite{35} and again found the transition to originate from an $\Omega''=4$ electronic state, with a bond length of $r_0=2.199\pm0.005$ Å. These experimental results, which assign the ground state as possessing $\Omega''=4$, differ from the predictions of both \textit{ab initio} and ligand-field theory. At this time we do not fully understand this discrepancy between experiment and theory. Perhaps the Ni$_2$ molecules are not sufficiently cooled in the supersonic expansion, thereby allowing the lowest $\Omega=4$ state, predicted to be about 800 cm$^{-1}$ above the ground electronic state, to remain populated. This state might well be resistant to cooling, since the only states predicted to lie below it in energy are $^2\Sigma^+$, $^2\Pi^+$, and $^2\Sigma$. Deactivation of an $\Omega=4$ state to a $^2\Sigma^-$ or $^2\Pi^+$ state would require a reversal of the orbital angular momentum of one of the $\delta$ holes in the $d^9$ core of one of the nickel atoms. This $\Delta\Omega=4$ transition might well have a very low collision cross section. Likewise, deactivation of an $\Omega=4$ state to the $\Omega=5$ state might be improbable because the $d^9$ cores are well shielded from the outside world by the $\sigma^2$ framework, making the conversion from a “$g$” coupling of the cores to a “$u$” coupling improbable as well. Of course, it would be ridiculous to think that the ground
TABLE VII. Comparison of \textit{ab initio} and ligand-field results for the gerade $d_{x^2+y^2}$ states of Ni.

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Combination in $%$ of the case (a) basis functions$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1$^1_G (\delta\delta)$</td>
</tr>
<tr>
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<tr>
<td>O$_{2}^+$</td>
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</tr>
<tr>
<td>1$^1_S$</td>
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<tr>
<td>2$^3_P$</td>
<td>1746 1850 1820</td>
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<tr>
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<td>2632 2666 2610</td>
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</tr>
<tr>
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<td>5356 5287 5193</td>
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<td>5604 5576 5552</td>
</tr>
<tr>
<td>2$^3_P$</td>
<td>6740 6874 6810</td>
</tr>
</tbody>
</table>

$^a$Ab initio results are from Ref. 30.

$^b$Ligand-field treatment with $Z_{Ni}=1.0$, $\zeta=603$ cm$^{-1}$, $(r^2)_u=0.3646$ Å$^2$, $(r^2)_d=0.3204$ Å$^4$, and $R=2.20$ Å.

$^c$Ligand-field energies resulting from a least-squares fit to the \textit{ab initio} energy levels, yielding $Z_{Ni}=+0.953$; $\zeta=623.92$ cm$^{-1}$.

$^d$The % contribution is given for the \textit{ab initio} result, followed by the percent contribution found from the ligand-field treatment with $Z_{Ni}=+1.0$, $\zeta=603$ cm$^{-1}$ in parentheses.
<table>
<thead>
<tr>
<th>State</th>
<th>$A_{initio}$</th>
<th>Ligand field $a$</th>
<th>Ligand field $b$</th>
<th>Combination in % of the case (a) basis functions $d$</th>
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<td>817</td>
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<td>3420</td>
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<td>3699</td>
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<td>16(8) 9(8)</td>
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<td>3989</td>
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$A_{initio}$ results are from Ref. 30.

$\text{Ligand-field treatment with } Z_{NI}=+1.0, \xi=603 \text{ cm}^{-1}, \langle \rho \rangle_{3d}=0.3466 \AA^2, \langle \rho \rangle_{4d}=0.3204 \AA^2, \text{ and } R=2.20 \AA.$

$\text{Ligand-field energies resulting from a least-square fit to the } ab \ initio \text{ energy levels, yielding } Z_{NI}=-0.935; \xi=633 \text{ 97 cm}^{-1}.$

The % contribution is given for the $ab \ initio$ result, followed by the result for the ligand-field calculation with $Z_{NI}=+1.0, \xi=603 \text{ cm}^{-1}$ in parentheses.
state of Ni$_2$ would not be populated in the jet-cooled molecular beam, so a more thorough investigation of Ni$_2$ should reveal the expected $\Omega=0^+_1$, $0^+_0$, and $2^+_1$ states which both $ab$ initio and ligand-field theory predict to be nearly degenerate, and are the strongest candidates for the ground state. Stimulated emission pumping experiments probably offer the greatest hope for untangling the $d^9 \sigma^2$ manifold of states in Ni$_2$, and this work will be critical for testing the ligand-field model of the electronic structure in this molecule.

Unlike nickel, the ground term of atomic palladium corresponds to the $4d^{10}5s^0$ configuration, and the ground state of Pd$_2$ probably derives from the singly promoted $4d^{10}5s^0+4d^95s^1$ separated atom limit. Both theory and experiment are in agreement that the ground state of Pd$_2$ is best described as $d^9 \sigma^2$, and $d^9 \sigma^2$ is the almost pure $g$ state of the ${\Sigma}^0_{\sigma}$, i.e., the $2^+$ state. The doubly promoted $d^9 \sigma^2$ states of Pd$_2$ fall at higher energies and have not yet been experimentally investigated. For this reason they will not be discussed further here.

The ground state of Pt$_2$ derives from two $d^9$ atoms, so the ligand-field model for the $d^9 \sigma^2$ manifold is applicable to this case. Unlike Ni$_2$, however, Pt$_2$ shows significant $\omega$-orbital contributions to its bonding. Strong evidence for this statement comes from the optical spectrum of Pt$_2$, which has been investigated in a jet-cooled molecular beam by the resonant two-photon ionization method. By observing the onset of predissociation in a very congested vibronic spectrum, Taylor et al. were able to determine the bond strength of diatomic platinum to be 3.14 eV. This is the ~f~d&~ states of Ptz. Nevertheless, we have calculated the ~f~d&~ states of Ptz. The emergence of $\Omega=0^+_1$, $0^+_0$, and $2^+_1$ states (arising from $\delta\delta$ configurations of holes) as the lowest lying states implies rather little $d$-orbital contributions to the chemical bonding in this calculation on Pt$_2$. Despite the quantitative differences, this is similar to the results of the ligand-field treatment described here. A major distinction, however, arises because the molecular-orbital-plus-configuration-interaction approach allows both covalent $d^9 \sigma^2$ and ionic $d^9 \sigma^2$ contributions, while the current implementation of ligand-field theory is similar to simple valence-bond theory in that only $d^9 \sigma^2$ configurations are considered. In light of the demonstrated contribution of the $d$ electrons to the bonding in Pt$_2$, however, it seems likely that neither calculation will be correct; this cannot be stated with certainty without a great deal of further experimental work on Pt$_2$, however.

### C. The $d^9 \sigma^2$ states of NiPt

Diatomic NiPt belongs to the category of a heteronuclear $d^9 \sigma^2$ molecule, which has been treated by the ligand-field plus spin–orbit method in Sec. II C. In addition, NiPt has been spectroscopically investigated in the gas phase and found to possess a ground electronic state with $\Omega=0^+$. It is not straightforward to determine if the ligand-field model is applicable to NiPt. It is true that an $\Omega=0^+$ state is one of the lowest electronic states coming from a $d^9 \sigma^2$ manifold of states in the ligand-field plus spin–orbit model, arising from spin-paired $\delta$ holes on the

### Table IX. Ligand field and $ab$ initio results for Pt$_2$

<table>
<thead>
<tr>
<th>States$^b$</th>
<th>Energy (cm$^{-1}$)</th>
<th>Ab initio$^b$</th>
<th>State</th>
<th>Energy (cm$^{-1}$)</th>
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<td>$0^+_1 (\Sigma^+\delta\delta)$</td>
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$^a$Ligand-field calculation employing $\Omega_2=+1.0$, $\xi_2=4052.8$ cm$^{-1}$, $R=2.471$ Å, $\langle r \rangle_2=0.9221$ Å, and $\langle r^2 \rangle_2=1.7300$ Å.

$^b$Complete-active-space self-consistent-field first order configuration interaction results from Ref. 41. States which consist of greater than 70% of a single configuration are identified by the full term symbol and orbital designation of the $d$ holes in the leading configuration. When spin–orbit or configurational mixing are more important, spin and orbital g/u designations are omitted.

$^c$States are designated by their $\Omega$, $+$, $-$, and g/u quantum numbers. In the ligand-field calculation many states with different quantum numbers are nevertheless degenerate. These would be split in a more realistic calculation.
TABLE X. Ligand-field predicted states of NiPt.a

<table>
<thead>
<tr>
<th>Stateb</th>
<th>Energy (cm⁻¹)</th>
<th>State</th>
<th>Energy (cm⁻¹)</th>
<th>State</th>
<th>Energy (cm⁻¹)</th>
</tr>
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<td>2,1</td>
<td>4,444</td>
<td>3,0⁺,₀⁻</td>
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<td>814</td>
<td>3,0⁺,₀⁻</td>
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<td>4</td>
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<td>3,2</td>
<td>4,908</td>
<td>3,0⁺,₀⁻</td>
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<td>2,1</td>
<td>6,283</td>
<td>2,1</td>
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<td>2,499</td>
<td>2,1</td>
<td>7,013</td>
<td>1,0⁺,₀⁻</td>
<td>16,189</td>
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<td>8,475</td>
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<td>17,012</td>
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<td>3,799</td>
<td>4</td>
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<td>1,0⁺,₀⁻</td>
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<td>4,194</td>
<td>1</td>
<td>11,020</td>
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</table>

aCalculation performed with \( Z_{\text{Ni}} = Z_{\text{Pt}} = +1.0 \), \( \xi = 603.0 \text{ cm}^{-1} \), \( \theta_{\text{Ni}} = 0.3466 \text{ Å}^2 \), \( \theta_{\text{Pt}} = 1.7306 \text{ Å}^2 \). States are designated by their \( \Omega \) quantum numbers. In many cases several states of different \( \Omega \) are degenerate.

Ni and Pt atoms. On the other hand, an \( \Omega = 0 \) term would be generated from the \( d^{9}d^{10}σ^{2} \) manifold of states in NiPt by a knowledge of the ground state, where the \( d \) orbitals were strongly split into bonding and antibonding orbitals.

Since the available experimental data for the splitting pattern of the \( d^{9}d^{11}σ^{2} \) manifold of states in NiPt is limited to a knowledge of the ground state, we must rely on comparisons of bond strengths and bond lengths to evaluate the \( d \)-orbital contributions to the chemical bonding in this molecule. As in Pt₂, the onset of predissociation in a very dense set of vibronic energy levels has allowed the bond strength of NiPt to be determined as \( D_0 \) (NiPt) = 2.798 eV.42 This may be compared to the analogous closed \( d \) subshell coinage metal diatomic, CuAu, which possesses a bond strength of \( D_0 \) (CuAu) = 2.344 eV.43 The greater bond strength of NiPt implies significant but not overwhelming contributions to the NiPt chemical bond by the \( d \) orbitals of the component atoms. This is further substantiated by the reduced bond length in NiPt (\( r_0 = 2.2078 \pm 0.0003 \text{ Å} \)) as compared to CuAu (\( r_0 = 2.3302 \pm 0.0006 \text{ Å} \)).43 On this basis the ligand-field plus spin–orbit model presented here, which omits metal–ligand orbital overlap, is probably not applicable to the NiPt diatomic molecule, since it appears that the \( d \) orbitals are split to some degree into bonding and antibonding pairs. Nevertheless, Table X presents the results of the ligand-field plus spin–orbit calculation for comparison to future ab initio or experimental results.

Finally, the analogous NiPd (Ref. 44) and PdPt (Ref. 44) diatomics have also been investigated in the gas phase, but the ground states of these molecules are thought to arise from \( d^{9}d^{10}d^{2} \) and \( d^{10}d^{10}d^{2} \) \( σ \) state configurations, respectively. This is due to the stable \( d^{10}d^{2} \) configuration of atomic palladium. Accordingly, a ligand-field model based on \( d^{9}d^{10}d^{2} \) manifold of states is inappropriate for these molecules, and they will not be considered further. Both molecules would find their counterparts in the \( d^{9}d^{10}d^{2} \) states of CoH, however, and the analysis of all of these systems in terms of a ligand-field theory will be quite interesting.

D. The \( d^{9}d^{10}d^{10}d^{2}σ^{2}σ^{2}σ^{2}σ^{2} \) states of NiCu

The single example of a manifold of experimentally well-known electronic states in a transition-metal diatomic molecule is the \( d^{9}d^{10}d^{10}d^{2}σ^{2}σ^{2} \) manifold of NiCu, which was experimentally investigated in the preceding paper.12 As such, this manifold provides an important test of the ligand-field theory developed in Sec. II E above. Accordingly, a calculation was attempted with \( Z_{\text{Cu}} = +1.0 \), \( \xi (\text{Ni},d^{8}d^{2}d^{2}) = 663 \text{ cm}^{-1},25 \langle \xi (\text{Ni},d^{9}d^{10}d^{2}) \rangle = 0.3466 \text{ Å}^2 \), \( \langle \xi (\text{Cu},d^{9}d^{10}d^{2}) \rangle = 0.3204 \text{ Å}^2 \), and with the 3dNi-σ exchange parameter \( G_2 \) allowed to vary. Despite the flexibility afforded by making \( G_2 \) an adjustable parameter, it was not possible to reproduce the experimentally observed electronic states of the \( d^{9}d^{10}d^{10}d^{2}σ^{2}σ^{2} \) manifold of NiCu with this model. This was troubling, particularly in light of the success of the ligand-field model in comparison with ab initio results for the \( d^{9}d^{10}d^{10}d^{2}σ^{2}σ^{2} \) manifold of NiCu, and the \( d^{9}d^{10}d^{2}σ^{2}σ^{2}σ^{2}σ^{2} \) manifold of Ni₂.

In the \( d^{9}d^{10}d^{10}d^{2}σ^{2}σ^{2}σ^{2}σ^{2} \) manifold of NiCu, however, one additional electron has been removed from the nickel core, so it might be reasonable for the copper to have an effective charge which is somewhat reduced from \( Z_{\text{Cu}} = +1.0 \). Accordingly, \( Z_{\text{Cu}} \) was varied along with \( G_2 \), and a reasonable fit to the experimental data was successfully obtained, as is listed in Table XI. Surprisingly, the calculation converged to values of \( G_2 = 511.6 \text{ cm}^{-1} \) [substantially reduced from \( G_2 \approx 1600 \text{ cm}^{-1} \) in the free \( d^{9}d^{10}d^{2}d^{2}d^{2} \) Ni⁺ ion] and \( Z_{\text{Cu}} = -0.666 \). A subsequent calculation also allowed \( \xi (\text{Ni},d^{8}d^{2}d^{2}) \) to vary, resulting in the fitted parameters of \( G_2 = 547.3 \text{ cm}^{-1}, Z_{\text{Cu}} = -0.686 \), and \( \xi (\text{Ni},d^{9}d^{10}d^{2}) \) = -592.3 cm⁻¹. Both fits are listed in Table XI. The emergence of a negative effective charge on the copper atom is surprising and is not presently understood. This suggests an improvement to the ligand-field treatment, in which one quantum mechanically solves for the \( σ^{2}σ^{2}σ^{2}σ^{2} \) system of three electrons in the presence of pseudopotentials describing the \( d^{9}d^{10}d^{2} \) cores, then calculates the electronic perturbation to the \( d^{9}d^{10}d^{2} \) core including both the point charge of the copper core and the influence of the \( σ^{2}σ^{2}σ^{2}σ^{2} \) electrons. Presumably this calculation would reveal why an effective negative charge resides on the copper atom in the \( d^{9}d^{10}d^{2}σ^{2}σ^{2}σ^{2}σ^{2} \) states of NiCu.

To show how the charge of the copper ligand affects the splitting in the \( d^{9}d^{10}d^{2}σ^{2}σ^{2}σ^{2}σ^{2} \) manifold of states. Fig. 1 displays the energies of the \( \Omega = 1/2, 5/2, \) and \( 3/2 \) levels as a function of ligand charge, holding the spin–orbit parameter and the exchange energy constant at 663 and 511.6 cm⁻¹, respectively. Again, it should be noted that this ignores the large configurational reordering effects which can result from variation of \( Z_{\text{Cu}} \). The figure shows that the pattern of \( \Omega \) states basically inverts in changing the ligand charge from +1 to -1, with the exception of a few avoided curve crossings. From this figure it is clear that we have not missed a minimum with \( Z_{\text{Cu}} > 0 \) in the nonlinear least-squares fit, since the pattern of states is totally wrong for \( Z_{\text{Cu}} > 0 \). A challenge for theorists is to
TABLE XI. Fitted ligand-field results for the \(d^8_\text{NiCu}(^{3}F)\) manifold of NiCu.

<table>
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<tr>
<th>State</th>
<th>Ext.</th>
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<th>Ligand fieldφ</th>
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<th>4Δ</th>
<th>4Π, α</th>
<th>4Π, β</th>
<th>3μ-1</th>
<th>3μ+1</th>
<th>3μ-1</th>
<th>3μ+1</th>
<th>3μ-1</th>
<th>3μ+1</th>
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<td>0(0)</td>
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<td>8(8)</td>
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<td>12 105.3</td>
<td>76(79)</td>
<td>15(12)</td>
<td>5(4)</td>
<td>2(1)</td>
<td>10(0)</td>
<td>2(3)</td>
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<tr>
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<td>63(68)</td>
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<td>1(1)</td>
<td>7(6)</td>
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<td>17(12)</td>
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<td>10 480.1 (−66)</td>
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<td>11(8)</td>
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<td>9 804.5</td>
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<tr>
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<tr>
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<td>9 664.3</td>
<td>5(5)</td>
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<td>12(12)</td>
<td>47(47)</td>
<td>0(0)</td>
<td>0(0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reference 12.

1. Molecular properties from ligand-field eigenvectors

Although the ligand-field fit to the \(d^8_\text{NiCu}(^{3}F)\) manifold of states of NiCu requires a seemingly unphysical negative charge on the copper atom, it nevertheless provides several convincing predictions. Both fits predict the existence of two states of \(\Omega=1.5\) states, located at approximately 13 200 and 13 300 cm\(^{-1}\), which were not observed in the spectroscopic work of Spain and Morse.\(^{12}\) However, absorption oscillator strength from the \(X^2\Delta_{3/2}\) ground state to the \(\Omega=1.5\) states derives entirely from the \(\Pi_{3/2}\) char-
character contained within the strongly mixed excited-state wavefunctions. The two unobserved \( \Omega = 1.5 \) states consist of only about 1%-3% \( ^3\Pi_{\Delta/2} \) character, whereas the observed \( \Omega = 1.5 \) states contain 11%-60% \( ^3\Pi_{\Delta/2} \) character. Thus the calculation predicts that these two unobserved band systems should have absorption intensities which are approximately one-tenth of that found in the other \( \Omega = 1.5 \) band systems. This readily accounts for their absence in the recorded spectra.

Another prediction of the ligand-field calculation is that an \( \Omega = 1.5 \) state should be found near 10 370 cm\(^{-1}\). Spain and Morse have detected a state in this energy range, which heterogeneously perturbs the \([10.4]_{2.5}\) state. It therefore must possess an \( \Omega \) value of either 1.5 or 3.5. Although rotationally resolved studies of this band system were inconclusive, the observation of a strong \( P \) branch suggested that the new state possessed \( \Omega = 1.5 \), and considerations of the vibrational factor of the perturbation matrix element placed the \( v = 0 \) level of this state at approximately 10 410.9 cm\(^{-1}\). Although this state was not included in the least-squares fit to the ligand-field model, it was nevertheless predicted to lie within 50 cm\(^{-1}\) of the observed energy of the \( v = 0 \) level.

2. Excited-state radiative lifetimes

The eigenvectors obtained in the ligand-field calculation should also at least qualitatively account for the radiative lifetimes measured in the resonant two-photon ionization experiments.\(^{12}\) The measured lifetimes fall into two categories, giving a range of 3.98-8.61 \( \mu s \) for the \( A-F \) states, and lifetimes greater than 40 \( \mu s \) for the low-lying \([10.8]_{3.5}, [10.4]_{2.5}, \) and \([10.4]_{1.5}(?)\) states. Since the ground \( d_{\alpha d}^{10} \) manifold is purely doublet \( (S = 1/2) \) character, the radiative decay rate should be roughly proportional to the total amount of doublet character in the excited-state wave function, which is given by the sum of the percentage contributions from the doublet states in Table XI. This gives values of 79%-96% doublet character for the \( B-F \) states, and only 12%-21% doublet character for the low-lying \([10.8]_{3.5}, [10.4]_{2.5}, \) and \([10.4]_{1.5}(?)\) states, in rough correspondence with the measured lifetimes. On the other hand, the \( A[11.5]_{2.5} \) state is not accurately represented by the ligand-field calculation, since its total doublet character is only 8%-12%, but its decay rate is comparable to that of the states which are calculated to be 79%-96% doublet character. Likewise, oscillator strength for the absorption \( A[11.5]_{2.5} \rightarrow X ^2\Delta_{\Delta/2} \) is entirely from the \( ^2\Delta_{\Delta/2} \) character of the \( A[11.5]_{2.5} \) state, and the ligand-field calculation predicts this to be only 1%-3%. This is far too low to explain the intensity of the \( A[11.5]_{2.5} \rightarrow X ^2\Delta_{\Delta/2} \) system in absorption.

3. Heterogeneous perturbation of the \( B[11.9]_{2.5} \) and \( C[11.9]_{1.5} \) states: L-uncoupling and S-uncoupling effects

If the ligand-field model is valid, the ligand-field eigenvectors should also predict the \( J \)-dependent perturbation between the \( B[11.9]_{2.5} \) (found to be primarily \( ^2\Delta_{\Delta/2} \) in the fits of Table XI) and \( C[11.9]_{1.5} \) (found to be primarily \( ^2\Pi_{\Delta/2} \) in the fits of Table XI) states of NiCu. The matrix elements for this rotationally induced heterogeneous perturbation, with selection rule \( \Delta \Omega = \pm 1 \), are

\[
\langle \Lambda, \Sigma, \Omega, v | -\beta F \lambda \Delta \rho^2/2 \mu R^2 | \Lambda \pm 1, \Sigma, \Omega, \pm 1, v' \rangle
\]

\[
= -B_{\text{sr}} \left( \sum_{i} T_{i} | \Lambda \pm 1, \Sigma, \Omega, \pm 1 \rangle [J(J+1) - \Omega(\Omega+1)]^{1/2}
\]

for the \( L \)-uncoupling operator, and

\[
\langle \Lambda, \Sigma, \Omega, v | -\beta F \lambda \Delta \rho^2/2 \mu R^2 | \Lambda, \Sigma, \Omega = 1, \Omega = 1, v' \rangle
\]

\[
= -B_{\text{sr}} \left| S(S+1) - \Sigma(\Sigma+1) \right|^{1/2} [J(J+1) - \Omega(\Omega+1)]^{1/2}
\]

25 evaluated with Hund's case (a) basis functions. As described in the preceding paper, the interaction matrix for the heterogeneous coupling of the \( B[11.9]_{2.5} \) and \( C[11.9]_{1.5} \) states is of the form

\[
H_{BC} = \begin{pmatrix}
T_{0,0}(B) + B_{\text{sr}}[J(J+1) - \frac{k}{4}]^{1/2} & k_{B}B_{\text{sr}}[J(J+1) - \frac{k}{4}]^{1/2} \\
kB_{\text{sr}}[J(J+1) - \frac{k}{4}]^{1/2} & T_{0,0}(C) + B_{\text{sr}}J(J+1)
\end{pmatrix}
\]

where \( k \) is a constant which combines all of the term-by-term interactions between the component Hund's case (a) states of the \([11.9]_{2.5} \) and \([11.9]_{1.5} \) states. With use of the ligand-field eigenvectors, which are linear combinations of the \( J \)-dependent perturbation, with selection rule \( \Delta \Omega = \pm 1 \), are

4. The \( d_{\alpha d}^{10} \) \((3F)\sigma^{2}\sigma^{*}\) excited states of NiH

The \( d_{\alpha d}^{10} \) \((3F)\sigma^{2}\sigma^{*}\) excited states of NiH are analogous to the \( d_{\alpha d}^{10} \) \((3F)\sigma^{2}\sigma^{*}\) excited states of NiCu, particularly if the \( d_{\alpha d}^{10} \) subshell is taken to remain closed. With this in mind, the ligand-field treatment applied to this manifold in NiCu may be immediately carried over to the corresponding excited states of NiH, where considerable experimental data is available.\(^{45}\) Indeed, the known electronic states of the two molecules fall into the same pattern, indicating that the electronic structure of the two molecules is determined by similar factors. Table XII presents the known electronic states of the \( d_{\alpha d}^{10} \) \((3F)\sigma^{2}\sigma^{*}\) manifold of NiH, along with the results of a least-squares fit of the experimental data to the ligand-field model described in Sec. II E above.

Table XII presents the composition of the wave function obtained in the fit, along with the fitted energy levels. In these calculations we have not considered the \( L \)- and \( S \)-uncoupling interactions which occur in the rotating molecule, and which can be quite significant in a light molecule such as a hydride. With further work to include these in-
TABLE XII. Fitted ligand-field results for the $d_{16}^{2}F^2$ manifold of NiH.

<table>
<thead>
<tr>
<th>State</th>
<th>Expt $^a$</th>
<th>1 ligand field $^b$</th>
<th>2 ligand field $^c$</th>
<th>$\tilde{\epsilon}$</th>
<th>$\tilde{\delta}$</th>
<th>$\tilde{\mu}$</th>
<th>$\tilde{\lambda}$</th>
<th>$\tilde{\zeta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G[18.4]2.5$</td>
<td>18.371</td>
<td>18.389 (-18)</td>
<td>18.342 (29)</td>
<td>2 (2)</td>
<td>(1)</td>
<td>(0)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>0.5</td>
<td>17.957</td>
<td>17.496</td>
<td></td>
<td></td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>$J[17.2]1.5$</td>
<td>17.250</td>
<td>17.366 (-116)</td>
<td>17.305 (-55)</td>
<td>4 (4)</td>
<td>(0)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>$F[17.0]3.5$</td>
<td>17.023</td>
<td>17.017 (25)</td>
<td>17.059 (-27)</td>
<td>5 (5)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
<tr>
<td>0.5</td>
<td>15.905</td>
<td>16.139</td>
<td></td>
<td></td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
<td>(1)</td>
</tr>
</tbody>
</table>

$^a$Reference 45.

$^b$Ligand-field calculation with $\tilde{\epsilon}_{j}=0.3466$ Å$^{-1}$, $\tilde{\delta}_{j}=0.3204$ Å$^{-1}$, and $\tilde{\mu}=1.644$ Å, $Z$ and $G_{1}$ were allowed to vary, and converged to $Z=0.439$ and $G=791.94$ Å$^{-1}$.

$^c$Ligand-field calculation with $\tilde{\epsilon}_{j}=0.3466$ Å$^{-1}$, $\tilde{\delta}_{j}=0.3204$ Å$^{-1}$, and $R=1.644$ Å, $\tilde{\mu}$, $Z$ and $G_{1}$ were allowed to vary, and converged to $\tilde{\mu}=614.64$ Å$^{-1}$, $Z=0.442$, and $G=783.61$ Å$^{-1}$.

$^d$The composition of the final wave function is given in percent for the fit described in footnote (b), and in parentheses for the fit described in footnote (c).

This contribution is responsible for the oscillator strength in absorption from the ground $X^2\Delta_{3/2}$ state.
ment, with the $A(15.5)2.5$ state having 75% $4\Phi_{5/2}$ character.

The general agreement between the experimentally deduced compositions of the wave functions and those obtained in the ligand-field fit is encouraging, and supports the validity of the ligand-field approach. Moreover, this level of agreement suggests that the results presented in Table XII will be useful in locating the remaining states of the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold of NiH. On the other hand, the charge state of the hydrogen atom obtained in the fit, $Z_H = -0.442$, is difficult to rationalize. The deperturbed term energies of the $3\Delta$ and $3\Pi$ states of the $d_{\sigma}^9(F)\sigma^6$ manifold of NiH correspond to an effective charge on the H atom of $Z_H = 1.053$, and it is difficult to understand why this parameter would change to $Z_H = -0.442$ in the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold, unless the $\sigma^*\sigma^4$ electron is totally localized on the hydrogen atom in the $d_{\sigma}^9(F)\sigma^6$ manifold. In any case, whatever is responsible for this severe change in the effective charge of the ligand is common to both the $d_{\sigma}^9(F)\sigma^0\sigma^4$ states of NiH and the $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ states of NiCu.

This mystery of the charge of the ligand will be best understood by examining the electronic structure of the $\sigma^0\sigma^4$ manifold of the NiCu and NiH molecules through $ab$ initio quantum-mechanical methods. A proper treatment would then allow the three $\sigma$ electrons to move in the potential of a $d_{\sigma}^9(F)Ni^{2+}$ ion in close proximity to a $d_{\sigma}^{10}(Cu)^{+}$ ion. Of course, the effects of the electrons of the cores of these ions would have to be included through pseudopotentials, but one could in principle obtain very reasonable wave functions for the $\sigma^0\sigma^4$ portion of the molecule in this fashion. It would then be possible to pursue a proper ligand-field treatment of the splitting among the states of the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold of NiCu and the $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ manifold of NiH by subjecting the $d_{\sigma}^9(F)\sigma^0\sigma^4$ core to an electrostatic perturbation derived from both the $+1$ point charge of the $d_{\sigma}^{10}\sigma$ core in addition to the field derived from the $\sigma^0\sigma^4$ framework. This generalization of the ligand-field treatment would still be far simpler than $ab$ initio quantum chemistry, and would perhaps provide an explanation of the negative effective charge found for the hydrogen and copper ligands.

IV. SUMMARY

In this paper ligand-field theory has been applied to the diatomic transition-metal molecules, focusing primarily on the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold of NiCu, the $d_{\sigma}^8(F)\sigma^0\sigma^2\sigma^2$ manifold of Ni and Cu$_2^+$, and the $d_{\sigma}^5(F)\sigma^0\sigma^6\sigma^4$ manifold of NiCu. In addition, comparisons to the $d_{\sigma}^9(F)\sigma^0\sigma^2\sigma^2$ and $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ manifolds of NiH have been made. The results of the theory applied to the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold of NiCu and the $d_{\sigma}^8(F)\sigma^0\sigma^2\sigma^2$ manifold of Ni$_2$ are impressive, showing essentially quantitative agreement with $ab$ initio quantum chemistry in a model with no free parameters. Most important is the fact that the ligand-field model provides a conceptual framework for understanding the electronic structure of these complicated molecules which does not require thousands (or even millions) of contributing electronic configurations for its application.

In the case of the $d_{\sigma}^9(F)\sigma^0\sigma^4$ manifold of NiCu and the $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ manifold of NiH the ligand-field Hamiltonian has been used as a fitting function to obtain an understanding of these electronic manifolds. The fitted results are robust, in the sense that they predict phenomena beyond those used to obtain the fit. Thus, for example, the composition of the wave functions of the $d_{\sigma}^9(F)\sigma^0\sigma^4$ states in NiH are generally in agreement with that deduced from spectroscopic work. Likewise, the ligand-field model correctly predicts the relative intensities and heterogeneous coupling between states in the $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ manifold of NiCu. Although the model fails in some details, it is clear that it provides a good zeroth-order description of these excited states of both NiH and NiCu. Further refinements to include ligand-induced configuration interaction, as was required in the treatment of LaF$_7^+$, for example, represent relatively straightforward extensions of this work, and can be incorporated readily.

The magnitude of the ligand charge found for the excited $d_{\sigma}^9(F)\sigma^0\sigma^4$ states of NiCu and the $d_{\sigma}^9(F)\sigma^0\sigma^0\sigma^4$ states in NiH is surprising and at this point unexplained. It is suggested that a quantum-mechanical treatment of the $\sigma^0\sigma^4$ framework in the pseudopotential created by the $d_{\sigma}^9(F)\sigma^0\sigma^4$ states of NiCu and the $d_{\sigma}^{10}(\sigma)\sigma^0\sigma^4$ states in NiH is an excellent probe of the degree of $d$-orbital bonding in the 3d transition-metal--Cu diatomic molecules. It will also be very interesting to apply the ligand-field model to NiCu congeners such as NiAg, NiAu, NiCu, CoCu, FeCu, CoNi, FeNi, NiAg, NiAu, etc. A comparison of a ligand-field calculation for CuCu and FeCu to experimental results would provide an interesting probe of the degree of $d$-orbital bonding in the 3d transition-metal--Cu diatomic molecules. It will also be very interesting to apply the ligand-field model to NiCu congeners such as NiAg, NiAu, NiAl, and PtCu, and to make a comparison to experimental results. In this regard we have recently determined the ground electronic states of NiAl$_{19}$, NiAl$_{20}$ and PtCu (Ref. 19) to be $\Delta_{5/2}$, but the optical spectra are complicated and unlike the spectra of NiCu. It seems likely that the ligand-field model may again succeed for the ground-state manifolds of these molecules, but may not be readily applicable to the excited electronic states.

ACKNOWLEDGMENTS

The authors wish to thank Professor K. W. Frank for engaging and fruitful discussions on the application of the ligand-field theory to diatomic molecules. We would like to...
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APPENDIX A: GENERATION OF WAVE FUNCTIONS

FOR A d₈g₉dσ² MANIFOLD OF STATES

The 3T₅(ω) (S=1, L=4, Σ=1, Ω=Λ+Σ=5) basis wave function (which is the only Ω=5 term deriving from a d₈g₉dσ² configuration), was written as a Slater determinant as

$$|3T₅(ω)⟩ = A₃|δ(1)α(1)δ(2)α(2)⟩.$$  \hspace{1cm} (A1)

Here A₃ is the antisymmetrization operator. The subscripts A or B label the atom, and δ indicates that m_l=+2. Application of the S⁻₇ lowering operator to this 3T₅(ω) wave function then generated the wave functions of the 1T₄(ω) (Σ=−2) and 1T₃(ω) (Σ=−1) terms. The 1T₄(ω) wave function was then obtained by forming the linear combination of the two Ω=4 Slater determinants that is orthogonal to the 3T₅(ω) wave function. Following this, application of L⁻ to the 1F₉/2 and 1F₇/2 wave functions generated the 3F₉/2 and 1F₇/2 wave functions corresponding to the δσ configuration. From these, the 3F₉/2 and 1F₇/2 wave functions (again belonging to the δσ configuration) were generated by reversal of the appropriate signs. The 3Δ(ω) and 3Δ(ω) wave functions belonging to the σσ configuration were then generated by application of L⁻ to the corresponding 1Δ(ω) and 3Δ(ω) wave functions, and the 3Δ(ω) and 3Δ(ω) wave functions deriving from the δσ configuration were obtained by reversal of the appropriate signs.

The 3Δ(ω) and 3Δ(ω) wave functions corresponding to the πσ configuration were constructed in analogy to the 3Γ(ω) and 1Γ(ω) wave functions of the δδ configuration by reducing the m_l quantum numbers of the occupied orbitals from 2 to 1, thereby completing the construction of the basis wave functions with Λ>2. Application of L⁻ to these 3Δ(ω) and 3Δ(ω) states then yielded the 3Π(ω) and 3Π(ω) states deriving from the πσ configuration, and from these the 3Π(ω) and 3Π(ω) basis functions were constructed by suitable changes in sign.

The 3Π(ω), 3Π(ω), 3Π(ω), and 3Π(ω) basis functions deriving from the δσ configuration were constructed by replacing m_l=+1 with m_l=−1 in the 3Φ(ω), 3Φ(ω), 1Φ(ω), and 3Φ(ω) basis functions deriving from the δσ configuration, respectively. This then completed the construction of all of the Hund's case (a) basis functions except for the Σ states.

The Ω=1 component of a 3Σ state derives from the α(1)α(2) combination of spins, so the 3Σ⁺(ω) (Ω=1(ω)) and 3Σ⁺(ω) (Ω=1(ω)) states deriving from the δδ configuration may be simply written as the plus and minus linear combinations of the [δ(1)α(1) δ(2)α(2)] and [δ(1)α(1) δ(2)α(2)] Slater determinants, with the assignment of the g/u symmetry determined by inspection. Here δ indicates m_l=−2, while δ indicates m_l=+2. Once these were determined, the Ω=0 components were generated by application of the S⁻₇ lowering operator. Finally, the 3Σ⁻(ω) (Ω=0(ω)) and 3Σ⁻(ω) (Ω=0(ω)) states deriving from the δδ configuration were obtained by reversing the appropriate signs in the 3Σ⁺(ω) (Ω=0(ω)) and 3Σ⁺(ω) (Ω=0(ω)) basis functions, respectively. The corresponding 3Σ⁻(ω), 3Σ⁻(ω), 3Σ⁻(ω), and 3Σ⁻(ω) basis functions deriving from the ππ configuration were then obtained by replacing all m_l=±2 values with m_l=±1. The last of the Σ basis wave functions (deriving from the σσ configuration) were then obtained by replacing the m_l=±1 values with m_l=0 in the 3Σ⁺(ω) and 3Σ⁺(ω) basis functions confirmed that the σσ configuration does not generate these terms, and verified that the procedure described above was correct. The final set of basis wave functions obtained is available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics or from one of the authors (M.D.M.).

APPENDIX B: GENERATION OF WAVE FUNCTIONS

FOR A d₈g₉dσ²+σ* MANIFOLD OF STATES

The basis set was derived by applying the lowering operators, L⁻ and S⁻, to the wave function of the 4Φ₉/2 state, which is unambiguously written as an antisymmetrized product of the hole spin orbitals as

$$|4Φ₉/2⟩ = A₃|δ(1)α(1)σ(2)α(2)σ*(3)α(3)⟩.$$  \hspace{1cm} (B1)

giving S=3/2, Σ=3/2, Λ=3, and Ω=9/2. By sequentially applying S⁻ to this function the 4Φ₇/2, 4Φ₅/2, and 4Φ₃/2 basis functions were generated. Application of L⁻ to the four components of the 4Φ term then generated the corresponding four components of the 4Δ term, and application of L⁻ once again yielded the four components of the 4Π term. Finally, application of L⁻ to the 4Π₇/2 and 4Π₅/2 terms gave the 4Σ⁻ and 4Σ⁻ terms, respectively. For application of the L⁻ operator, the σ* orbital was taken as an s orbital, so it could not be lowered in angular momentum. This method ensured that the basis wave functions correspond to a F term of the d₈ configuration on atom A, and are not contaminated by 1S, 3P, 1D, or 1G couplings of the d₈ electrons.

The S=1/2 terms of the 3Σ₅/2 configuration were slightly more difficult to derive. These were obtained by first writing the wave function of the 2Φ₉/2 term which results from the d₈((3G)d₈σ²σ*¹) configuration, which is uniquely generated as

$$|2Φ₉/2⟩ = A₅|δ(1)α(1)α(2)β(2)σ*(3)α(3)⟩.$$  \hspace{1cm} (B2)

The lowering operator, L⁻, was then applied to generate the 2Φ₇/2 term of the d₈((3G)d₈σ²σ*¹) configuration. The 2Φ₇/2 term of the d₈((F)d₈σ²σ*¹) configuration was then determined as the linear combination of the three Slater...
determinants which give \( M_L = 3 \) and \( M_S = 1/2 \) which is orthogonal to both the \( 2\Phi_{7/2} \) term of the \( \mathcal{d}^3 \mathcal{G} \) configuration and the \( 4\Phi_{7/2} \) term of the \( \mathcal{d}^6 \mathcal{G} \) configuration, as

\[
\begin{align*}
|2\Phi_{7/2}(3F)\rangle &= \hat{A}_3 |\phi_1(1)\psi_2(2)\rangle \beta(2)\alpha^*(3)\alpha(3) | \\
&\quad + C_2 |\phi_1(1)\psi_2(2)\alpha^*(2)\alpha(3) | \beta(3) | \\
&\quad + C_3 |\phi_1(1)\psi_2(2)\alpha(2)\alpha^*(3) \beta(3) |.
\end{align*}
\]

(B3)

Application of \( \hat{S}^- \) to \( |2\Phi_{7/2}(3F)\rangle \) then generated \( |2\Phi_{5/2}(3F)\rangle \), and repetitive application of \( \hat{L}^- \) to these functions generated the remaining \( \Delta, \Pi, \) and \( \Sigma^- \) basis wave functions, which correspond to pure \( 3F \) states of the \( \mathcal{d}^6 \) ion embedded in the molecule. The 21 basis wave functions obtained by this procedure are available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics or from one of the authors (M.D.M.).

21. See AIP document No. PAPS JCP97-4641-3 for 3 pages of tables giving the Hund's case (a) basis functions for a \( \mathcal{d}^6 \mathcal{G} \) system and a \( \mathcal{d}^6 \mathcal{F} \) system. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (60 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
30. I. Shim (personal communication).