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ELECTRONIC STRUCTURE IN SMALL INORGANIC MOLECULES: SOME RESULTS OBTAINED FROM X-RAY PHOTOELECTRON SPECTROSCOPY

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ELECTRONIC STRUCTURE IN SMALL INORGANIC MOLECULES: SOME RESULTS OBTAINED FROM X-RAY PHOTOELECTRON SPECTROSCOPY

Winfield Blount Perry
(Ph.D. thesis)

October, 1974

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ELECTRONIC STRUCTURE IN SMALL INORGANIC MOLECULES:
SOME RESULTS OBTAINED FROM X-RAY PHOTOELECTRON SPECTROSCOPY

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ELECTRONIC STRUCTURE IN SMALL INORGANIC MOLECULES:
SOME RESULTS OBTAINED FROM X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

X-ray photoelectron spectroscopy is used to study aspects of
electronic structure in a number of primarily small, volatile inorganic
compounds. Core and valence electron binding energies and Auger electron
energies have been measured, and these data are interpreted using simple
theoretical models.

Core binding energies were measured for a number of volatile carbon,
silicon, and germanium compounds. The chemical shifts are interpreted
using the electrostatic potential equation together with charge
distributions from extended-Hückel and CNDO/2 molecular orbital calculations
and from an electronegativity equalization procedure. The core binding
energy chemical shifts can be rationalized without the inclusion of
valence d orbitals on silicon or germanium. Core binding energies were
also measured for a series of primarily tetracovalent compounds of
nitrogen and phosphorus. Again the chemical shifts are interpreted
using the electrostatic potential equation together with charge distributions
from extended-Hückel and CNDO/2 molecular orbital calculations. Although
pπ→dπ bonding does not seem to be important in determining the charge distributions in the phosphorous compounds, pπ→pπ bonding may be important in some of these molecules. It is necessary to include the effects of electronic relaxation to quantitatively rationalize the chemical shifts. Atomic charges were calculated for a number of small molecules from core binding energy chemical shifts using the electrostatic potential equation. A modification of that equation is proposed which includes the effects of electronic relaxation on core binding energies for the purpose of calculating more realistic atomic charges.

Valence electron binding energies for some volatile silicon compounds were measured, and are interpreted using the eigenvalues and eigenfunctions from extended-Hückel molecular orbital calculations. A simple model for spectral intensity analysis aids in assigning the spectral bands. Binding energies and spectral intensities can be rationalized without assuming that the silicon valence d orbitals were important in the chemical bonding of these compounds.

The L2M45N45 and L3M45M45 Auger spectra of GeH4 were measured and are interpreted using a semi-empirical model. A method to estimate relaxation energy differences from Auger and core electron chemical shifts is proposed and results using this method for a number of germanium compounds are presented.

A method of calculating lattice potentials for ionic solids in the point charge approximation is presented. The application of these potentials in the interpretation of solid state core binding energy chemical shifts is discussed. A computer program to calculate atomic charges in molecules using an electronegativity equalization procedure is presented.
This program will also correlate the calculated atomic charges with core binding energy chemical shifts using the potential equation.
INTRODUCTION

X-ray photoelectron spectroscopy (ESCA or XPS) is a versatile tool for investigating the electronic structure of atoms, molecules and crystalline and amorphous solids.\(^1\)\(^-\)\(^3\) This thesis is primarily concerned with the electronic structures and, most often, with the charge distributions in relatively small, volatile inorganic molecules. The experimental data and the interpretations of this data found in this thesis may be classified under one of three subject areas: core electron binding energy chemical shifts, valence electron binding energies and Auger electron energies. On a fundamental level, all three phenomena can be treated using much the same physics. However, we shall describe each phenomenon with a separate model, both for the sake of simplicity, and because it is often easier to appreciate the chemical significance of such data when they are presented using simple, straightforward models, rather than in the abstract language of \textit{ab initio} theory.

Both core electron binding energies and valence electron binding energies are measured by making use of the photoelectric effect. An atom or a molecule absorbs a photon, in this case from an X-ray, and ejects an electron, the photoelectron. The kinetic energy of this electron can be measured with some instrument, and in the case of a free atom or a free molecule, the energy conservation equation, neglecting only a small momentum transfer term, is expressed:

\[
E_B = h\nu - E_k
\]

where \(E_B\) is the binding energy, or, equivalently, the ionization potential
of the photoelectron, \( h\nu \) is the energy of the photon and \( E_K \) is the kinetic energy of the photoelectron. In actual experiments, because the energy zero of our spectrometer is irreproducible, a standard is used, and binding energies are given by the following expression:

\[
E_B(x) = E_B(s) + [E_K(s) - E_K(x)]
\]  

(2)

where \( E_B(x) \) is the unknown binding energy, \( E_B(s) \) is the known binding energy of the standard and \( [E_K(s) - E_K(x)] \) is the measured kinetic energy difference between the photoelectrons from the standard and from the sample molecule.

Although specific models for the interpretation of both core and valence electron binding energies are presented in the body of this thesis, all of these models assume that the Born-Oppenheimer approximation remains valid during the photoelectric process, and that only electronic effects contribute appreciably to a binding energy or even to the chemical shifts associated with core electron binding energies. Some justification can be offered for these assumptions.

In the most general terms, a binding energy for a given electronic shell is given by the difference in the total energies of the ground state species and the ion having a hole in the appropriate electronic shell, that is:

\[
E_B = E_{\text{ion}} - E_0
\]  

(3)

For a free molecule, both the ground and ionic states of the molecules can be specified by a product wavefunction of the form:

\[
\Psi_{\text{tot}} = \Psi_{\text{elec}} \cdot \Psi_{\text{vib}} \cdot \Psi_{\text{rot}} \cdot \Psi_{\text{trans}}
\]  

(4)
The energy of such a state is just equal to:

\[ E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}} \]

Thus an electron binding energy may be expressed:

\[ E_B = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} + \Delta E_{\text{trans}} \]

The last two terms, the differences in the rotational and translational energies of the ion and the neutral species, are very small compared to a binding energy and may be neglected. The vibrational energy difference, \( \Delta E_{\text{vib}} \), could have a magnitude of several tenths of an electron volt.\(^4\)

In addition, because photoemission is a vertical, Franck-Condon process,\(^2,4\) if the vibrational potential energy functions of the ion and of the neutral species have different equilibrium nuclear coordinates, several vibrational states of the ion may become populated. This effect is believed to be important in determining spectral line widths.\(^4\) However, binding energies range from about 10–50 eV for a valence shell electron\(^2,3\) to thousands of electron volts for a k shell electron in a heavy atom,\(^1\) and even core electron chemical shifts can exceed 10 eV.\(^2,3\)

Thus, the predominate term in Eq. (6) is \( \Delta E_{\text{elec}} \), the difference in the energies of the electronic states of the ion and the neutral species.

The timescale for the photoelectron process is rather crudely estimated to be about \( 10^{-16} \) seconds.\(^1\) This figure was obtained by noting that ESCA linewidths are around 1 eV and then applying the uncertainty principle. Since much of the linewidth is due to the linewidth of the incident X-ray and to instrumental broadening,\(^4\) the quoted figure is really an upper bound. Thus it is believed that when a high energy
photon source, such as X-rays, is used to ionize molecules, the photoelectric process takes place faster than the time required for nuclear relaxation, and that the nuclear coordinates of the ground state species are also appropriate for the final state ion.

Auger electrons result from a somewhat different process than photoelectrons. The initial state for the Auger process is not a ground state neutral species, but an excited state ion with a hole in a core electronic shell. Thus the initial state for the Auger process is one of the final states of the photoelectric process. In order to lower the energy of the ion, an electron from a lower energy core shell or from a valence shell "falls" into the core hole. The energy released by this process promotes another relatively low energy electron to a continuum state, and it is the kinetic energy of the Auger electron that is measured. Because the final state species is doubly ionized, having two holes in its electronic shells, a greater number of multiplet states are often observed for many Auger spectral bands than for photoelectric spectral bands, and electronic relaxation is more pronounced during an Auger ionization than during a comparable photoionization.
References


I. CORRELATION OF CORE ELECTRON BINDING ENERGIES WITH
CHARGE DISTRIBUTIONS FOR COMPOUNDS OF
CARBON, SILICON, AND GERMANIUM

Abstract
Core electron binding energies for analogous compounds of carbon, silicon, and germanium have been measured by X-ray photoelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Hückel theory, CNDO/2, and an electronegativity equalization method. The data can be rationalized without any consideration of $p\pi \rightarrow d\pi$ bonding in the silicon and germanium compounds.

Introduction
The chemical shift associated with atomic core electron binding energies is an electrostatic effect associated with the coulombic potential at the nucleus of the core-ionized atom or, more exactly, at the hole site itself. These shifts are usually interpreted, using Koopmans' theorem, in terms of ground-state electronic distributions. We have measured the core binding energies for analogous carbon, silicon, and germanium compounds and have correlated the chemical shifts with changes in the calculated charge distributions of the compounds. A principal aim of the work was to determine whether the valence-shell d orbitals of silicon and germanium are important in determining the charge distributions in compounds of these elements. Morgan and Van Wazer have studied the binding energies of carbon, silicon, and germanium in solids. Because of the solid-state problems of work function, charging, and
surface impurities and the difficulty of accounting for the Madelung potential in solids, we have restricted our study to compounds in the gas phase.

**Experimental Section**

**Materials**

The carbon compounds were obtained from commercial sources and were used as received. The $\text{CH}_4$, $\text{C}_2\text{H}_6$, $(\text{CH}_3)_2\text{O}$, $\text{CF}_4$, $\text{CH}_3\text{Cl}$, and $\text{CH}_3\text{Br}$ were obtained from the Matheson Company; research grade $\text{C(CH}_3)_4$ was obtained from the Phillips Petroleum Company, analytical reagent grade $\text{CCl}_4$ was obtained from Mallinckrodt Chemical Works, and $\text{CBr}_4$ was obtained from the Eastman Kodak Company.

Silane was prepared by the reactions of $\text{SiCl}_4$ with $\text{LiAlH}_4$; the infrared spectrum agreed with the literature. Methylsilane was prepared by treating $\text{SiCl}_3\text{CH}_3$ with $\text{LiAlH}_4$ using a procedure similar to that used for $\text{SiH}_4$. The vapor pressure (190 Torr at $-83.6^\circ$) and infrared spectrum agreed with the literature. A sample of Matheson, Coleman and Bell practical grade $\text{Si(CH}_3)_4$ was used and was found to be pure by infrared spectrometry. Disiloxane was prepared by the hydrolysis of $\text{SiH}_3\text{Cl}$ and was purified by vacuum distillation. Its vapor pressure (15 Torr at $-83.6^\circ$) and infrared spectrum agreed with the literature. Silicon tetrafluoride was prepared by pyrolysis of $\text{BaSiF}_6$; the infrared spectrum agreed with the literature. Silyl chloride was prepared by the reaction of $\text{SiH}_4$ and $\text{AgCl}$; its vapor pressure (39 Torr at $-83.6^\circ$) and infrared spectrum agreed with the literature values. Silicon tetrachloride (99.8%, from Matheson, Coleman and Bell) was vacuum distilled and checked for purity by infrared spectrometry.
bromide was prepared by treating SiH$_3$Cl with excess HBr; its vapor pressure (82 Torr at -45.2°) and infrared spectrum agreed with the literature. Silicon tetrabromide was prepared by the reaction of Si with Br$_2$ and was vacuum distilled; the boiling point (150°) agreed with the literature.

Germane was prepared by a standard procedure; its vapor pressure (180 Torr at -111.6°) and infrared spectrum agreed with the literature. Methylgermane was prepared by treating GeH$_3$Cl with LiCH$_3$ and was purified by vacuum distillation; the infrared spectrum agreed with the literature. Tetramethylgermane was kindly provided by Dr. C. Riddle; its infrared spectrum agreed with the literature. Germanium tetrafluoride was prepared by the pyrolysis of BaGeF$_6$; the infrared spectrum agreed with the literature. Germyl chloride was prepared from GeH$_4$ and AgCl; the vapor pressure (68 Torr at -22.8°) and infrared spectrum agreed with the literature. Germanium tetrachloride was prepared by the reaction of GeO$_2$ with HCl; its vapor pressure (23 Torr at 0°) agreed with the literature. Germyl bromide was prepared by treating GeH$_3$Cl with excess HBr; the vapor pressure (28 Torr at -22.8°) and infrared spectrum agreed with the literature. Germanium tetrabromide was prepared by treating Ge with Br$_2$ and was purified by vacuum distillation. The melting point (25°) agreed with the literature.

Hydrogen chloride and HBr were obtained in lecture bottles from the Matheson Co. Chlorine and bromine were obtained from the J. T. Baker Chemical Co.
X-Ray Photoelectron Spectra

Spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer. Magnesium Kα X-rays (1253.6 eV) were used for all spectra except those of germanium compounds, for which aluminum Kα X-rays (1486.6 eV) were used. The spectra were measured with sample pressures of 30–40 μ in the spectrometer irradiation chamber. Argon, at 20–30 μ was simultaneously leaked into the irradiation chamber for a reference. The argon 2p$_{3/2}$ core binding energy (248.45 eV) was used as a standard for all our measurements. Binding energies were determined by a least-squares fitting of both sample and reference experimental data to Lorentzian line shapes. The reproducibility of the data was determined for several compounds to be about ±0.05 eV. The energies correspond to absolute free-molecule ionization potentials inasmuch as they were measured at low pressure in the gas phase and were calibrated against a standard of known energy.

Most of the carbon 1s shifts have been previously reported by other workers. However, to obtain a series strictly comparable with respect to reference and precision, we remeasured these binding energies.

Calculations

Atomic Charges

Charge distributions for use in the potential model were calculated using three different methods: extended Hückel theory (EHT), CNDO/2, and an electronegativity equalization method (CHELEQ) devised by the authors.

The simple extended Hückel theory of Hoffmann was used.
diagonal elements of the Hamiltonian matrix were one-electron orbital
energies from atomic, *ab initio* calculations by Clementi,\(^{32}\) rather than
empirical valence-state ionization potentials. The off-diagonal elements
used the relation

\[ H_{ij} = 0.875(H_{ii} + H_{jj})S_{ij} \]  

(1)

The overlap integrals were calculated from Slater-type orbitals, using
exponents and principal quantum numbers fitted to near Hartree-Fock
atomic wave functions by Cusachs and Corrington.\(^{33}\) The basis set in-
cludes d orbitals on silicon and germanium atoms as parameterized by
Corrington.\(^{34}\) Atomic charges and orbital populations were obtained by
Mulliken analysis.

Our program for the CNDO/2 molecular orbital method was very similar
to that found by Pople and Beveridge.\(^{30}\) We have not altered Pople's
parameters for the first-row elements and for hydrogen. We have followed
Segal and Santry's\(^{35}\) method for parameterization of the second-row
elements but have utilized Hinze and Jaffe's\(^{36,37}\) orbital ionization
energies and electron affinities and Cusachs and Corrington's\(^{33}\) valence
s-orbital wave functions. As discussed previously, these wave functions
came from near Hartree-Fock results and are less arbitrary for a second-
and third-row elements than are exponents obtained using Slater's rules.\(^{38}\)

The CNDO/2 program was expanded to third-row nontransition elements by
this same method. Because CNDO/2 uses the same radial function for all
basis functions on a given atom, d orbitals are poorly described, and
one obtains results which are quite different from those of *ab initio*
calculations.\(^{39}\) Consequently, for all elements above hydrogen we used
only an \( s,p \) basis set. Orbital populations in CNDO/2 are directly obtained from the diagonal elements of the density matrix.

The CHELEQ method for estimating atomic charges is based on the equalization of orbital electronegativities.\(^{31}\) This empirical method is based on the Iczkowski and Margrave definition of electronegativity\(^ {40} \) and, as far as possible, uses Hinze and Jaffe's orbital electronegativities.\(^ {16,17} \) There is no provision for \( d \) orbitals in this method. The method has successfully correlated binding energies for a large number of first-row elements.

The Potential Model

Using Koopmans' theorem, one may easily derive the potential model from the Roothan equations. The binding energy of a \( 1s \) electron, for example, is given by the expression\(^ 3 \)

\[
E^A_{1s} = - \langle x_{1s} | H + G | x_{1s} \rangle 
\]

(2)

where, for simplicity, we have assumed that the core molecular orbital is the \( 1s \) orbital, \( x_{1s} \), of atom A. If we neglect the exchange integrals of atoms not directly bonded to atom A, Eq. (2) may be expanded and arranged as\(^ {2,3} \)

\[
E^A_{1s} = - \sum_{i \in A \neq 1s} \sum_j p_{ij} [(1s1s|ij) - \frac{1}{2}(1s|1s)] - \\
[ \sum_{i \neq A} \sum_j p_{ij} (1s1s|ij) - \sum_{B \neq A} Z_B (1s|r_{1sB}^{-1}|1s) ] - \\
[H_{1s1s} + \frac{1}{2}(1s1s|1s1s)] 
\]

(3)
The empirical point charge potential equation is written

\[ E_B = kQ + V + \ell \]

where \( V \) represents the point charge electrostatic potential due to the ligands. The term \( kQ \) corresponds to the first double summation of Eq. (3); hence \( k \) has the value

\[ k = \sum \left[ F_0(1s,2\ell) - \frac{1}{2} G_1(1s,2\ell) \right] \]

where \( N_\ell \) is the fractional occupancy of the \( \ell \)th valence subshell \( (s,p,d,\ldots) \) and \( F_0 \) and \( G_1 \) are two-electron Slater integrals from atomic Hartree-Fock calculations. The \( V \) in Eq. (4) and the terms in the second set of brackets of Eq. (3) represent an electrostatic potential at \( A \).

The last terms in Eq. (3) and Eq. (4) are constants for a given element.

Schwartz has further identified Eq. (3) with the "external potential" \( \phi_{\text{ext}} \), plus a constant. This may be written as

\[ E_{1s}^A = \phi_{\text{ext}} + \ell = - \sum_{i,j} P_{ij}(1|r_A^{-1}|j) + \sum_{B\neq A} Z_AR_AB^{-1} + \ell \]

Equation 6 is applicable to semiempirical calculations by restricting the first summation to valence electrons and by substituting \( Z_{\text{core}} \) for \( Z \). This modified potential is called \( \phi_{\text{val}} \), the valence potential. For use with CNDO/2 semi-empirical calculations (to retain invariance and to simplify calculations), the diagonal two-centered matrix elements are approximated as \( r^{-1} \) and Eq. (6) becomes

\[ E_B = - \sum_{i \in A} P_{ii}(r_i^{-1}) + \sum_{B \neq A} Q_{BR_AB}^{-1} + \ell \]

The empirical point charge potential equation is written

\[ E_B = kQ + V + \ell \]

where \( V \) represents the point charge electrostatic potential due to the ligands. The term \( kQ \) corresponds to the first double summation of Eq. (3); hence \( k \) has the value

\[ k = \sum \left[ F_0(1s,2\ell) - \frac{1}{2} G_1(1s,2\ell) \right] \]

where \( N_\ell \) is the fractional occupancy of the \( \ell \)th valence subshell \( (s,p,d,\ldots) \) and \( F_0 \) and \( G_1 \) are two-electron Slater integrals from atomic Hartree-Fock calculations. The \( V \) in Eq. (4) and the terms in the second set of brackets of Eq. (3) represent an electrostatic potential at \( A \).

The last terms in Eq. (3) and Eq. (4) are constants for a given element.

Schwartz has further identified Eq. (3) with the "external potential" \( \phi_{\text{ext}} \), plus a constant. This may be written as

\[ E_{1s}^A = \phi_{\text{ext}} + \ell = - \sum_{i,j} P_{ij}(1|r_A^{-1}|j) + \sum_{B\neq A} Z_AR_AB^{-1} + \ell \]

Equation 6 is applicable to semiempirical calculations by restricting the first summation to valence electrons and by substituting \( Z_{\text{core}} \) for \( Z \). This modified potential is called \( \phi_{\text{val}} \), the valence potential. For use with CNDO/2 semi-empirical calculations (to retain invariance and to simplify calculations), the diagonal two-centered matrix elements are approximated as \( r^{-1} \) and Eq. (6) becomes

\[ E_B = - \sum_{i \in A} P_{ii}(r_i^{-1}) + \sum_{B \neq A} Q_{BR_AB}^{-1} + \ell \]
This very simple form\textsuperscript{42} may be used with extended Hückel theory by using Mulliken gross orbital populations in place of the CNDO/2 density matrix terms $P_{ii}$. Equation 7 has the form of the pont charge potential model, where $k$ may be written for a Slater-type orbital as

$$k = \sum N_i \xi_i n^{-1}$$

where $\xi_i$ is the valence orbital exponent and $n$ is the valence orbital quantum number.

Another method of estimating the free-atom value of $k$ uses the principle of equivalent cores.\textsuperscript{43} The chemical shift between the gaseous atom $A$ and the gaseous ion $A^+$ is the energy of the reaction

$$A^{4+} + A^+ = A + A^{2+} \quad \Delta E = \Delta E_B$$

where the asterisks refer to core holes. If we let $B$ stand for the element following $A$ in the periodic table, we may write another equation having practically the same energy as that of Eq. (9), i.e.

$$B^+ + A^+ = A + B^{2+} \quad \Delta E = \Delta E_B$$

For a free atom

$$k = \frac{\Delta E_B}{\Delta q} = \frac{\Delta E_B}{\Delta q}$$

From Eqs. (10) and (11) one obtains

$$k_A = I_2(B) - I_1(A)$$

where $I_2(B)$ is the second ionization potential of atom $B$ and $I_1(A)$ is the first ionization potential of atom $A$.

Relaxation effects during photoionization may be accounted for by use of the principle of equivalent cores and an approximation due to
Hedin and Johansson.\textsuperscript{5} The corrected binding energy is written

$$E_{B}^{\text{rel}} = \frac{1}{2} (\phi_{\text{val}}(Z^0) + \phi_{\text{val}}[(Z + 1)^+]) + \ell$$ \hspace{1cm} (13)

where $\phi_{\text{val}}(Z^0)$ is the potential of the ground-state neutral molecule and $\phi_{\text{val}}[(Z + 1)^+]$ is the potential of the isoelectronic cation in which the ionized core has been replaced by the core of the next higher element in the periodic table.

\textbf{Results and Discussion}

Core binding energies for the central carbon, silicon, and germanium atoms are given in Table I. The experimental values were correlated with values calculated by several methods. The CNDO/2 and EHT methods were applied to the valence potential model. The calculated binding energies were expressed as

$$E_{B}^{\text{calcd}} = c\phi_{\text{val}} + \ell$$ \hspace{1cm} (14)

where $c$ and $\ell$ are parameters determined by a least-squares fitting of experimental binding energies to the calculated valence potentials. Although $c$ should be unity, we have allowed it to be an adjustable scaling parameter to compensate somewhat for the approximate nature of our calculations and for inadequacies of parameterization. Both ground-state and relaxed-state correlations were made for C 1s, Si 2p, and Ge 3p binding energies. Table II lists the potentials, parameters, standard deviations, and correlation coefficients from the EHT correlations, and Table III lists similar data from the CNDO/2 correlations. Figures 1, 2 and 3 are plots of CNDO/2 ground-state correlations for carbon, silicon, and germanium binding energies, respectively.
### Table I

**Experimental Core Binding Energies for Carbon, Silicon, and Germanium**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$M = C$ (1s)</th>
<th>$M = Si$ (2p)</th>
<th>$M = Ge$ (3p$_{3/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MH}_4$</td>
<td>290.73</td>
<td>107.28</td>
<td>129.33</td>
</tr>
<tr>
<td>$\text{MH}_3\text{CH}_3$</td>
<td>290.57</td>
<td>106.82</td>
<td>128.92</td>
</tr>
<tr>
<td>$\text{M(CH}_3)_4$</td>
<td>290.31</td>
<td>105.94</td>
<td>128.04</td>
</tr>
<tr>
<td>$(\text{MH}<em>3)</em>{2}O$</td>
<td>292.13</td>
<td>107.81</td>
<td>--</td>
</tr>
<tr>
<td>$\text{MF}_4$</td>
<td>301.68</td>
<td>111.79</td>
<td>133.75</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Cl}$</td>
<td>292.31</td>
<td>108.11</td>
<td>130.23</td>
</tr>
<tr>
<td>$\text{MCl}_4$</td>
<td>296.22</td>
<td>110.39</td>
<td>132.12</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Br}$</td>
<td>291.95</td>
<td>108.08</td>
<td>123.04</td>
</tr>
<tr>
<td>$\text{MBr}_4$</td>
<td>294.64</td>
<td>109.73</td>
<td>131.35</td>
</tr>
</tbody>
</table>

*The uncertainty in these energies is approximately ±0.05 eV.*
Table II

EHT Valence Potentials for Carbon, Silicon, and Germanium (eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{val}(C)$</th>
<th>$\phi_{val}(S)</th>
<th>\phi_{val}(Si)$</th>
<th>$\phi_{val}(Ge)</th>
<th>\phi_{rel}(Ge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH$_4$</td>
<td>-95.19</td>
<td>-112.90</td>
<td>-48.02</td>
<td>-53.63</td>
<td>-46.56</td>
</tr>
<tr>
<td>MH$_3$CH$_3$</td>
<td>-94.39</td>
<td>-112.96</td>
<td>-46.86</td>
<td>-52.79</td>
<td>-45.36</td>
</tr>
<tr>
<td>M(CH$_3$)$_4$</td>
<td>-92.41</td>
<td>-113.62</td>
<td>-42.89</td>
<td>-49.85</td>
<td>-41.31</td>
</tr>
<tr>
<td>(MH$_3$)$_2$O</td>
<td>-88.27</td>
<td>-104.95</td>
<td>-48.41</td>
<td>-53.44</td>
<td></td>
</tr>
<tr>
<td>MF$_4$</td>
<td>-57.83</td>
<td>-68.22</td>
<td>-39.58</td>
<td>-41.80</td>
<td>-37.07</td>
</tr>
<tr>
<td>MH$_3$Cl</td>
<td>-88.84</td>
<td>-107.36</td>
<td>-45.66</td>
<td>-51.26</td>
<td>-44.27</td>
</tr>
<tr>
<td>MCl$_4$</td>
<td>-72.81</td>
<td>-92.63</td>
<td>-38.22</td>
<td>-43.86</td>
<td>-37.02</td>
</tr>
<tr>
<td>MH$_3$Br</td>
<td>-91.16</td>
<td>-110.77</td>
<td>-46.12</td>
<td>-52.12</td>
<td>-44.76</td>
</tr>
<tr>
<td>MBr$_4$</td>
<td>-80.09</td>
<td>-103.47</td>
<td>-39.10</td>
<td>-45.67</td>
<td>-37.92</td>
</tr>
<tr>
<td>c</td>
<td>0.295</td>
<td>0.247</td>
<td>0.333</td>
<td>0.356</td>
<td>0.347</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>318.31</td>
<td>318.83</td>
<td>123.07</td>
<td>126.04</td>
<td>144.98</td>
</tr>
<tr>
<td>Std dev</td>
<td>0.46</td>
<td>0.64</td>
<td>1.28</td>
<td>0.95</td>
<td>1.24</td>
</tr>
<tr>
<td>Correl coeff</td>
<td>0.992</td>
<td>0.985</td>
<td>0.723</td>
<td>0.858</td>
<td>0.774</td>
</tr>
</tbody>
</table>
Binding energies were also calculated from Eq. (4) and CHELEQ atomic charges, using values of $k$ and $l$ obtained by least-squares fitting of $Q$ and $V$ to the experimental data. Only ground-state charges were used with this method. Table IV lists the charges, potentials, parameters, standard deviations, and correlation coefficients from the CHELEQ correlations. Figures 4 through 6 show plots of $(\Delta E_B - V)$ vs $Q$ for the carbon, silicon, and germanium data, respectively. The chemical shifts, $\Delta E_B$, shown in these figures are referred to the hydrides $MH_4$.

All three methods for calculating ground-state charge distributions give good correlations with carbon binding energies, as expected from previous work. The chemical shifts between corresponding pairs of silicon and germanium compounds are almost identical. This result is not surprising in view of the similar chemistries and structures of silicon and germanium compounds. The silicon and germanium shifts are qualitatively similar to the carbon shifts, although the former are smaller than the latter.

**EHT Correlations**

The EHT parameterizations for silicon and germanium are nearly identical. The EHT correlation of $E_B$ with $\Phi_{val}$ is not as satisfactory for the silicon and germanium compounds as it is for the carbon compounds. The poorer correlation is partly caused by excessive calculated polarization, which is partially corrected by the scaling parameter $c$ of Eq. (14). In all three correlations, this parameter took a value near 0.3 and served to "depolarize" the charges. For carbon this worked quite well, but for silicon and germanium, polarization was more extreme—especially for the tetrahalides—and the simple linear correction given by $c$ was
Table III

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{\text{val}}(C)$</th>
<th>$\phi_{\text{rel}}(C)$</th>
<th>$\phi_{\text{val}}(\text{Si})$</th>
<th>$\phi_{\text{rel}}(\text{Si})$</th>
<th>$\phi_{\text{val}}(\text{Ge})$</th>
<th>$\phi_{\text{rel}}(\text{Ge})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MH}_4$</td>
<td>-88.86</td>
<td>-104.76</td>
<td>-57.44</td>
<td>-64.84</td>
<td>-58.31</td>
<td>-63.41</td>
</tr>
<tr>
<td>$\text{MH}_3\text{CH}_3$</td>
<td>-88.49</td>
<td>-105.07</td>
<td>-57.30</td>
<td>-65.14</td>
<td>-58.20</td>
<td>-63.73</td>
</tr>
<tr>
<td>$\text{M(CH}_3\text{)_4}$</td>
<td>-87.56</td>
<td>-105.75</td>
<td>-56.88</td>
<td>-65.78</td>
<td>-57.92</td>
<td>-64.52</td>
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<td>$(\text{MH}_3\text{)}_2\text{O}$</td>
<td>-87.25</td>
<td>-104.04</td>
<td>-56.54</td>
<td>-64.89</td>
<td>-58.82</td>
<td>-66.85</td>
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<tr>
<td>$\text{MF}_4$</td>
<td>-79.37</td>
<td>-94.90</td>
<td>-50.90</td>
<td>-57.38</td>
<td>-51.66</td>
<td>-56.43</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Cl}$</td>
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<td>-104.03</td>
<td>-56.08</td>
<td>-63.84</td>
<td>-56.95</td>
<td>-62.46</td>
</tr>
<tr>
<td>$\text{MCl}_4$</td>
<td>-82.83</td>
<td>-52.84</td>
<td>-61.30</td>
<td>-53.82</td>
<td>-60.06</td>
<td>-59.72</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Br}$</td>
<td>-87.22</td>
<td>-105.04</td>
<td>-56.42</td>
<td>-64.43</td>
<td>-57.32</td>
<td>-63.02</td>
</tr>
<tr>
<td>$\text{MBr}_4$</td>
<td>-84.64</td>
<td>-54.03</td>
<td>-63.01</td>
<td>-55.19</td>
<td>-62.04</td>
<td>-58.72</td>
</tr>
<tr>
<td>c</td>
<td>1.171</td>
<td>1.048</td>
<td>0.778</td>
<td>0.665</td>
<td>0.742</td>
<td>0.684</td>
</tr>
<tr>
<td>#</td>
<td>393.99</td>
<td>401.11</td>
<td>151.55</td>
<td>150.61</td>
<td>172.14</td>
<td>172.85</td>
</tr>
<tr>
<td>Std dev</td>
<td>0.63</td>
<td>0.49</td>
<td>0.54</td>
<td>0.62</td>
<td>0.51</td>
<td>0.53</td>
</tr>
<tr>
<td>Correl coeff</td>
<td>0.985</td>
<td>0.993</td>
<td>0.957</td>
<td>0.942</td>
<td>0.962</td>
<td>0.959</td>
</tr>
</tbody>
</table>
inadequate. Also, electronic relaxation during photoemission may affect the chemical shifts of second- and third-row elements more than those of carbon, leading to poorer results with ground-state charges.

**CNDO/2 Correlations**

Excessive polarization is not obtained with a self-consistent field theory like CNDO/2. Thus the fitting parameter $c$ for the CNDO/2 carbon compound correlation is close to unity. However, for the silicon and germanium compounds, the plots (Figs. 2 and 3) exhibit more scatter than that for the carbon compounds (Fig. 1), and the parameter $c$ is approximately 0.7. These results may be due to errors in parameterization for silicon and germanium. The orbital ionization potentials and, especially, electron affinities are uncertain for these elements. However, the CNDO/2 correlations are much better than those given by EHT, indicating that the relative CNDO/2 charge distributions are reasonable.

**CHELEQ Correlations**

The CHELEQ correlations for the silicon and germanium compounds, shown in Figs. 5 and 6, are similar to those obtained with CNDO, perhaps because both methods are parameterized with essentially the same Hinze and Jaffe data. The CHELEQ correlations are based on the point charge potential model, Eq. (4), and it is of interest to compare the least-squares determined values of $k$ with various theoretical estimates of this parameter. Table V lists the empirical $k$ values and theoretical $k$ values obtained from Eqs. 5, 8 and 12. The ratios $k_{Si}/k_C$, $k_{Ge}/k_C$, and $k_{Ge}/k_{Si}$ are also tabulated. Ground-state ionization potentials, corresponding to $s^2p^2$ structures, were used with the equivalent cores method of
Table IV
CHELEQ Correlation Data for Carbon, Silicon, and Germanium

<table>
<thead>
<tr>
<th>Compound</th>
<th>$Q_C$</th>
<th>$V_C$, eV</th>
<th>$Q_{Si}$</th>
<th>$V_{Si}$, eV</th>
<th>$Q_{Ge}$</th>
<th>$V_{Ge}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MH}_4$</td>
<td>-0.060</td>
<td>0.79</td>
<td>-0.029</td>
<td>0.29</td>
<td>-0.091</td>
<td>0.86</td>
</tr>
<tr>
<td>$\text{MH}_3\text{CH}_3$</td>
<td>-0.047</td>
<td>0.52</td>
<td>-0.013</td>
<td>0.08</td>
<td>-0.076</td>
<td>0.64</td>
</tr>
<tr>
<td>$\text{M(CH}_3)_4$</td>
<td>-0.011</td>
<td>-0.33</td>
<td>0.035</td>
<td>-0.36</td>
<td>-0.030</td>
<td>-0.04</td>
</tr>
<tr>
<td>$(\text{MH}_3)_2\text{O}$</td>
<td>0.049</td>
<td>-0.76</td>
<td>0.099</td>
<td>-1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{MF}_4$</td>
<td>0.498</td>
<td>-5.42</td>
<td>0.633</td>
<td>-5.92</td>
<td>0.602</td>
<td>-5.19</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Cl}$</td>
<td>0.020</td>
<td>0.15</td>
<td>0.071</td>
<td>-0.40</td>
<td>0.012</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{MCl}_4$</td>
<td>0.256</td>
<td>-2.08</td>
<td>0.368</td>
<td>-2.63</td>
<td>0.316</td>
<td>-2.17</td>
</tr>
<tr>
<td>$\text{MH}_3\text{Br}$</td>
<td>0.007</td>
<td>0.28</td>
<td>0.057</td>
<td>-0.26</td>
<td>-0.003</td>
<td>0.28</td>
</tr>
<tr>
<td>$\text{MBr}_4$</td>
<td>0.202</td>
<td>-1.50</td>
<td>0.309</td>
<td>-2.03</td>
<td>0.250</td>
<td>-1.57</td>
</tr>
<tr>
<td>$k$</td>
<td>30.07</td>
<td>16.59</td>
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<td>15.42</td>
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<td>$\ell$</td>
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<td>107.02</td>
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<td></td>
<td></td>
<td>129.46</td>
</tr>
<tr>
<td>Std dev</td>
<td>0.62</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>Correl coeff</td>
<td>0.994</td>
<td>0.989</td>
<td></td>
<td></td>
<td></td>
<td>0.992</td>
</tr>
</tbody>
</table>
Table V

Theoretical and Empirical Values of the Potential Model Parameter k (eV/e)

<table>
<thead>
<tr>
<th></th>
<th>CHELEQ empirical</th>
<th>Equation 13</th>
<th>Equation 5</th>
<th>Equation 8 cation</th>
<th>Equation 8 neutral</th>
<th>Equation 8 anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_C</td>
<td>30.07</td>
<td>18.34</td>
<td>19.54</td>
<td>23.83</td>
<td>21.80</td>
<td>20.47</td>
</tr>
<tr>
<td>k_Si</td>
<td>16.59</td>
<td>11.58</td>
<td>11.78</td>
<td>13.84</td>
<td>12.84</td>
<td>12.17</td>
</tr>
<tr>
<td>k_Ge</td>
<td>15.42</td>
<td>10.73</td>
<td>11.37</td>
<td>13.09</td>
<td>12.31</td>
<td>11.71</td>
</tr>
<tr>
<td>k_Si/k_C</td>
<td>0.55</td>
<td>0.63</td>
<td>0.60</td>
<td>0.58</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>k_Ge/k_C</td>
<td>0.51</td>
<td>0.59</td>
<td>0.58</td>
<td>0.55</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>k_Ge/k_Si</td>
<td>0.93</td>
<td>0.93</td>
<td>0.97</td>
<td>0.95</td>
<td>0.96</td>
<td>0.96</td>
</tr>
</tbody>
</table>
estimating $k$ (Eq. 12). Slater integrals calculated by Mann for Hartree-Fock calculations were used to obtain $k$ values from Eq. (5), and single STO atomic wave functions tabulated by Cusachs were used to obtain $k$ values from Eq. (8). Because cation and anion STO wave functions were also available, we included values of $k$ for these species to illustrate the charge dependency of $k$. The estimated $k$ values calculated from Slater integrals and those calculated from nuclear attraction integrals correspond to sp$^3$ atoms. All of the ground-state estimates of $k$ are in approximate agreement. The empirical CHELEQ values are about 50% higher than the theoretical estimates, but the ratios of empirical values are close to the theoretical ratios. The discrepancies in absolute values are probably due to the arbitrary nature of assigning absolute charges to atoms in molecules by CHELEQ or any method. 31

Relaxation Effects

Electronic relaxation is complete in the time required for the photoelectric process. Relaxation during photoemission occurs because the remaining electrons are attracted to the hole left by the photoelectron, with the result that the photoelectron acquires a higher kinetic energy than expected from a frozen-orbital Koopmans' theorem description of photoemission. The success of ground-state wave functions and charge distributions in correlating ESCA chemical shifts is due not to this relaxation energy being small but rather to its having about the same magnitude for a variety of compounds. However, when relaxation is neglected for certain molecules (CO is an example), predicted shifts are much different from the experimental values. Using Eq. (13), we corrected the EHT and CNDO/2 potentials for relaxation and thereby
eliminated a recurrent anomaly in the uncorrected correlations. In all three series the experimental binding energies increase in the order $M(CH_3)_4 < MH_3CH_3 < MH_4$. The effect is quite pronounced for $M = Si$, Ge. However, all the ground-state methods wrongly predict $MH_4 < MH_3CH_3 < (CH_3)_4$. For $M = C$, both EHT and CNDO relaxation-corrected calculations give the proper order. For $M = Si$, Ge, the EHT relaxation-corrected calculations only partially correct the error. The CNDO/2 relaxation-corrected potentials, however, give the experimental order for both silicon and germanium. These qualitative results strongly suggest that the spurious order predicted by the ground-state correlations was caused by the neglect of relaxation. The success of the relaxation correction in quantitatively improving the correlations, as measured by the standard deviations and correlation coefficients, largely depends upon the adequacy of the central atom parameterization for both elements and upon the ability of the semi-empirical method to describe correctly cationic molecules. Our CNDO carbon $^{47}$ and EHT silicon and germanium correlations were improved by including the relaxation correction, but the EHT carbon and the CNDO silicon and germanium correlations were made slightly worse when corrected for relaxation. In spite of these difficulties we believe that Eq. (13) will correct major discrepancies caused by neglect of electron relaxation.

**d-Orbital Bonding**

There is considerable speculation as to the importance of the valence-shell d orbitals in the chemistry of silicon and germanium. One aim of our study was to determine, if possible, the importance of d-orbital participation by a comparison of the silicon and germanium shifts with the corresponding carbon shifts. The participation of the valence-shell d orbitals of silicon or germanium in $\pi + d\pi$ bonding corresponds to a
transfer of negative charge from the ligand atoms to the central atom: 
\( R_3Si^- = X^+ \). If such \( \pi \) bonding is significant, the core binding energy of the silicon or germanium atom would be expected to be lower than in the absence of such bonding. Silicon and germanium d orbitals were included in the EHT basis set, but the EHT method is too crude to yield a meaningful solution to the problem. Neither the CHELEQ method nor our version of CNDO/2 had any provision for d orbitals. However, certain systematic deviations in the CHELEQ and CNDO/2 plots (Figs. 2, 3, 5 and 6) may be interpreted as an indication that d orbitals are important in the bonding.

Let us first consider the CHELEQ plots, Figs. 5 and 6. The solid lines in these figures were determined by least-squares fitting of the data. If d orbitals are not important in the bonding of these compounds, the slopes of these lines, i.e., the \( k_{Si} \) and \( k_{Ge} \) values, should be equal to the slope of the corresponding plot for carbon compounds, \( k_C \), times the theoretical ratios \( k_{Si}/k_C \) and \( k_{Ge}/k_C \), respectively. We have calculated these theoretical values of \( k_{Si} \) and \( k_{Ge} \) using the average \( k_{Si}/k_C \) and \( k_{Ge}/k_C \) values from Table V. The dashed lines in Figs. 5 and 6 have slopes equal to these calculated \( k \) values. These lines were drawn through the points for the hydrides \( SiH_4 \) and \( GeH_4 \) because \( p\pi + d\pi \) bonding in these compounds is assumed to be negligible. Negative deviations of \( (\Delta E_B - V) \) from the dashed lines may be attributed to negative charge on silicon or germanium due to \( p\pi + d\pi \) bonding which was neglected in the charge calculations. The CNDO/2 plots for silicon and germanium, Figs. 2 and 3, have been similarly treated. In these plots, the dashed lines passing through the hydrides have unit slope, the theoretically
correct value of the fitting constant c. Again all the remaining points lie below these lines.

Although the above interpretation suggests appreciable d orbital bonding, other considerations suggest the opposite conclusion. The solid straight-line correlations which neglect d orbitals are fairly good. Small errors in the parameterization of silicon and germanium in both the CNDO/2 and CHELEQ methods may cause the low empirical values of k and c. Perhaps relaxation effects can account for at least part of the deviations from the dashed lines, especially in the cases of M(CH₃)₄, MBr₄, and MCl₄. Inasmuch as the silicon and germanium correlations (without consideration of d orbitals) are almost as good as the carbon correlations, it seems unlikely that any treatment including d-orbital bonding could significantly improve the silicon and germanium correlations relative to the carbon correlation. All in all, the data offer little support for the participation of d orbitals in the bonding of silicon and germanium compounds.

Chlorine and Bromine Chemical Shifts

Core binding energies for the halogen, oxygen, and methyl carbon atoms in the compounds which we have discussed and also for molecular chlorine, bromine, hydrogen chloride, and hydrogen bromide were measured and are given in Table VI. No correlations were made for the oxygen or fluorine binding energies because there were insufficient data for these elements. The EHT, CNDO/2, and CHELEQ correlation data for the chlorine binding energies are listed in Table VII. The data from the bromine correlations, listed in Table VIII, closely parallel the chlorine. All of these correlations have considerable scatter, as indicated by the
Table VI
Experimental Core Binding Energies for Carbon, Oxygen, Fluorine, Chlorine, and Bromine

<table>
<thead>
<tr>
<th>Compound</th>
<th>Binding energy, a eV</th>
<th>X = CH₃</th>
<th>X = O</th>
<th>X = F</th>
<th>X = Cl</th>
<th>X = Br</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(1s)</td>
<td>(1s)</td>
<td>(1s)</td>
<td>(2p₃/₂)</td>
<td>(3d₅/₂)</td>
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<tr>
<td>CH₃X</td>
<td></td>
<td>290.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>(CH₃)₂X</td>
<td></td>
<td></td>
<td>538.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cₓ₄</td>
<td></td>
<td>290.31b</td>
<td>695.36</td>
<td></td>
<td>206.84</td>
<td>76.57</td>
</tr>
<tr>
<td>SiH₃ₓ</td>
<td></td>
<td>290.31</td>
<td></td>
<td></td>
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<td>(SiH₃)₂ₓ</td>
<td></td>
<td></td>
<td>538.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siₓ₄</td>
<td></td>
<td>289.61</td>
<td>694.56</td>
<td></td>
<td>206.77</td>
<td>76.47</td>
</tr>
<tr>
<td>GeHₓ₃</td>
<td></td>
<td>290.19</td>
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<td></td>
<td>205.50</td>
<td>75.65</td>
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<tr>
<td>Geₓ₄</td>
<td></td>
<td>289.50</td>
<td>694.11</td>
<td></td>
<td>206.42</td>
<td>76.24</td>
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<tr>
<td>X₂</td>
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<td></td>
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<td></td>
<td>207.64</td>
<td>77.10</td>
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<tr>
<td>HX</td>
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<td></td>
<td></td>
<td></td>
<td>207.22</td>
<td>77.06</td>
</tr>
</tbody>
</table>

aThe uncertainty in these energies is approximately ±0.05 eV.

bOnly one carbon peak was observed for C(CH₃)₄. The line width of 1.2 eV was slightly greater than the normal carbon width of approximately 1.1 eV.
### Table VII

**EHT, CNDO/2, and CHELEQ Correlation Data for Chlorine**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{\text{val}}^{\text{EHT}}$</th>
<th>$\phi_{\text{val}}^{\text{CNDO/2}}$</th>
<th>$q^{\text{CHELEQ}}$</th>
<th>$\nu^{\text{CHELEQ}}$</th>
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<td>-142.19</td>
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<td>0.00</td>
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<td>ClH</td>
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<td>-143.69</td>
<td>-0.090</td>
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<td>-144.33</td>
<td>-0.081</td>
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<tr>
<td>Cl₄C</td>
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<td>-142.45</td>
<td>-0.064</td>
<td>1.13</td>
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<tr>
<td>ClSiH₃₃</td>
<td>-136.43</td>
<td>-144.36</td>
<td>-0.109</td>
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<tr>
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<td>-142.94</td>
<td>-0.092</td>
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<tr>
<td>ClGeH₃₃</td>
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<td>-144.29</td>
<td>-0.096</td>
<td>0.48</td>
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<tr>
<td>C</td>
<td></td>
<td>0.591</td>
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<tr>
<td>k</td>
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<td></td>
<td>21.99</td>
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<td>$\ell$</td>
<td>260.83</td>
<td>291.26</td>
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<td>207.44</td>
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<tr>
<td>Std. Dev.</td>
<td>0.39</td>
<td>0.45</td>
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<td>0.40</td>
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**Correl. Coeff.** | 0.823 | 0.759 | 0.880
Table VIII

EHT, CNDO/2, and CHELEQ Correlation Data for Bromine

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{\text{EHT}}^{\text{val}}$</th>
<th>$\phi_{\text{CNDO/2}}^{\text{val}}$</th>
<th>$Q_{\text{CHELEQ}}$</th>
<th>$V_{\text{CHELEQ}}$</th>
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<td>Br$_2$</td>
<td>-116.48</td>
<td>-127.59</td>
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<tr>
<td>BrH</td>
<td>-117.47</td>
<td>-128.50</td>
<td>-0.076</td>
<td>0.78</td>
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<tr>
<td>BrCH$_3$</td>
<td>-116.93</td>
<td>-129.03</td>
<td>-0.066</td>
<td>0.39</td>
</tr>
<tr>
<td>Br$_4$C</td>
<td>-116.41</td>
<td>-127.73</td>
<td>-0.050</td>
<td>0.81</td>
</tr>
<tr>
<td>BrSiH$_3$</td>
<td>-117.98</td>
<td>-128.92</td>
<td>-0.093</td>
<td>0.54</td>
</tr>
<tr>
<td>Br$_4$Si</td>
<td>-117.32</td>
<td>-127.99</td>
<td>-0.077</td>
<td>1.12</td>
</tr>
<tr>
<td>BrGeH$_3$</td>
<td>-118.44</td>
<td>-128.78</td>
<td>-0.078</td>
<td>0.35</td>
</tr>
<tr>
<td>Br$_4$Ge</td>
<td>-117.81</td>
<td>-127.89</td>
<td>-0.063</td>
<td>0.85</td>
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<td>C</td>
<td>0.438</td>
<td>0.508</td>
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<tr>
<td>k</td>
<td>--</td>
<td>--</td>
<td>16.54</td>
<td></td>
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<tr>
<td>$\ell$</td>
<td>128.10</td>
<td>141.90</td>
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<tr>
<td>Std. Dev.</td>
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<td>0.38</td>
<td>0.36</td>
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<tr>
<td>Correl. coeff.</td>
<td>0.656</td>
<td>0.603</td>
<td>0.792</td>
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</table>
correlation coefficients. The low standard deviations are a consequence of the small range of binding energies involved. Some of the experimental shifts (which may be obtained from the data in Table VI) deserve comment. The chemical shift $E_B(HX) - E_B(X_2)$ is much smaller for $X = Cl, Br$ than was observed by other workers for $X = F$. The halogen binding energies for corresponding silicon and carbon compounds are quite close, whereas those for the corresponding germanium compounds are shifted to lower energy. One might have expected the halogens on corresponding silicon and germanium compounds to have nearly the same energies. More satisfactory correlation methods, probably including relaxation effects, seem to be necessary to understand these halogen chemical shifts.
References


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(45) C. E. Moore, NSRDS-NBS34 (Sept., 1970).


(47) The relaxed potentials for carbon are incomplete because calculations for NCl$_4^+$ and NBr$_4^+$ did not converge even after many iterations. The corresponding standard deviation for the ground state potentials of the carbon series minus CCl$_4$ and CBr$_4$ was 0.61 eV.

(48) P. Finn, W. L. Jolly, and T. D. Thomas, unpublished data.
Figure Captions

Fig. 1. Plot of carbon 1s binding energy vs $\Phi_{\text{val}}$ from CNDO/2 method.

Fig. 2. Plot of silicon 2p binding energy vs $\Phi_{\text{val}}$ from CNDO/2 method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

Fig. 3. Plot of germanium 3p<sub>3/2</sub> binding energy vs $\Phi_{\text{val}}$ from CNDO/2 method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

Fig. 4. Plot of $E_B - V$ vs Q for relative carbon 1s binding energies. Charges calculated by CHELEQ method.

Fig. 5. Plot of $E_B - V$ vs Q for relative silicon 2p binding energies. Charges calculated by CHELEQ method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

Fig. 6. Plot of $E_B - V$ vs Q for relative germanium 3p<sub>3/2</sub> binding energies. Charges calculated by CHELEQ method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)
Fig. 1

E_B (eV) vs. \( \Phi_{val} \) (eV)

- \( \text{CH}_4 \)
- \( \text{CH}_3 \text{Br} \)
- \( \text{CH}_3 \text{Cl} \)
- \( \text{C}_2\text{H}_5 \)
- \( \text{C} (\text{CH}_3)_4 \)
- \( \text{CBr}_4 \)
- \( \text{CCl}_4 \)
- \( \text{CF}_4 \)

\( (\text{CH}_3)_2\text{O} \)
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
II. AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF CHARGE DISTRIBUTIONS IN TETRACOVALENT COMPOUNDS OF NITROGEN AND PHOSPHORUS

Abstract

Core electron binding energies for ten phosphorus and four nitrogen compounds have been measured by X-ray photoelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Huckel theory and CNDO/2 molecular orbital calculations. The data indicate that formally charged resonance structures of the type

$$\text{R} - \Theta \text{X}$$

contribute significantly to the charge distributions in the tetracovalent compounds. The data for the phosphorus compounds can be quantitatively rationalized without the inclusion of any $p\pi + d\pi$ bonding between the central atom and the X ligand, but the effects of electronic relaxation upon the core binding energy chemical shifts must be included.

Introduction

The possible types of bonding found in tetracovalent compounds of phosphorus and nitrogen have stirred much interest and created some controversy.\(^1\)-\(^4\) If the bonding in these compounds is described using valence bond concepts, the most straightforward resonance structure, shown below, implies a considerable charge separation about one bond.
However, because some of these compounds have short M-X bond lengths and high M-X stretching frequencies, multiple bond character has been postulated for the M-X bond. Such multiple bonding could be explained by the following no-bond resonance structure.

When the central atom is phosphorus, however, it is possible that the phosphorus 3d orbitals participate in the bonding. In this case, the central phosphorus would be hybridized $sp^3d$, and a resonance structure having no formal charges, such as the following, would be appropriate.

This last bonding description, which involves $p\pi + d\pi$ bonding between the central phosphorus atom and the peripheral X ligand, has been offered as an explanation for the stability of the tetracovalent phosphorus compounds relative to those of nitrogen.
To help resolve this speculation, we have measured the core binding energy chemical shifts by means of X-ray photoelectron spectroscopy (ESCA)\(^5\) of the following tetracovalent compounds \(\text{N(CH}_3\text{)}_3\text{BH}_3\), \(\text{N(CH}_3\text{)}_3\text{O}\), \(\text{P(CH}_3\text{)}_3\text{BH}_3\), \(\text{P(CH}_3\text{)}_3\text{CH}_2\), \(\text{P(CH}_3\text{)}_3\text{NH}\), \(\text{P(CH}_3\text{)}_3\text{O}\), \(\text{P(CH}_3\text{)}_3\text{S}\), \(\text{POCl}_3\), and \(\text{PSCl}_3\). We have also measured binding energies for the trivalent "precursors" \(\text{N(CH}_3\text{)}_3\), \(\text{P(CH}_3\text{)}_3\), and \(\text{PCl}_3\) and for the hydrides \(\text{NH}_3\) and \(\text{PH}_3\). These binding energies were measured for gas phase samples and represent true molecular ionization potentials, free from solid state effects such as sample charging, contact potentials, and lattice potentials. We have interpreted the ESCA chemical shifts from the compounds qualitatively using simple electronegativity concepts, and quantitatively using results from extended Hückel theory\(^6\) (EHT) and CNDO/2\(^7\) molecular orbital calculations.

**Experimental Section**

Anhydrous \(\text{NH}_3\) and \(\text{N(CH}_3\text{)}_3\) were obtained from the Matheson Company and were used as received. \(\text{PCl}_3\) was obtained from the Mallinckrodt Chemical Works; \(\text{POCl}_3\) was obtained from the Matheson, Coleman, and Bell Company; \(\text{PSCl}_3\) was obtained from the Research Organic/Inorganic Chemical Corporation. All three were distilled under dry nitrogen, and their boiling points (76°, 106°, and 123°, respectively) agree with literature values.\(^8\) Trimethylamine-N-oxide dihydrate was obtained from the Eastman Kodak Company and dehydrated by distillation with dimethylsulfoxide followed by vacuum sublimation; the melting point (96°-98°) of trimethylamine-N-oxide agrees with the literature value\(^8\) for the anhydrous form. Trimethylamine borane from the Callery Chemical Company
was used as received. Phosphine was prepared from hypophosphorous acid, its vapor pressure (170 torr at -111\degree) agrees with the literature. Trimethylphosphine was prepared from PCl$_3$ and LiCH$_3$; its vapor pressure (156 torr at 0\degree) agreed with the literature.

Trimethylphosphine borane was prepared by the reaction of stoichiometric amounts of B$_2$H$_6$ and P(CH$_3$)$_3$. Trimethylphosphinemethyldiide was prepared by a modification of the procedure of Koester et al. First, P(CH$_3$)$_4$I was obtained as a white precipitate from the reaction of excess CH$_3$I with P(CH$_3$)$_3$ in ether. Then, the P(CH$_3$)$_4$I (10.3 g) was added under nitrogen to an excess of freshly precipitated KNH$_2$ dispersed in about 200 ml of triglyme. The product was taken off under vacuum while the reaction mixture was refluxed. The product vapors were passed through cold traps at -23\degree, -78\degree, and -196\degree, respectively. The pyrophoric product, P(CH$_3$)$_3$CH$_2$, was obtained from the -78\degree trap. The yield was 2.64 g [62.1\% theoretical yield based on P(CH$_3$)$_4$I]. The product's mass spectrum had a parent peak at m/e = 90. The proton nmr spectrum of the neat product showed two doublets; one at $\delta = -0.7$ with respect to TMS, $J = 6$Hz, intensity 1, the other at $\delta = 1.38$ with respect to TMS, $J = 12$Hz, intensity 4.5.

Trimethylphosphineimide was isolated in an attempt to prepare P(CH$_3$)$_3$CH$_2$ in liquid ammonia. Tetramethylphosphonium iodide, 15.4 g (70.6mM), was added to 100 mM of freshly precipitated KNH$_2$ in about 100 ml of liquid ammonia. The reaction mixture was stirred for an hour, by which time the ammonia had all evaporated. The flask containing the products was then attached to a vacuum line and the volatile materials were passed through cold traps at -23\degree, -78\degree, and -196\degree, respectively.
An oily material which solidified upon standing and which evolved CH₄ was collected in the -23° and -78° traps. After two days, by which time all gas evolution had ceased, the product material was separated into a viscous, oily liquid, and a white, air-sensitive solid. The latter was identified as P(CH₃)₃NH. The yield was 0.28 g [4.4% theoretical yield based on P(CH₃)₄O]. The product's melting point (58°-59) agreed with the literature. In addition, the product's mass spectrum showed a parent peak at m/e = 91 and a strong, pressure-dependent P + 1 peak. A proton nmr spectrum of the neat material showed a singlet at δ = 0.1 relative to TMS of intensity 1, and a doublet at δ = 1.65 relative to TMS with J = 13 Hz and an intensity of 9. Trimethylphosphineoxide was prepared from POCl₃ and CH₃MgBr; its melting point (136°-138°C) agreed with the literature. Trimethylphosphine sulfide was prepared from P(CH₃)₃·HgCl₂ and ammonium polysulfide; its melting point (152-153°C) agreed with the literature.

The spectra were obtained from the gas phase on the Berkeley iron-free, double focusing magnetic spectrometer. Samples having sufficient vapor pressure were leaked into the irradiation chamber together with argon gas. Sample pressures and argon pressure in the irradiation chamber were approximately 40-50 µ and 20-30 µ respectively. The less volatile solid samples were placed directly inside the irradiation chamber, which resembles an effusion cell, and spectra were taken of the vapors above the solid. Argon was simultaneously leaked into the irradiation chamber at about 10 µ pressure. The spectra were taken with magnesium Kα radiation. Core levels from the sample and the reference gas, argon, were alternately scanned.
The spectra were fit by a least-squares analysis to Lorentzian lineshapes using a computer program described by Fadley. The absolute ionization potentials were calculated on the basis of 248.45 eV for the 2p\textsubscript{3/2} level in argon.\textsuperscript{5*} The reproducibility of the data was determined for several compounds to be about ±0.05 eV. We were unable to measure the N ls level in N(CH\textsubscript{3})\textsubscript{3}O in several attempts, despite being able to measure the C ls and O ls levels. To ensure that the vapor from the solid was indeed N(CH\textsubscript{3})\textsubscript{3}O, the sample was removed from the ESCA spectrometer and analyzed by mass spectroscopy. The mass spectrum showed a strong parent peak for N(CH\textsubscript{3})\textsubscript{3}O at m/e = 75 and peaks corresponding to the loss of methyl groups at m/e = 60, 45, and 30. We believe that the N ls spectrum was obscured by noise.

Experimental values of molecular geometries and internuclear distances, which were used in the molecular orbital calculations and potential correlations, were taken from the literature\textsuperscript{19-24} whenever possible. In a few cases, where accurate geometries were not available, values were estimated from data for similar compounds.

\textsuperscript{*}The Uppsala group has re-evaluated the binding energies of the noble gases and now believe the correct value for the argon 2p\textsubscript{3/2} level is 248.62 eV.\textsuperscript{18} Our energies may be adjusted to this reference by adding 0.17 eV to each value.
Binding Energy Correlations

ESCA chemical shifts are due to the changes in the coulombic potential felt at a core electron shell in atoms of a given element which have different chemical environments. The simplest interpretation states that changes in core binding energies for an element are simply proportional to changes in the charge of the atom. That is:

\[ E_B(A) = kQ_A + \ell \]  

where \( k \) and \( \ell \) are parameters. A more sophisticated model, the point charge potential equation involves the relation

\[ E_B(A) = kQ_A + \sum_{B\neq A} \frac{Q_B}{R_{AB}} + \ell \]  

This model includes the potential due to the other atoms in the molecule, which are treated as point charges separated from the ionized atom by the internuclear distances. As before, \( k \) and \( \ell \) are parameters, usually evaluated by a least-squares fit of the charge to the binding energies. The parameter \( k \) may be interpreted as the average \( \langle r^{-1} \rangle \) expectation value for the valence orbitals on atom \( A \) and \( \ell \) represents the binding energy of a free atom of \( A \).

If the charge distribution of a molecule is determined from a molecular orbital calculation, the quantum mechanical potential at atom \( A \) can be calculated from the density matrix and the appropriate \( r^{-1} \) integrals. A simpler approach, which is especially applicable to semi-empirical MO calculation, uses a valence potential first proposed by Schwartz where:

\[ \Phi_{val} = - \sum_{jA} P_{jA} \langle r^{-1} \rangle_{jA} + \sum_{B\neq A} \frac{Q_B}{R_{AB}} \]  

(3)
Here $P_i$ is the gross population in the $i^{th}$ valence orbital and $Q_B$ is the net charge on atom B, both determined from Mulliken population analysis. This form is similar to equation 2, except that the one-center ($r^{-1}$) integrals are calculated from the wavefunctions rather than evaluated empirically. Using equation 3, the binding energies are calculated:

$$E_B (A) = c \phi_{\text{val}} (A) + \ell$$  \hspace{1cm} (4)

where $c$ is an adjustable parameter which helps to compensate for the approximate nature of most semi-empirical MO theories and $\ell$ now represents the binding energy for a hypothetical atomic core stripped of all valence electrons.

The previous discussion has assumed that chemical shifts may be interpreted strictly in terms of ground state charge distributions. However, during photoionization, the remaining electrons in the molecule are attracted toward the core hole, and ESCA chemical shifts are more accurately described in terms of charge distributions for electronically relaxed transition states. Although the electronic relaxation produces a large change in the coulombic potential from that of the ground state, fortunately for a given element, this change is nearly the same for a wide variety of molecules, thus allowing the use of ground state charge distributions. The transition state may, however, be approximated in the valence potential model, equation 4, by using a result of Hedin and Johansson together with the principle of equivalent cores. The hole state binding energy may be expressed as:

$$E_B (A) = c \times \frac{1}{2} [\phi_{\text{val}} (A) + \phi_{\text{val}} (B^+) ] + \ell$$  \hspace{1cm} (5)
where $\phi_{\text{val}}(B^+)$ is the potential calculated for the isoelectronic cation obtained by substituting the core of atom A with the core of atom B, the next higher atom on the periodic table.

Results and Discussion

Central atom and ligand atom core binding energies for the nitrogen compounds are found in Table I. These data for the series of phosphorus compounds appear in Table II. The chemical shifts, relative to the hydrides, for the central N and P atoms also explicitly appear in Tables I and II, respectively, for the readers' convenience. The order of these binding energies could almost be predicted using two simple notions: that, for a given element, the charge on an atom should be approximately proportional to the summed (Pauling) electronegativities of the other atoms to which the first atom is bonded, and, that the binding energy is proportional to charge. For the nitrogen compounds, the binding energies should thus be ordered:

$$\text{NH}_3 < \text{N(CH}_3)_3 < \text{N(CH}_3)_3\text{BH}_3$$

For the phosphorus series, the order should be:

$$\text{PH}_3 < P(\text{CH}_3)_3 < \text{PCl}_3 < P(\text{CH}_3)_3\text{BH}_3 < P(\text{CH}_3)_3\text{CH}_2 \approx P(\text{CH}_3)_3\text{S}$$

$$< P(\text{CH}_3)_3\text{NH} > P(\text{CH}_3)_3\text{O} < \text{PSCl}_3 < \text{POCl}_3$$

Except for the misplacement of $\text{NH}_3$ and $\text{PH}_3$ and the gross misplacement of $\text{PCl}_3$, these orders were observed experimentally. More quantitative treatments of the chemical shifts, given in the next sections, require a more quantitative knowledge of charge distributions, and give more
### TABLE I

Experimental Core Binding Energies for Some Compounds of Nitrogen (in eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_B(\text{N }1\text{s})^a$</th>
<th>$\Delta E_B(\text{N})$</th>
<th>$E_B(\text{C }1\text{s})^a$</th>
<th>$E_B(\text{X})^a,b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>405.43</td>
<td>0.0</td>
<td>---</td>
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</tr>
<tr>
<td>N(CH$_3$)$_3$</td>
<td>404.63</td>
<td>-1.20</td>
<td>291.09</td>
<td>---</td>
</tr>
<tr>
<td>N(CH$_3$)$_3$BH$_3$</td>
<td>406.51</td>
<td>1.08</td>
<td>291.80</td>
<td>193.20</td>
</tr>
<tr>
<td>N(CH$_3$)$_3$O</td>
<td>---</td>
<td>---</td>
<td>291.60</td>
<td>537.5</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$NH</td>
<td>---</td>
<td>-3.05</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

---

*a* The uncertainty in our experimental values is approximately ±0.05 eV, except for ±0.1 for the O 1s binding energy in N(CH$_3$)$_3$O.

*b* The entered binding energies are for the B 1s and O 1s levels, respectively.
TABLE II
Experimental Core Binding Energies for Some Compounds of Phosphorus (in eV)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_B(P_{2p3/2})^{a}$</th>
<th>$\Delta E_B(P)$</th>
<th>$E_B(R)^{a,b}$</th>
<th>$E_B(X)^{a,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH$_3$</td>
<td>136.87</td>
<td>0.0</td>
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<td>---</td>
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<tr>
<td>P(CH$_3$)$_3$</td>
<td>135.76</td>
<td>-1.11</td>
<td>290.13</td>
<td>---</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$BH$_3$</td>
<td>137.00</td>
<td>0.13</td>
<td>290.79</td>
<td>192.76</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$CH$_2$</td>
<td>137.03</td>
<td>0.16</td>
<td>290.40</td>
<td>287.83</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$NH</td>
<td>137.39</td>
<td>0.52</td>
<td>290.63</td>
<td>402.38</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$O</td>
<td>137.63</td>
<td>0.76</td>
<td>290.57</td>
<td>535.88</td>
</tr>
<tr>
<td>P(CH$_3$)$_3$S</td>
<td>137.45</td>
<td>0.58</td>
<td>290.60</td>
<td>166.91</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>139.60</td>
<td>2.73</td>
<td>206.27</td>
<td>---</td>
</tr>
<tr>
<td>POCl$_3$</td>
<td>140.87</td>
<td>4.00</td>
<td>207.16</td>
<td>537.80</td>
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<tr>
<td>PSCl$_3$</td>
<td>140.45</td>
<td>3.58</td>
<td>206.71</td>
<td>168.70</td>
</tr>
</tbody>
</table>

$^{a}$ The uncertainty in our experimental values is approximately $\pm 0.05$ eV.

$^{b}$ The first six entered binding energies are for the C 1s level in the methyl groups; the last three binding energies are for the Cl 2p$_{3/2}$ level.

$^{c}$ The entered binding energies are for the B 1s, C 1s, N 1s, O 1s, S 2p$_{3/2}$, O 1s and S 2p$_{3/2}$ levels respectively.
insight into the chemical bonding found in these compounds.

**EHT Correlations.** The valence potential model, equation 4, was used to correlate binding energies with EHT charge distributions. The original formulation of the EHT method by Hoffmann was used for these calculations. The ionization energies and wavefunctions used in our program have been described previously. A valence s, p basis set was used for all the atoms in the calculations except for hydrogen (an s basis set) and phosphorus (for which valence d orbitals were also included in the basis set). The valence potentials evaluated at all the atoms present in these compounds excepting hydrogen appear in Table III. This table also includes values of the parameters c and l for each element, and, where more than two binding energies for a given element were correlated, the standard deviation and the correlation coefficient. The correlations of the carbon, nitrogen, and phosphorus binding energies involve enough data to warrant individual discussion.

The carbon ls binding energy correlation, illustrated in Fig. 1, shows that the ground state potentials are, to a good approximation, linearly related to the binding energies. The binding energy of the + methylene carbon in $P(CH_3)_3CH_2$ is very low, as might be expected from its negative formal charge. The other points all represent methyl carbons. The value of $c_C$, 0.185, is much smaller than unity, and indicates that the EHT charge separations are exaggerated. However, since methyl binding energies from both the nitrogen and phosphorus compounds fit on one correlation line, the degree of calculated excess bond polarity seems to be constant for all these trimethyl compounds. The nitrogen correlation, although not illustrated, was quite good.
TABLE III

Ground State Valence Potentials\(^a\) from EHT Calculations and Data from the Correlations of Core Binding Energies with EHT Potentials

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{val}^{(P)}$</th>
<th>Dev. ($P$)(^b)</th>
<th>$\phi_{val}^{(N)}$</th>
<th>Dev. ($N$)(^b)</th>
<th>$\phi_{val}^{(C)}$</th>
<th>Dev. ($C$)(^b)</th>
<th>$\phi_{val}^{(B)}$</th>
<th>$\phi_{val}^{(O)}$</th>
<th>$\phi_{val}^{(S)}$</th>
<th>$\phi_{val}^{(Cl)}$</th>
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</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>---</td>
<td>---</td>
<td>153.68</td>
<td>0.09</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>N(CH(_3))(_3)</td>
<td>---</td>
<td>---</td>
<td>157.22</td>
<td>-0.01</td>
<td>91.60</td>
<td>0.12</td>
<td>---</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>N(CH(_3))(_3)BH(_3)</td>
<td>---</td>
<td>---</td>
<td>147.59</td>
<td>-0.07</td>
<td>89.65</td>
<td>0.45</td>
<td>55.98</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>N(CH(_3))(_3)O</td>
<td>---</td>
<td>---</td>
<td>131.37</td>
<td>c</td>
<td>87.48</td>
<td>-0.13</td>
<td>---</td>
<td>222.55</td>
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</tr>
<tr>
<td>PH(_3)</td>
<td>74.83</td>
<td>1.10</td>
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</tr>
<tr>
<td>P(CH(_3))(_3)</td>
<td>72.94</td>
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<td>---</td>
<td>95.81</td>
<td>0.0</td>
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</tr>
<tr>
<td>P(CH(_3))(_3)BH(_3)</td>
<td>65.48</td>
<td>-0.94</td>
<td>---</td>
<td>---</td>
<td>93.24</td>
<td>0.10</td>
<td>58.09</td>
<td>---</td>
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<tr>
<td>P(CH(_3))(_3)CH(_2)</td>
<td>65.39</td>
<td>-0.93</td>
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<td>---</td>
<td>93.06</td>
<td>-0.27</td>
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</tr>
<tr>
<td>P(CH(_3))(_3)NH</td>
<td>---</td>
<td>---</td>
<td>108.97</td>
<td>0.05</td>
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</tr>
<tr>
<td>P(CH(_3))(_3)O</td>
<td>64.41</td>
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<td>168.04</td>
<td>-0.03</td>
<td>93.00</td>
<td>-0.10</td>
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<tr>
<td>P(CH(_3))(_3)S</td>
<td>62.55</td>
<td>-0.99</td>
<td>---</td>
<td>---</td>
<td>92.40</td>
<td>-0.24</td>
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<td>227.39</td>
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<td>-0.03</td>
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<td>107.66</td>
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<td>POCl(_3)</td>
<td>58.74</td>
<td>1.36</td>
<td>---</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>224.01</td>
<td>---</td>
<td>131.57</td>
</tr>
<tr>
<td>PSCl(_3)</td>
<td>57.96</td>
<td>0.76</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>108.60</td>
<td>132.06</td>
<td></td>
</tr>
</tbody>
</table>

| c | 0.232 | 0.204 | 0.185 | 0.209 | 0.376 | -1.904 | 0.188 |
| l | 153.16 | 436.66 | 307.90 | 204.87 | 621.45 | -38.10 | 231.73 |
| Std. Dev. | 1.15 | 0.07 | 0.21 | --- | 0.44 | --- | 0.18 |
| Corr. Coeff. | 0.737 | 0.999 | 0.981 | --- | 0.903 | --- | 0.914 |

\(^a\) All potentials are negative and in eV.
\(^b\) Dev($X$) = $E_B(X) - [c_X\phi_{val}^{(X)} + \ell_X]$ (eV).
\(^c\) This binding energy was not measured.
as can be determined from the correlation coefficient. The value of $c_N$, 0.205, is fairly close to the value of $c_C$, although both c's are smaller than was expected from previous work.\textsuperscript{30} The EHT correlation of phosphorus binding energies, shown in Fig. 2, exhibits quite a bit of scatter, and the value of $c_P$, 0.232, is higher than either $c_C$ or $c_N$. The compounds in the phosphorus correlations may be divided into three groups: the six trimethyl compounds, the three trichloro compounds, and phosphine. The two dashed lines in Fig. 2 represent correlations for just the trimethyl and trichloro compounds. The respective results from these are $c_{P(CH_3)}: 0.179$, std. dev. $P(CH_3): 0.07$ eV, corr. coeff. $P(CH_3): 0.994$ and $c_{P(Cl)}: 0.125$, std. dev. $P(Cl): 0.260$, corr. coeff. $P(Cl): 0.916$. These values indicate much better correlations than the total correlation and suggest that, although the EHT calculations correctly give relative charge distributions for fairly homogeneous series, the method is less useful in quantitatively predicting changes in markedly different molecules.

The boron, oxygen, sulfur and chlorine binding energy correlations found in Table III do not include enough points to be especially significant. However, the boron and chlorine correlations which include only trimethyl and trichloro compounds respectively give c values near those of carbon, nitrogen, and phosphorus, whereas the oxygen and sulfur correlations, which include both trimethyl and trichloro compounds, give c's with much different values. Again, this suggests that the two correlations for the phosphorus binding energies represented by the dashed lines are artifacts of the EHT charge calculations.
Transition state potentials for phosphorus were calculated using Eq. 5. The potentials and the correlation data are listed in Table IV. A slight improvement in the correlation was obtained by this method. However, because EHT does not give good representations of ionic species, and because potentials for the isoelectronic cations must be used in Eq. 5, electronic relaxation effects are poorly described by EHT. If, however, the hole state potentials for the six trimethyl and the three trichloro phosphorus compounds are correlated separately with the phosphorus binding energies, better fits are obtained than with the ground state potentials. The hole state correlations give the following results:

\[
\begin{align*}
\sigma_\text{P(CH}_3\text{)} & : 0.168, \text{std. dev. } P(\text{CH}_3) : 0.05, \text{corr. coeff. } P(\text{CH}_3) : 0.998, \\
\sigma_\text{P(Cl)} & : 0.126, \text{std. dev. } P(\text{Cl}) : 0.21 \text{ and corr. coeff. } P(\text{Cl}) : 0.944.
\end{align*}
\]

Thus, the inclusion of even crudely estimated relaxation effects corrects the potentials somewhat, and they more nearly describe the transition state which is measured by ESCA.

Although phosphorous valence d orbitals were included in the EHT basis sets, they had little effect on the composition of the filled molecular orbitals and hence on the calculated charge distributions. The very good correlation of EHT potentials with the P 2p\text{3/2} binding energies of the organo-phosphorus compounds may then be interpreted as showing either a constant amount of d orbital bonding in that series, or that such bonding is unimportant, at least in determining charge distributions.

**CNDO/2 Correlations.** The valence potential model was also used to correlate binding energies with CNDO/2 charge distributions. The
TABLE IV

Hole State Valence Potentials\(^a\) for Phosphorus from EHT Calculations and Data from the Correlation of Phosphorus Binding Energies with the EHT Potentials

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\phi_{\text{val}}(P))</th>
<th>Dev(P)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PH}_3)</td>
<td>80.66</td>
<td>1.07</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3)</td>
<td>79.51</td>
<td>-0.31</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3\text{BH}_3)</td>
<td>72.26</td>
<td>-0.76</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3\text{CH}_2)</td>
<td>71.70</td>
<td>-0.86</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3\text{NH})</td>
<td>70.29</td>
<td>-0.83</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3\text{O})</td>
<td>68.18</td>
<td>-1.09</td>
</tr>
<tr>
<td>(\text{P(CH}_3\text{)}_3\text{S})</td>
<td>69.65</td>
<td>-0.92</td>
</tr>
<tr>
<td>(\text{PCl}_3)</td>
<td>72.26</td>
<td>1.84</td>
</tr>
<tr>
<td>(\text{POCl}_3)</td>
<td>63.88</td>
<td>1.15</td>
</tr>
<tr>
<td>(\text{PSCl}_3)</td>
<td>63.83</td>
<td>0.72</td>
</tr>
<tr>
<td>(\text{C}_p)</td>
<td></td>
<td>0.234</td>
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<tr>
<td>(\ell_P)</td>
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<td>154.64</td>
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<tr>
<td>Std. Dev.</td>
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<tr>
<td>Corr. Coeff.</td>
<td></td>
<td>0.770</td>
</tr>
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</table>

\(^a\) All potentials are negative and in eV.

\(^b\) Dev(P) = E_8(P 2p_{3/2}) - [k_P \phi_{\text{val}}(P) + \ell_P] (eV).
theory of and the approximations involved in the well-known CNDO/2 molecular orbital theory are described in detail in the book by Pople and Beveridge. For atoms lighter than neon, the procedures and parameters described in that book were followed exactly. For molecules which contained second row elements (P, S and Cl), four sets of CNDO/2 calculations were made using different parameters and valence basis sets for these elements. Two sets of parameters for the second row elements were used: those proposed by Santry and Segal and included in the Pople and Beveridge book, and another set which we had previously used for calculations which included second and third row elements.

These latter parameters used orbital ionization potentials and electron affinities determined by Hinze and Jaffe together with Slater orbital wavefunctions proposed by Cusachs and Corrington for valence s orbitals. Values of $\beta_o$ were estimated using the method of Santry and Segal. In the s,p,d calculations using these parameters, $\frac{1}{2}(I_d + A_d)$ was simply set to zero for P, S and Cl; that is, the d orbitals were assumed to be nonbonding in the neutral free atoms.

Four sets of ground state binding energy correlations were made using CNDO/2 valence potentials. Potentials for the first set were determined using calculations in which second row atoms used an s,p,d basis set and Santry-Segal parameters. Potentials for the second set of correlations also included s,p,d basis sets on second row elements, but used the Hinze-Jaffé based parameters. The third and fourth sets of correlations used s,p basis set calculations. Potentials for the third set were obtained from calculations using Santry-Segal parameters;
potentials for the fourth sets came from calculations using the Hinze-Jaffe based parameters. As measured by the correlations coefficients and standard deviations, either of the two sets of correlations using s,p,d potentials were worse than either of the two sets of correlations using s,p potentials. Of the two s,p,d correlations, the first set was significantly worse than the second. We believe this is largely due to the poor representation of virtual orbitals in general, and virtual d orbitals in particular, by CNDO/2. Because such orbitals are allowed to have too much bonding character in CNDO/2, our simple expedient of letting \( \frac{1}{2}(I_d + A_d) \) equal zero in calculations for the second set of correlations helps to compensate for this inadequacy of CNDO/2. However, because both s,p,d correlations were inferior to either of the two s,p correlations, we suspect that the valence d orbitals on phosphorus are not important in determining the charge distributions of these compounds. Phosphorus d orbitals are certainly not important in these molecules at the level of description represented by either EHT or CNDO/2.

The third and fourth set of ground state correlations of s,p potentials against binding energies are of comparable quality. The principal difference between the two sets of second row element parameters is that the Hinze-Jaffe-based parameters represent the second row elements as more electronegative than the Santry-Segal parameters. In order to better differentiate between the two sets of parameters, we made correlations of the approximate hole state potentials against binding energy for (nearly) all of the different cores by using Eq. 5. Because CNDO/2 is a self-consistent field theory, unlike EHT, the electronic structure of cations should be given nearly as well as that of neutral molecules. These hole state potentials, which
should better represent the charge distributions actually "measured" by the chemical shifts, did in fact improve the correlations for the carbon, nitrogen, and phosphorus binding energies, the three series for which we have meaningful quantities of data. Again the quality of the correlations from the two sets of parameters were comparable, but the hole state s,p potentials using the Hinze-Jaffe-based parameters gave the best correlations. For brevity, we shall discuss only these results in detail.

The ground state valence potentials calculated at each atom in a molecule (excepting hydrogens) are found in Table V for both the nitrogen and the phosphorus compounds. Table V also contains the values of the parameters \( c \) and \( \ell \), the standard deviations and the correlation coefficients from the binding energy correlations for each element. These data for the hole state correlations appear in Table VI. No hole state potentials could be determined for chlorine atoms because the necessary parameters for argon are not available.

The values of the parameter \( c_C \) for the ground state binding energy correlation, 0.386, and for the hole state correlation, 0.499, are larger than the value for \( c_C \) from the EHT correlation, indicating that the CNDO/2 charge distributions are, as expected, less polarized than the EHT charge distributions. However, even for the hole state correlation, \( c_C \) is considerably less than one, indicating that although the calculated potentials are proportional to the measured binding energies, a 2 eV change in potential corresponds to approximately a 1 eV change in binding energy. This result is difficult to explain since other carbon binding energy correlations using CNDO/2 potentials gave values of \( c_C \) much nearer
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\phi_{\text{val}}(P)$</th>
<th>Dev(P)$^b$</th>
<th>$\phi_{\text{val}}(N)$</th>
<th>Dev(N)$^b$</th>
<th>$\phi_{\text{val}}(C)$</th>
<th>Dev(C)$^b$</th>
<th>$\phi_{\text{val}}(B)$</th>
<th>$\phi_{\text{val}}(O)$</th>
<th>$\phi_{\text{val}}(S)$</th>
<th>$\phi_{\text{val}}(Cl)$</th>
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<td>$\text{NH}_3$</td>
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<td>---</td>
<td>135.66</td>
<td>0.75</td>
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</tr>
<tr>
<td>$\text{N(CH}_3)_3$</td>
<td>---</td>
<td>---</td>
<td>134.63</td>
<td>-0.44</td>
<td>87.84</td>
<td>0.47</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_3\text{BH}_3$</td>
<td>---</td>
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<td>130.55</td>
<td>-0.12</td>
<td>86.17</td>
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<td>56.85</td>
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<td>c</td>
<td>86.66</td>
<td>0.53</td>
<td>---</td>
<td>197.28</td>
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<td>$\text{PH}_3$</td>
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<td>---</td>
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<td>88.34</td>
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<td>87.04</td>
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<td>$\text{P(CH}_3)_3\text{S}$</td>
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<td>-0.19</td>
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<td>-0.47</td>
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<td>143.11</td>
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<td>143.11</td>
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<td>191.84</td>
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<td>142.31</td>
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<td>$\ell$</td>
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<td>456.54</td>
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<td>401.65</td>
<td>559.99</td>
<td>236.11</td>
<td>259.74</td>
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<tr>
<td>Std. Dev.</td>
<td>0.61</td>
<td>0.52</td>
<td>0.38</td>
<td>0.98</td>
<td>0.315</td>
<td>0.576</td>
<td>0.36</td>
<td>0.576</td>
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<tr>
<td>Corr. Coeff.</td>
<td>0.933</td>
<td>0.955</td>
<td>0.936</td>
<td>0.315</td>
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<td>---</td>
<td>0.36</td>
<td>0.576</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

---

$^a$ All potentials are negative and in eV.

$^b$ Dev(X) = $E_B(X) - [c_X \phi_{\text{val}}(X) + \ell_X]$ (eV).

$^c$ This binding energy was not measured.
### Table VI

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Phi_{\text{val}}(P) )</th>
<th>Dev(P) (^b)</th>
<th>( \Phi_{\text{val}}(N) )</th>
<th>Dev(N) (^b)</th>
<th>( \Phi_{\text{val}}(C) )</th>
<th>Dev(C) (^b)</th>
<th>( \Phi_{\text{val}}(B) )</th>
<th>( \Phi_{\text{val}}(O) )</th>
<th>( \Phi_{\text{val}}(S) )</th>
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<tr>
<td>( \text{NH}_3 )</td>
<td>---</td>
<td>---</td>
<td>154.39</td>
<td>-0.13</td>
<td>---</td>
<td>---</td>
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<tr>
<td>( \text{N(CH}_3\text{)}_3 )</td>
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<td>---</td>
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<td>-0.18</td>
<td>104.99</td>
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<tr>
<td>( \text{N(CH}_3\text{)}_3\text{BH}_3 )</td>
<td>---</td>
<td>---</td>
<td>152.74</td>
<td>0.22</td>
<td>103.59</td>
<td>-0.04</td>
<td>68.63</td>
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</tr>
<tr>
<td>( \text{N(CH}_3\text{)}_3\text{O} )</td>
<td>---</td>
<td>---</td>
<td>152.34</td>
<td>c</td>
<td>104.13</td>
<td>0.05</td>
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<td>( \text{PH}_3 )</td>
<td>91.23</td>
<td>-0.12</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>220.04</td>
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</tr>
<tr>
<td>( \text{P(CH}_3\text{)}_3 )</td>
<td>92.85</td>
<td>0.04</td>
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<td>106.53</td>
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<td>( \text{P(CH}_3\text{)}_3\text{BH}_3 )</td>
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<td>69.22</td>
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<td>90.63</td>
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<td>90.74</td>
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<td>161.84</td>
<td>0.09</td>
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<tr>
<td>( \text{P(CH}_3\text{)}_3\text{O} )</td>
<td>91.00</td>
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<td>220.33</td>
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</tr>
<tr>
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<td>216.70</td>
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</tr>
<tr>
<td>( \text{PSCl}_3 )</td>
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<td>-0.23</td>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>124.19</td>
<td>---</td>
</tr>
<tr>
<td>( c )</td>
<td>0.782</td>
<td>0.439</td>
<td>0.499</td>
<td>0.746</td>
<td>0.346</td>
<td>0.633</td>
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<tr>
<td>( \ell )</td>
<td>208.36</td>
<td>473.41</td>
<td>343.50</td>
<td>244.38</td>
<td>612.78</td>
<td>247.25</td>
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<tr>
<td>Std. Dev.</td>
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<td>0.19</td>
<td>0.13</td>
<td>---</td>
<td>0.76</td>
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<tr>
<td>Corr. Coeff.</td>
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<td>0.994</td>
<td>0.993</td>
<td>---</td>
<td>0.675</td>
<td>---</td>
<td>---</td>
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</tr>
</tbody>
</table>

---

\(^a\) All potentials are negative and in eV.

\(^b\) Dev(X) = E_B(X) - [c_X \Phi_{\text{val}}(X) + \ell_X] \text{ (eV)}.

\(^c\) This binding energy was not measured.

\(^d\) The equivalent core calculation for this hole state potential did not achieve self consistency.
to unity, the theoretical value.\textsuperscript{25,26} The hole state potentials for carbon gave a much better correlation than the ground state potentials. In the hole state correlation, illustrated in Fig. 3, the carbon data from both the nitrogen and phosphorus compounds fit a single line very well, whereas, in the ground state correlation, the carbon points representing $\text{N}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_3\text{BH}_3$, and $\text{N}(\text{CH}_3)_3^0$ all are appreciably above the least-squares line. This observation suggests that there is a greater amount of electronic relaxation in the ionization of a methyl carbon atom of a phosphorus compound than of the corresponding nitrogen compound. In other words, $\text{PR}_2$ and $\text{PR}_2\text{X}$ are more electronically polarizable groups than are $\text{NR}_2$ and $\text{NR}_2\text{X}$.

The $c_N$ values parallel the $c_C$ values. For the ground state correlation $c_N$ equals 0.382, while for the hole state correlation $c_N$ equals 0.439. Again, the chemical shifts in the calculated potentials are larger than the shifts in binding energies. A comparison of the ground state and hole state correlations discloses a fairly common failing of ground state correlations.\textsuperscript{29} For ground state potentials, $\Phi_{\text{val}}(\text{NH}_3) < \Phi_{\text{val}}(\text{CH}_3)_3$, whereas $E_B(\text{NH}_3) > E_B(\text{CH}_3)_3$. The hole state potentials, however, do show the correct order: $\Phi_{\text{val}}(\text{NH}_3) > \Phi_{\text{val}}(\text{CH}_3)_3$. The incorrect prediction of this shift using ground state potentials is caused by the greater electronic relaxation of a $\text{CH}_3$ group adjacent to an atom undergoing photoemission than of a $\text{H}$ group adjacent to an atom undergoing photoemission.

The $c_p$ values, 0.681 for the ground state potentials and 0.782 for the hole state potentials, are somewhat larger than the corresponding values of $c_C$ and $c_N$. A larger value for $c_p$ than for either $c_C$ or $c_N$
was also obtained from the EHT correlations. However, in that instance, it resulted from the inability of the simple EHT calculations to correctly accommodate both the trimethyl and the trichloro compounds of phosphorus in the same correlation. In the CNDO/2 correlation of phosphorus binding energies, shown in Fig. 4, binding energies from both the trimethyl and the trichloro compounds fall on or close to the correlation line. Thus, the higher value for $c_P$ compared to those for $c_C$ and $c_N$ must result from subtle deficiencies in the CNDO/2 calculations. As was also the case for the CNDO/2 carbon and nitrogen binding energy correlations, the hole state correlation for the phosphorus binding energies is appreciably better than the ground state correlation. Although all but two binding energies are better correlated by the hole state potentials, the most dramatic example is again the hydride, in this case PH$_3$. The ground state potentials predict the order $\Phi_{\text{val}}(\text{PH}_3) < \Phi_{\text{val}}(\text{P(CH}_3)_3) < \Phi_{\text{val}}(\text{P(CH}_3)_3\text{BH}_3)$, whereas $E_B(\text{P(CH}_3)_3) < E_B(\text{PH}_3) < E_B(\text{P(CH}_3)_3\text{BH}_3)$. When the hole state potentials are considered, however, both the direction and the magnitude of the shifts are accounted for. Thus essentially the entire 1 eV shift in binding energy between PH$_3$ and P(CH$_3$)$_3$ is due to the changes in the potentials upon photoemission and not to differences between the ground state potentials.

Because the difference between the ground state and hole state potentials for a given molecule is due to electrons relaxing toward the positively charged ionized core, one expects that the difference between these potentials, that is the valence relaxation energy for that molecule, should depend upon the number of ligands bonded to the core ionized atom, and the polarizabilities of these ligands. We previously
found in a study of germanium compounds that Cl and CH₃ groups have similar valence relaxation energies, and that both were larger than that of H. Thus for the trivalent phosphorus compounds, PH₃, P(CH₃)₃, and PCl₃, one expects that \( \phi_{\text{val}}(\text{PCl}₃) - \phi_{\text{val}}(\text{P(CH₃)}₃) \) should have about the same value for ground potentials (\( \Delta \phi_{\text{val}} \approx 3.9 \) eV) as for hole state potentials (\( \Delta \phi_{\text{val}} \approx 3.7 \) eV). However, for \( \phi_{\text{val}}(\text{PCl}₃) - \phi_{\text{val}}(\text{PH}₃) \), the ground state potential difference is \( \Delta \phi_{\text{val}} = 3.9 \) eV, while for hole state potentials \( \Delta \phi_{\text{val}} = 2.1 \) eV. These two figures differ by more than an eV because of the greater polarizability of Cl relative to H. A tetracovalent molecule P(CH₃)₃X ought to have larger valence relaxation energy than trivalent P(CH₃)₃. If X = NH, for example, the difference \( \phi_{\text{val}}[\text{P(CH₃)₃NH}] - \phi_{\text{val}}[\text{P(CH₃)₃}] \) for the ground state potentials is 2.4 eV, and for the hole state potentials is 2.1 eV. The relaxation energy in the potentials due to the NH group is the difference of the two figures, -0.3 eV. Multiplying this figure by the average \( c_p \) for the ground state and hole state potentials, one crudely estimates that the valence relaxation energy contribution of the NH group to the binding energy is about 0.2 eV.

The binding energy correlations for boron, oxygen, sulfur, and chlorine have too few data points to justify detailed analysis. In the ground state correlations of these elements, the parameter c varies from 0.118 to 3.667. Both of these extreme values indicate that the appropriate ground state potentials poorly describe the chemical shifts. Although c varies from 0.346 to 0.746 for the correlations using hole state potentials, these values for c are closer to those from the more significant carbon, nitrogen, and phosphorus correlations. Thus, it
again appears necessary to consider the transition state potentials in order to quantitatively interpret the chemical shifts for these compounds.

The thermodynamic method for predicting chemical shifts, based upon the equivalent cores concept can be used to predict ESCA shifts if the necessary thermodynamic quantities are accurately known. The total energies determined by molecular orbital calculations provide a way to estimate these quantities. It is easily seen, that in this approach, a binding energy is given by:

\[ E_B(A) = E_{\text{tot}}(B^+) - E_{\text{tot}}(A) + \ell \]

(6)

where \( E_{\text{tot}}(A) \) is the total energy calculated for the molecule, and \( E_{\text{tot}}(B^+) \) is the total energy calculated for the isoelectronic cation obtained by substituting atom B for A, as was also done in Eq. 5, as usual, \( \ell \) is a constant. Good correlations of binding energies for first row elements have been obtained with this approach using total energies from ab initio and MINDO molecular orbital calculations. Using CNDO/2 energies, the results have been poor. However, we thought that it might be interesting to compare the hole state potential equation correlations of the phosphorus and nitrogen binding energies using Eq. 5 with correlations based on the total energies from the same CNDO/2 ground state and equivalent core calculations used to calculate the hole state potentials. The total energies from CNDO/2 include both one and two electron integrals and one might expect that this model would be at a higher level of sophistication than the potential model which uses only one electron integrals. Both methods include the same level of relaxation correction. As is the case with the potential correlations, we
allow an adjustable parameter in the CND0/2 total energy correlations, using, instead of Eq. 6, the following equation:

\[ E_B(A) = c[E_{\text{tot}}(B^+) - E_{\text{tot}}(A)] + \ell \]  

The results from these correlations, found in Table VII, show that CND0/2 total energies give much poorer correlations than do the potentials from the same calculations. Thus it appears that while CND0/2 is quite useful for obtaining charge distributions, it is not especially reliable in calculating heats of reactions involving these compounds. In other words, the calculated heats of reactions, being relatively small energies obtained by subtracting two large energy terms, seem to be much more sensitive to small changes in electronic distribution than are the potentials.

Conclusions

The simplest valence bond structures for these tetracovalent group Va compounds suggest that the central atom should have an unusually high positive charge while the peripheral BH\(_3\), CH\(_2\), NH, O, or S ligand should acquire a considerable negative charge. Our binding energy data support this idea because the central atom binding energies of all the tetracovalent compounds are higher than the binding energies for their respective trivalent precursors. In addition, the binding energies of the ligand atoms which have formal charges are unusually low for those elements. The calculated charges, which are given in Table X for all of the atoms in these compounds except for hydrogens, help quantify the extent of this charge separation. Although the EHT charges are much too polarized, "truer" charges for a molecule can be obtained using a simple interpretation of the valence potential model. These more
Table VII

Binding Energy Correlations Using CNDO/2 Total Energies and the Equivalent Cores Thermodynamic Model

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_{tot}(M)^a$</th>
<th>$\Delta E_{tot}(M)^a$</th>
<th>$M=N$</th>
<th>Dev(M)$^b$</th>
<th>$M=P$</th>
<th>Dev(M)$^b$</th>
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<tr>
<td>$\text{MH}_3$</td>
<td>6.41424</td>
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<td>$\text{M(CH}_3)_3$</td>
<td>6.39484</td>
<td>-0.46</td>
<td>3.68190</td>
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<tr>
<td>$\text{M(CH}_3)_3\text{BH}_3$</td>
<td>6.25961</td>
<td>-0.03</td>
<td>3.61481</td>
<td>-0.95</td>
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<tr>
<td>$\text{M(CH}_3)_3\text{CH}_2$</td>
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<td>---</td>
<td>3.65158</td>
<td>-0.26</td>
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<tr>
<td>$\text{M(CH}_3)_3\text{NH}$</td>
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<td>0.65</td>
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<td>$\text{M(CH}_3)_3\text{O}$</td>
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<td>---</td>
<td>3.69795</td>
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<td>$\text{M(CH}_3)_3\text{S}$</td>
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<tr>
<td>$\text{MSCl}_3$</td>
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<td>3.46194</td>
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<tr>
<td>$\epsilon$</td>
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<td>17.907</td>
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<tr>
<td>$\epsilon$</td>
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<td></td>
<td>202.68</td>
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<tr>
<td>Std. Dev. $(\text{eV})$</td>
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<td>1.03</td>
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<td>0.794</td>
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$^a$ All values are negative and in a.u.

$^b$ $\text{Dev}(M) = E_B(M) - [c\Delta E_{tot}(M) + \epsilon](\text{eV})$

$^c$ Value is for $\text{P(CH}_3)_3\text{NH}$
<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>EHT</th>
<th>CNDO/2</th>
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<tbody>
<tr>
<td>PH₃</td>
<td>P</td>
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<tr>
<td>P(CH₃)₃</td>
<td>P</td>
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<td>C</td>
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<tr>
<td>P(CH₃)₃BH₃</td>
<td>P</td>
<td>1.545</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>-0.333</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-0.109</td>
<td>-0.126</td>
</tr>
<tr>
<td>P(CH₃)₃CH₂</td>
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<td>1.910</td>
<td>0.291</td>
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<tr>
<td></td>
<td>C</td>
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<tr>
<td></td>
<td>C'</td>
<td>-1.327</td>
<td>-0.453</td>
</tr>
<tr>
<td>P(CH₃)₃NH</td>
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<td>0.294</td>
</tr>
<tr>
<td></td>
<td>C</td>
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<td>-0.029</td>
</tr>
<tr>
<td></td>
<td>N</td>
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<td>-0.449</td>
</tr>
<tr>
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<td>P</td>
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<td>0.249</td>
</tr>
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<td></td>
<td>C</td>
<td>-0.358</td>
<td>-0.023</td>
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<td>O</td>
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<tr>
<td>P(CH₃)₃S</td>
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<td>C</td>
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<td>S</td>
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<td>O</td>
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<td>PSCl₃</td>
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<td></td>
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<tr>
<td></td>
<td>S</td>
<td>-1.186</td>
<td>-0.419</td>
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</table>
realistic charges are found by multiplying the calculated charges times the average of the values of c (from Eq. 4) for all of the elements in the molecule for which binding energy correlations were made. If this procedure is followed, one still obtains relatively high charges on the central atoms and on the ligands having negative formal charges.

The ESCA data for these compounds suggest considerable charge polarization in the tetracovalent molecules. (Of course, the atomic charges do not reach values of unity corresponding to some of the formal charges.) Valence bond structures give electron distributions for hypothetical molecules exhibiting pure covalent bonding, and it is only for such cases that the magnitudes of the formal charges have any meaning. Thus additional ionic effects due to heternuclear bonding and induction are also important in determining the charge distributions and hence in determining the core electron binding energies for these molecules. For example, trivalent PCl₃ has a higher P 2p 3/2 binding energy than any of the tetracovalent trimethyl phosphorus compounds despite the valence bond structures which assign phosphorus a zero formal charge in PCl₃ and a +1 formal charge in the (CH₃)₃PX molecules.

Although direct evidence supporting or opposing the presence of multiple bonding in these compounds is not obtained from ESCA chemical shifts, certain conclusions may be inferred from our data. For the phosphorus compounds, one would expect that the phosphorus valence 3d orbitals might participate in the bonding, if at all, by pπ+ dπ interactions. These interactions would tend to increase the electron density of phosphorus at the expense of the formally charges peripheral ligand. Because we were able to obtain good correlations of the phosphorus core
binding energies and of core binding energies of the electron deficient ligands by three different methods, all of which neglected or minimized pπ→dπ interactions, the following proposition seems likely. Either the d orbitals are of comparable importance in determining the charge distributions for all of the phosphorus compounds including PH₃, P(CH₃)₃, and PCl₃, or they do not contribute significantly to the charge distributions of any of the compounds which we studied. We believe that the latter hypothesis is correct. Certain experimental data also directly argue against d orbital bonding. For the pairs of compounds M(CH₃)₃BH₃ and M(CH₃)₃O, where M = N,P, the B 1s and O 1s binding energies of the phosphorus compounds are lower than the B 1s and O 1s binding energies of the nitrogen compounds. This strongly suggests a greater negative charge on the BH₃ and O ligands for the phosphorus compounds than for the nitrogen compounds, in agreement with simple electronegativity effects. This behavior is not consistent with the presence of appreciable pπ→dπ bonding in the two phosphorus compounds.

Multiple bonding between the central atom and the formally charged ligand is still possible for both the phosphorus and nitrogen compounds if one is willing to consider no-bond hyperconjugated resonance structures such as the following:

```
R
/  
R→M=X
```

For these structures, charge is not transferred from the X ligand to the central atom as for pπ→dπ bonding, but rather charge is transferred from the X ligand to the other peripheral ligands. Although bond order is
not a particularly well-defined concept in the molecular orbital description of chemical bonding, we have carefully examined the EHT and CNDO/2 calculations for POC\textsubscript{3} and PSC\textsubscript{3} in order to infer bond orders for these molecules. Examining the results of the EHT Mulliken analyses shows little π electron density in the P-O and P-S overlap populations, and the π\textsuperscript{v} orbitals on oxygen and sulfur are nearly filled and exhibit primarily lone pair characteristics. Although there are no overlap populations in CNDO/2, the π\textsuperscript{v} orbitals of oxygen and sulfur are again nearly filled, and an examination of the eigenvectors for the filled molecular orbitals again suggests that these orbitals are largely lone pairs. Thus, simple molecular orbital descriptions of the ground state of these two molecules shows primarily σ bonding and considerable charge polarization. However, more sophisticated calculations should be made if the importance of hyperconjugation in these molecules is to be theoretically determined. In addition, the calculation of localized molecular orbitals might be especially applicable to determining the extent of hyperconjugation.

Our best correlations of binding energies with charge distributions were obtained when the effect of electronic relaxation due to the core hole was explicitly included in the charge distributions. We feel that the effects of electronic relaxation during photoemission on core binding energies will become more apparent as more gas phase ESCA binding energies for compounds including elements heavier than neon are measured. These heavier atoms are more polarizable than most first row elements, and such atoms should thus be more perturbed by positively charged holes in either their own cores, or the cores of adjacent atoms. Furthermore, the increased size of these heavier elements implies smaller one center
< r⁻¹> expectation values and thus smaller chemical shifts. Thus, the effects of valence electron relaxation should become more pronounced. However, the equivalent cores approach, in both the thermodynamic and potential applications of this idea, provides a simple method of accounting for most of the valence electron charge polarization which occurs during photoemission.
References


Figure Captions

Fig. 1. Plot of phosphorus $2p_{3/2}$ binding energies vs binding energies calculated from ground state EHT valence potentials, where $E_B^{(\text{calc})} = c \Phi + \ell$. The two dashed lines represent correlations of just the trimethyl and just the trichloro compounds.

Fig. 2. Plot of carbon $1s$ binding energies vs binding energies calculated from ground state EHT valence potentials, where $E_B^{(\text{calc})} = c \Phi + \ell$.

Fig. 3. Plot of phosphorus $2p_{3/2}$ binding energies vs binding energies calculated from hole state CNDO/2 valence potentials, where $E_B^{(\text{calc})} = c \Phi + \ell$.

Fig. 4. Plot of carbon $1s$ binding energies vs binding energies calculated from hole state CNDO/2 valence potentials, where $E_B^{(\text{calc})} = c \Phi + \ell$. 
Fig. 2
Fig. 3
Fig. 4
III. THE CALCULATION OF ATOMIC CHARGES FROM CORE BINDING ENERGY CHEMICAL SHIFTS

Introduction

The point charge electrostatic potential equation of Siegbahn, et al.\(^1\) has been used to correlate core binding energy chemical shifts for free molecules for a number of different elements.\(^1,2\) Although the original use of the potential equation was restricted to frozen-orbital, Koopmans' theorem descriptions of chemical shifts, the effects of electronic relaxation during photoionization may be included into the potential equation\(^3\) through the use of the equivalent cores approximation.\(^4\) Thomas, et al.\(^5\) have recently shown that the frozen-orbital expression of the potential equation may also be used to calculate atomic charges more or less directly from the experimental chemical shifts. This technique of calculating atomic charges from binding energy chemical shifts will be re-evaluated by including a much larger and more diverse body of experimental data than was originally used. In addition, a modification of the potential equation will be proposed which will include, at least partially, the effects of electronic relaxation during photoemission. Because the primary aim of this procedure is to determine ground state atomic charges, and also, in order to be able to solve the equations used by this procedure, it is necessary that the relaxation correction to the potential equation be a function of the ground state atomic charges. Thus, the equivalent cores approximation, which requires atomic charges corresponding to the final state ion, could not be used to account for relaxation effects.
The Potential Equation

The frozen orbital expression of the electrostatic potential equation which we shall use in this work has a slightly different form from that used by Siegbahn, but the physical descriptions represented by both equations are equivalent. Our equation may be easily derived from a classical electrostatic model of photoionization. For the purpose of this model, an atom is represented by a point charge core of charge \( +Z_A e \), located at the center of a rigid, conducting, spherical shell of charge \( -Z_A e \), which represents the valence electronic shells of the atom. A molecule is represented by an assembly of these atoms where the nucleus-like cores at the centers of each atom are located at fixed coordinates given by the ground state equilibrium geometry of the real molecule. In a molecule, the valence shells of the atom need not have charges of \( -Z_A e \), but may have the charges \( -(Z_A - q_A)e \), with the condition that:

\[
\sum_A q_A = 0
\]  

(1)

where the summation is over all the atoms \( A \) in the molecule. The quantity \( q_A \), then, is just the net charge of an atom \( A \).

The binding energy of a core electron in some given atom \( A \) is equal to a constant energy term, \( \ell_A \), which represents the energy necessary to remove the core electron from an isolated core of atom \( A \), plus the change in the total electrostatic energy of the "molecule" upon the removal of a core electron from atom \( A \). The energy is expressed:

\[
E_B(A) = \ell_A + [(Z_A + 1) - Z_A]e\{-(Z_A - q_A)e_{r_A} + \sum_{B \neq A} \left[ (Z_B - (Z_B - q_B))\frac{e}{R_{AB}} \right] \} (2)
\]

where \( r_A \) is the radius of the valence shell of atom \( A \), and \( R_{AB} \) is the internuclear distance between atoms \( A \) and \( B \). Equation 2 may be rewritten in a simpler form:

\[
E_B(A) = -\frac{1}{r_A}(Z_A - q_A) + \sum_{B \neq A} \frac{q_B}{R_{AB}} + \ell_A
\]  

(3)
where we are now assuming that $e^2 = 1$. If the ionized atom, atom A, is described using some concepts from quantum mechanics, and a hybrid atomic orbital valence shell is assumed, $\frac{1}{r_A}$ would be given by the integral $<n\ell m|r_{A}^{-1}|n\ell m>$, where $|n\ell m>$ is a valence shell hybrid atomic orbital.

In this work, we shall let $\frac{1}{r_A}$ be a parameter $k_A$, but the empirical values which are determined will be compared to theoretical estimates for $k_A$.

The electronic relaxation which occurs during photoionization can be described as the polarization of charge density towards the newly created positive hole in a core shell of the ionized atom. Most of this rearrangement of electron density occurs in the core shells of the ionized atom, and in the valence shells of atoms more or less throughout the molecule. The electronic rearrangement in the core shells of the ionized atom would be expected to give rise to a constant energy for given elements and be insensitive to different chemical environments. It is surely the electronic rearrangement in valence shell electron density which affects core binding energy chemical shifts. At least some of this valence shell electronic rearrangement will be described by the following, essentially classical model of electronic relaxation.

There are two kinds of atoms in this model. A core ionized atom is represented by a point charge core of charge $+Z_Ae$ at the center of a partially collapsible conducting spherical shell of charge $-Z_Ae$, i.e. the valence shell. A nonionized atom is represented by a point charge core of charge $+Z_Be$ at the center of a polarizable conducting sphere of charge $-Z_Be$. A molecule is defined as before. When atom A is core ionized, that is, when its core charge is increased by one unit, the
valence shell of atom A contracts from a radius of \( r \) to one of \( r_A - \Delta r_A \). The valence shells of the non-ionized atoms B are displaced towards atom A from an internuclear distance \( R_{AB} \) to \( R_{AB} - \Delta R_B \). The cores of the atoms B remain at the original coordinates. This process is illustrated for a triatomic molecule in figure 1. Both the contraction and the displacements of the valence shells allow charge to be polarized towards the ionized core and reduce the difference between the electrostatic potential energy of the ion and that of the neutral molecule. Adding these concepts to those of equation 2, a core binding energy is now given by the expression:

\[
E_B(A) = E_A + e^2 \left\{ (Z_A + 1) - \frac{(Z_A - q_A)}{r_A - \Delta r_A} + \sum_{B \neq A} \left( \frac{Z_B}{R_{AB}} - \frac{Z_B - q_B}{R_{AB} - \Delta R_B} \right) \right\}
\]

\[
Z_A \left[ -\frac{Z_A - q_A}{r_A} + \sum_{B \neq A} \frac{Z_B - (Z_B - q_B)}{R_{AB}} \right]
\]

(4)

this expression can be rewritten in a form more like that of equation 3, again letting \( e^2 = 1 \):

\[
E_B(A) = -(Z_A - q_A) \frac{1}{r_A} - \left\{ (Z_A - q_A) (Z_A + 1) \left[ \frac{1}{r_A^0 - \Delta r_A} - \frac{1}{r_A} \right] \right\} + \sum_{B \neq A} \left[ \frac{q_B}{R_{AB}} - \left( \frac{Z_B - q_B}{R_{AB} - \Delta R_B} - \frac{1}{R_{AB}} \right) \right]
\]

(5)

where the terms in the first curly brackets represent the reduction in electrostatic potential energy due to the contraction of the valence shell of atom A, i.e. the atomic or one-center relaxation. In a quantum mechanical description of the atom, again assuming hybrid valence orbitals, this energy is given by the valence shell electron population times a
Fig. 1. A schematic presentation of the photoionization of a core electron from atom A in a triatomic molecule.
polarization potential, \( \frac{1}{2} \langle \eta \ell \mu | v_R | \eta \ell \mu \rangle \). When evaluated for a single electron in an sp\(^3\) hybrid valence orbital, we shall denote this term as \( \langle v_R \rangle \). The terms in the second curly brackets represent the reduction in electrostatic potential energy due to the displacements of the valence shells of the atoms B, that is the two-center relaxation. We shall continue to express these terms using classical electrostatics for point charges. If the parameter \( k_A \) is defined as before, our final expression for a binding energy is given by:

\[
E_B(A) = -(k_A + \langle v_R \rangle_A)(Z_A - q_A) + \sum_{B \neq A} \left[ \frac{q_B}{R_{AB}} - \left( \frac{1}{R_{AB} - \Delta R_B} - \frac{1}{R_{AB}} \right) \right] + \xi_A \tag{6}
\]

If \( \Delta R_B = 0 \), that is, if there is assumed to be no two-center relaxation, then equation 6 is identical to equation 3, except that \( k_A \) in equation 3 is replaced by \( k_A + \langle v_R \rangle_A \) in equation 6.

Several features of this model should be discussed. Like the frozen-orbital potential equation, our relaxation corrected potential equation assumes that the charge distribution in a molecule may be adequately approximated by a number of nonpenetrating spherical charge distributions centered on the atomic nuclei of the molecule. There is much precedent for this assumption, but this may be a poor description for some molecules. Because two-center relaxation is treated classically by this model, there are no provisions for chemical bonding in the model. All charge polarization occurs "through space" and chemical factors, such as whether two atoms are bonded to each other and, if so, what is the effect of bond order, are neglected.
Calculations

If a molecule does not contain hydrogen atoms, which have no core electrons, it is possible to measure a core binding energy for every chemically unique atom in the molecule. However, in the point charge approximation, only \( n - 1 \) atomic charges are necessary to specify the complete charge distribution of a molecule having \( n \) chemically unique atoms, since all the charges must sum to a known total charge. For a free molecule, this total charge is of course zero. Thus, if an appropriate set of molecules is selected, it is possible to measure enough binding energies to determine, using equation 6, all the charges in each molecule, plus the values of the parameters \( k \) and \( \ell \) for each elements represented in the data set. In our case, the data set contains 77 core binding energies from 35 molecules. Only 62 atomic charges are necessary to describe the charge distributions in the data set, but because the data set includes ten different elements, a total of 20 values for the parameters \( k \) and \( \ell \) must also be determined.

Because this data set, when used with equation 6, constitutes an overdetermined set of equations, the method of general least squares analysis was used to solve the equations for the best values of the \( k \)'s, \( \ell \)'s and \( q \)'s. Thus, one can evaluate the generality and usefulness of this model of photoionization to some extent from the calculated error in a core binding energy correlation and from the statistical uncertainty in the charges and in \( k \) and \( \ell \).

RESULTS

We first applied equation 6 to the xenon fluoride binding energy data
of Thomas, et al. Table I lists the results of our analysis for an essentially frozen-orbital description of photoionization, i.e. $\Delta R_B = 0$. Our values nearly duplicate the previously reported values, as should be the case. Because this procedure is heavily parameterized, the results are unfortunately sensitive to the choice of data set. If the binding energy for $F_2$ is removed from the xenon fluoride data set, and the equations are solved as before, the calculated charges and $k_{Xe}$ change somewhat, but the value of $k_F$ changes drastically. The new value, a relatively large, negative number is not consistent with the physical description of photoionization given by the potential equation. These results also appear in Table I.

The essentially frozen-orbital expression of equation 6, which includes only effects from one-center relaxation, was next used to calculate charges for the molecules in the large data set. The experimental core binding energies, the atomic charges, together with their statistical uncertainties, and the rms and standard errors from the binding energy calculations appear in Table II. The values for the $k$ and $\ell$ parameters from these calculations are listed in Table III.

Two sets of theoretical values for $k$ for the elements included in the large data set are listed in Table IV. Both sets of $k$'s were calculated for $sp^3$ valence orbitals using the expression:

$$k_{sp^3} = \frac{1}{4}<ns|r^{-1}|ns> + \frac{3}{4}<np|r^{-1}|np>$$

(7)

where $n$ is the principal quantum number of the valence shell. The first set of $k$'s was calculated from atomic Slater type orbital (STO) wavefunctions.
TABLE I
Calculated Charges for the Xenon Fluorides$^a$ from Equation 6 with $\Delta R_B = 0$.
(Statistical Uncertainties Appear Parenthetically)

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<th>q^c</th>
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<td>Xe</td>
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</tr>
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<td>$\ell_{Xe}$ (eV)</td>
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</tr>
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</table>


$^b$ Binding energy correlation data: Std. Error = 0.100 eV, RMS Error = 0.035 eV.

$^c$ Binding energy correlation data: Std. Error is undefined because the set of equations is exactly determined. Thus, RMS Error = 0.
TABLE II

Experimental Binding Energies (in eV) and Atomic Charges Calculated from Equation 6 with $\Delta R_B = 0$. (Statistical Uncertainties Appear Parenthetically).

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</tr>
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</table>

The core binding energies in this table are for the following levels:

- C = C 1s, N = N 1s, O = O 1s, F = F 1s, Si = Si 2p$_{3/2}$, P = P 2p$_{3/2}$
- S = S 2p$_{3/2}$, Cl = Cl 2p$_{3/2}$, Ge = Ge 3p$_{3/2}$, and Br = Br 3d$_{5/2}$

$^a$ Binding energy correlation data: Std. Error = 0.228 eV, RMS Error = 0.101 eV.
$^b$ Dr. M. S. Lazarus, unpublished data.
$^c$ Dr. R. R. Rietz, unpublished data.
$^d$ K. Siegbahn, et al., "ESCA Applied to Free Molecules," North Holland Publishing Co., Amsterdam, 1969. Absolute ionization potentials are based upon the following values: C 1s:CH$_4$ = 290.7, N 1s:N$_2$ = 409.8, O 1s:O$_2$ = 543.2, F 1s:CF$_4$ = 695.4, S 2p$_{3/2}$:CS$_2$ = 169.8 (all in eV).
Empirically Determined Values for the Parameters $k$ and $\ell$.

(Statistical Uncertainties Appear Parenthetically).

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*a* In units of eV/e.

*b* In units of eV.
TABLE IV
Theoretical Estimates of Some Quantities

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<th>( k_{sp}^a,b )</th>
<th>( k_{sp}^a,c )</th>
<th>( \langle v_R \rangle^{a,d} )</th>
<th>( \langle r_{sp}^3 \rangle^{e,f} )</th>
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\( a \) In units of eV/e.

\( b \) Calculated from STO wavefunctions, Ref. 8.

\( c \) Calculated from RHFS \( \langle r^{-1} \rangle \), Ref. 9.

\( d \) Calculated from Slater integrals, Ref. 10 using the method of Ref. 7.

\( e \) In units of \( a_0 \) (Bohr radius).

\( f \) Calculated from atomic HF valence \( \langle r \rangle \), Ref. 8.

\( g \) In units of \( a_0^3 \).
and the second set of k's were calculated using tabulated $r^{-1}$ orbital expectation values from relativistic Hartree-Fock-Slater (RHFS) calculations for atoms. Both sets of k's, thus, are for neutral free atoms and may not be entirely appropriate for atoms in molecules. In addition, the two sets of k's are not perfectly consistent. However, these values should be useful benchmarks to compare against empirically determined values for k. Other theoretically evaluated quantities, which are used in equation 6, also appear in Table IV. The values for $\langle V_R \rangle$ were calculated using two-electron Slater integrals from Hartree-Fock calculations for free atoms. The radical expectation values, $\langle r \rangle$, and their cubes were calculated for sp$^3$ valence orbitals from tabulated ab initio $\langle r \rangle$ values for free atoms.

A comparison of the theoretical values of k with the empirically determined values for the calculations where $\Delta R_B = 0$ shows, that the empirical values are too large. However, except for the values of $k_c$ and $k_p$, there is at least a crude proportionality between the theoretical and empirical values. As will be the case in all our calculations, the statistical uncertainties for most values of k, $l$, and q are high relative to the magnitudes of these quantities. Because the values for k were calculated to be too high, one would expect, given the form of equation 6, that the calculated charges would be too low. Although the relative values of the charges in Table II do not offend our chemical intuition, they are smaller than the charges which are calculated using other procedures.

In order to include the effects of two-center relaxation, it is
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<td>0.220</td>
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<td>Cl</td>
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<td>0.0</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.104(0.026)</td>
<td>-0.110(0.024)</td>
<td>Br(_2)</td>
<td>Br</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>C</td>
<td>0.116</td>
<td>0.110</td>
<td>O(_2)</td>
<td>O</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.058(0.024)</td>
<td>-0.055(0.027)</td>
<td>N(_2)</td>
<td>N</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>S</td>
<td>0.256</td>
<td>0.293</td>
<td>C(_2)F(_4)</td>
<td>C</td>
<td>0.164</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>-0.128(0.028)</td>
<td>-0.147(0.028)</td>
<td>F</td>
<td>-0.082(0.019)</td>
<td>-0.087(0.018)</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Charges calculated using \( \Delta R_B = 0.0004<r>_B^3 \) in equation 6. Binding energy correlation data: Std. Error = 0.314 eV, RMS Error = 0.139 eV.

\( b \) Charges calculated using \( \Delta R_B = 0.001<r>_B \) in equation 6. Binding energy correlation data: Std. Error = 0.306 eV, RMS Error = 0.135 eV.
necessary to evaluate the $\Delta R_B$ term in equation 6. This term should be a function of the polarizability of the valence shell. For a given element, the polarizability of the valence shell could be reasonably expected to be approximately proportional to the atomic volume or similarly to a quantity like $<r>^3$, where $<r>$ is taken to be the radial expectation value for the valence shell. Thus a simple, plausible expression for $\Delta R_B$ is given by:

$$\Delta R_B = \alpha <r>^3$$

where $\alpha$ is a proportionality constant. This expression was used in equation 6 for several values of $\alpha$. The values for the $k$ and $\ell$ parameters are listed in Table III for $\alpha = 0.0002$ and $\alpha = 0.0004$. These values for $k$ are considerably lower than the values which resulted when $\Delta R_B$ was entirely neglected. The values for $k$ when $\alpha = 0.0004$ are in reasonable agreement with the theoretical estimates again excepting $k_c$ and $k_p$. However, the standard error from these calculations is higher than for the case where $\Delta R_B = 0$, and a few of the calculated atomic charges, such as the negative charge on silicon in SiCl$_4$, are clearly not reasonable. On the other hand, the magnitudes of the atomic charges are generally larger and more consistent than those obtained from other procedures. The charges, their statistical uncertainties, and the rms and standard errors for the calculations where $\alpha = 0.0004$ are listed in Table V.

The results of these last calculations motivated, in part, the choice of an alternate expression for $\Delta R_B$. Because the displacement
represented by $\Delta R_B$ is a one-dimensional translation of charge, perhaps $\Delta R_B$ might better be described by the cube root of the atomic polarizability. This concept is expressed:

$$\Delta R_B = \alpha \langle r \rangle_B$$  \hspace{1cm} (9)

where $\alpha$ is again a proportionality constant. Several values of $\alpha$ were tried, and the $k$ and $\ell$ values from the calculations where $\alpha = 0.0010$ and $\alpha = 0.0015$ are listed in Table III. Again the $k$ values from calculations assuming non-zero values for $\Delta R_B$ are in better agreement with the theoretical estimates than those from the calculations neglecting two-center relaxation. The charges, their statistical uncertainties, and the rms and standard errors from the calculations where $\alpha = 0.0010$ are listed in Table V. These last charges have comparable magnitudes to those calculated using equation 8 with $\alpha = 0.0004$, but there are no obviously unreasonable charges in this set.

Although the agreement between the empirical and theoretical values for $k$ is improved by including effects from two-center relaxation, the agreement is by no means perfect. In order to learn what charges are calculated when theoretical values of $k$ are used, the RHFS estimates for $k$ were used in equation 6 as constants rather than as parameters. Two sets of charge calculations were made using these $k$'s. In the first set of calculations, two-center relaxation was neglected, i.e. $\Delta R_B = 0$. For the second set of calculations, $\Delta R_B$ was treated as a parameter, and empirical, best least squares values for $\Delta R_B$ were determined. The calculated charges, their statistical uncertainties,
Atomic Charges Calculated from Equation 6 and Using Theoretically Estimated Values for $k_A$. (Statistical Uncertainties Appear Parenthetically.)

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<tr>
<th></th>
<th>$q^a$</th>
<th>$q^b$</th>
<th></th>
<th>$q^a$</th>
<th>$q^b$</th>
</tr>
</thead>
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<tr>
<td>CF$_4$</td>
<td>C</td>
<td>0.578</td>
<td>F</td>
<td>-0.144(0.013)</td>
<td>-0.147(0.036)</td>
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<tr>
<td></td>
<td>F</td>
<td>-0.144(0.013)</td>
<td></td>
<td>0.639</td>
<td>0.643</td>
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<tr>
<td>CCl$_4$</td>
<td>C</td>
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<td>Cl</td>
<td>-0.043(0.011)</td>
<td>-0.068(0.027)</td>
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<tr>
<td></td>
<td>Cl</td>
<td>-0.043(0.011)</td>
<td></td>
<td>0.732</td>
<td>0.760</td>
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<tr>
<td>CBr$_4$</td>
<td>C</td>
<td>0.073</td>
<td>Br</td>
<td>-0.018(0.011)</td>
<td>-0.051(0.043)</td>
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<tr>
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<td>Br</td>
<td>-0.018(0.011)</td>
<td></td>
<td>0.054</td>
<td>0.095</td>
</tr>
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<td>SiF$_4$</td>
<td>Si</td>
<td>0.500</td>
<td>F</td>
<td>-0.125(0.026)</td>
<td>-0.174(0.079)</td>
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<tr>
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<td>-0.125(0.026)</td>
<td></td>
<td>0.650</td>
<td>0.650</td>
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<td>SiCl$_4$</td>
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<td>-0.124(0.069)</td>
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<td></td>
<td>Cl</td>
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<td></td>
<td>0.581</td>
<td>0.748</td>
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<td>-0.034(0.025)</td>
<td>-0.118(0.090)</td>
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<td></td>
<td>Br</td>
<td>-0.034(0.025)</td>
<td></td>
<td>0.217</td>
<td>0.217</td>
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<tr>
<td>PF$_3$</td>
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<td>-0.099(0.047)</td>
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<tr>
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<td>F</td>
<td>-0.133(0.019)</td>
<td></td>
<td>0.095</td>
<td>0.072</td>
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<td>POF$_3$</td>
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<td>0.563</td>
<td>O</td>
<td>-0.239(0.022)</td>
<td>-0.206(0.051)</td>
</tr>
<tr>
<td></td>
<td>O</td>
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<td></td>
<td>0.671</td>
<td>0.598</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>P</td>
<td>0.164</td>
<td>Cl</td>
<td>-0.055(0.020)</td>
<td>-0.054(0.035)</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
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<td></td>
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<td>POCl$_3$</td>
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<td>0.334</td>
<td>O</td>
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<td>-0.207(0.050)</td>
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<tr>
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<td>O</td>
<td>-0.243(0.022)</td>
<td></td>
<td>0.270</td>
<td>0.307</td>
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<tr>
<td>PSCl$_3$</td>
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<td>0.247</td>
<td>S</td>
<td>-0.138(0.035)</td>
<td>-0.085(0.051)</td>
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<tr>
<td></td>
<td>S</td>
<td>-0.138(0.035)</td>
<td></td>
<td>0.163</td>
<td>0.249</td>
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</table>
\begin{table}[h]
\centering
\begin{tabular}{cccccc}
\hline
 & $q^a$ & $q^b$ & & $q^a$ & $q^b$
\hline
ONF$_3$ & N & 0.412 & 0.222 & OSF$_2$ & S & 0.494 & 0.499
 & O & -0.131(0.020) & -0.031(0.038) & & O & -0.207(0.020) & -0.213(0.045)
 & F & -0.094(0.008) & -0.064(0.021) & & F & -0.143(0.014) & -0.143(0.040)
NO$_2$ & N & 0.181 & -0.011 & OCS & C & 0.150 & 0.167
 & O & -0.091(0.014) & 0.006(0.034) & & O & -0.140(0.023) & -0.151(0.064)
 & S & -0.010(0.033) & -0.016(0.059)
NNO & N & -0.082 & -0.118 & Cl$_2$ & Cl & 0.0 & 0.0
 & N & 0.186(0.026) & 0.127(0.037) & & Br$_2$ & Br & 0.0 & 0.0
 & O & -0.104(0.020) & -0.008(0.037)
CO$_2$ & C & 0.317 & 0.332 & O$_2$ & O & 0.0 & 0.0
 & O & -0.158(0.023) & -0.166(0.068)
CS$_2$ & C & -0.008 & 0.017 & N$_2$ & N & 0.0 & 0.0
 & S & 0.004(0.023) & -0.008(0.053) & C$_2$F$_4$ & C & 0.168 & 0.180
 & F & -0.084(0.017) & -0.090(0.041)
SO$_2$ & S & 0.380 & 0.386 & & & & &
 & O & -0.190(0.019) & -0.193(0.047)
SF$_6$ & S & 0.850 & 0.848 & & & & &
 & F & -0.142(0.008) & -0.141(0.034)
\hline
\end{tabular}
\caption{Charge distribution (\textsuperscript{a}) and binding energy correlation data (\textsuperscript{b}).}
\end{table}

\textsuperscript{a} Charge calculated for $\Delta R_B = 0$ in Equation 6. Binding Energy correlation data: Std. Error = 0.475, RMS Error = 0.270.

\textsuperscript{b} Charges calculated from Equation 6 and allowing $\Delta R_B$ to be an adjustable parameter. The empirically determined values for $\Delta R_B$ (\times 10\textsuperscript{3} \text{Å}) are: C = 0.70(2.39), N = 6.84(1.42), O = -0.01(1.36), F = 0.01 (1.28), Si = -3.74 (8.21), P = 4.07(2.37), S = 0.90(1.46), Cl = 2.49(1.13), Ge = 5.21 (6.46), Br = 4.13(4.01). Binding energy correlation data: Std. Error = 0.332 eV, RMS Error = 0.146 eV.
and the rms and standard errors from both sets of calculations plus the empirical values for $\Delta R_B$ from the second set appear in Table VI. For many molecules, the atomic charges from both sets of calculations are nearly identical. The standard error of the calculations including two-center relaxation is, as expected, lower than the standard error of the calculations neglecting two-center relaxation. The negative value for $\Delta R_{Si}$ is not consistent with the physical description of $\Delta R_B$ in our relaxation corrected potential equation. Attempts to use equation 6 and to allow values for both $k_A$ and $\Delta R_B$ to be adjustable parameters failed. Because of the excessive number of parameters in such a procedure, we were unable to find the least squares solution to that system of equations.

**Conclusions**

Several conclusions may be reached by examining the different sets of calculated charges which have been presented in this chapter. Although our set of experimental core binding energies is fairly large, these experimental chemical shifts are distributed over ten elements. This fact may cause our calculated charges to be sensitive to the choice and number of molecules in the data set as was the case for the xenon fluorides. In addition, there is a great deal of statistical uncertainty for most of the charges and for the $k$ and $l$ parameters. However, the following results may be inferred from the charge calculations. When the effects from two-center relaxation are entirely neglected, and when $k$ is allowed to be an adjustable parameter, the calculated values for the $k$'s and the charges combine to minimize the effect on binding energies of the electrostatic potential due to the nonionized atoms in a molecule. More specifically, in terms of equation 6, when $\Delta R_B$ was neglected the resulting large values
of k and the small charges caused the \((k_A + \langle w_R \rangle_A)(Z_A - q_A)\) term to dominate the summation, \(\sum_{B \neq A} q_B/R_{AB}\). Although early workers with ESCA did assume that binding energies were simply proportional to the charge of the ionized atom,\(^{11}\) it has been shown that the electrostatical potential equation is a more correct description of ESCA chemical shifts.\(^6\)

The inclusion into the potential equation of a simple expression for two-center relaxation helps to correct this behavior. However, our electrostatic, through-space model for two-center relaxation may be too simple to quantitatively account for all of the electronic rearrangement that occurs during photoionization. If more experimental data were available, it might be possible to improve the model by using a more sophisticated expression for \(\Delta R_B\), perhaps by letting \(\Delta R_B\) be a function of such chemical quantities as bond order and formal charge as well as of polarizability.

For our set of data and using equation 6, the best procedure for calculating charges probably is to use the theoretically estimated values for k and allow \(\Delta R_B\) to be an adjustable parameter. Even when \(\Delta R_B\) is neglected, reasonable values for most charges are calculated using the theoretical values for k in equation 6. Thus it may be worthwhile to obtain better theoretical values for k. For example, by using wavefunctions for atoms in molecular environments to calculate k rather than using free atom wavefunctions.

Finally, in order to provide an independent set of charges to compare against the charges calculated using equation 6, we have made CND0/2\(^{12}\) semi-empirical molecular orbital calculations for the molecules in our
data set. The parameters which we used in CNDO/2 calculations have been previously described. The CNDO/2 charges are listed in Table VII. An overall comparison of the CNDO/2 charges with those calculated using the electrostatic potential equation shows that the CNDO/2 charges have greater magnitudes than even the charges listed in Table VI. However, we believe that the CNDO/2 calculations for many molecules are too polarized, that is that the charges are too large. It is more important to notice that many of the trends in atomic charges along series of related molecules from the data set are the same for the CNDO/2 charges and for those found in Tables V and VI. We believe that it should be possible to calculate atomic charges in molecules from core binding energy chemical shifts which approach physically "real" quantities. In order to develop this approach, more experimental data is definitely required. The inclusion of core binding energies from more molecules should reduce the sensitivity of the calculated charges as to the choice and size of the data set. Finally, it is necessary to explicitly include the effects of two-center relaxation, especially if the values for \( k \) are to be calculated empirically. More work needs to be done in developing a model to quantitatively describe this relaxation.
<table>
<thead>
<tr>
<th></th>
<th>Atomic Charges from CNDO/2 Molecular Orbital Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₄</td>
<td>C  0.804 PSCl₃ P 0.665 GeBr₄ Ge 0.280</td>
</tr>
<tr>
<td></td>
<td>F -0.201 S -0.419 Br -0.070</td>
</tr>
<tr>
<td>CCl₄</td>
<td>C  0.400 Cl -0.082 ONF₃ N 0.709</td>
</tr>
<tr>
<td></td>
<td>Cl -0.100 SO₂F₂ S 0.882 O -0.133</td>
</tr>
<tr>
<td>CBr₄</td>
<td>C  0.256 O -0.127 NO₂ N 0.410</td>
</tr>
<tr>
<td></td>
<td>Br -0.064 F -0.314</td>
</tr>
<tr>
<td>SiF₄</td>
<td>Si 1.288 SF₅Cl S 1.360</td>
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<tr>
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<td>POF₃</td>
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<td>C₂F₄ C 0.396</td>
</tr>
<tr>
<td></td>
<td>F -0.198</td>
</tr>
</tbody>
</table>

*a Calculation was not self-consistent.*
REFERENCES


(4) W. L. Jolly, in D. A. Shirley (editor); "Electron Spectroscopy," North Holland, Amsterdam, 1972, p. 629.


(13) Our CNDO/2 parameters are described in Chapter 1 of this thesis in the section on calculations.
Except for one instance, the correlations of CNDO/2 valence potentials with core binding energy chemical shifts reported in Chapters 1 and 2 of this thesis gave values of less than unity for c, the parameter which scales the valence potentials. See also the CNDO/2 correlations reported in reference 6.
APPENDIX A

A Description of Program ESCHAR

Program ESCHAR is a Fortran IV computer program which calculates atomic charges in molecules from core binding energy chemical shifts using a form of the electrostatic potential equation. Program ESCHAR requires approximately 62,600 (octal) core memory to load and 52,300 (octal) core memory to execute using the RUN76 Fortran compiler for the CDC 7600 computer at the Lawrence Berkeley Laboratory. The program determines atomic charges from core binding energies by the method of general least squares analysis, where the atomic charges and certain other terms in the potential equation are treated as parameters. As dimensioned in this writeup, the program can accept up to 150 parameters, of which up to 120 may be varied. The program can accept molecules having up to 10 atoms, and the number of binding energies plus the number of molecules in the data set must be equal to or less than 200.

Program ESCHAR is derived from the Oak Ridge general least squares computer program, program ORGLS. A complete description of this program is given in: W. R. Busing and H. A. Levy, "ORGLS, A General Fortran Least Squares Program," Oak Ridge National Laboratory Report ORNL-TM-271, 1962. The electrostatic potential equation used in program ESCHAR has the form:

\[ E_B(A) = \ell_A - (k_A + <V_{R>}_A)(Z_A - q_A) + e^2 \sum_{B \neq A} \frac{q_B}{R_{AB}} - \]

\[ (Z_B - q_B)(Z_A + 1)[(R_{AB} - \alpha P_B)^{-1} - R_{AB}^{-1}] \]  

(1)

where \( \ell, k, q, P, \) and \( \alpha \) are parameters. The partial derivatives of the binding energy with respect to the different parameters, which are required
by the program, are calculated analytically. Least squares refinement of the parameters continues until some specified maximum number of cycles is reached or until the analysis converges. A converged solution for the equations is assumed when the standard error changes by less than 0.0001 or by 0.01%, whichever is greater, for three consecutive cycles.

Data input for this program is fairly complex. Therefore, an entire data set is presented for an example of how to prepare data for the program. The xenon fluoride data of T. D. Thomas, et al., consists of five compounds, Xe, XeF$_2$, XeF$_4$, XeF$_6$, and F$_2$, for which eight binding energies were measured. The charge distributions in these molecules are specified by eight charges. However, only three of these charges are independent quantities. We shall take these to be $q_{Xe}(XeF_2)$, $q_{Xe}(XeF_4)$, and $q_{Xe}(XeF_6)$. The remaining charges are known, e.g. $q_F(F_2) = 0$ and $q_F(XeF_2) = -\frac{1}{2}q_{Xe}(XeF_2)$. Other parameters are $\ell_F$, $k_F$, $\ell_{Xe}$, $k_{Xe}$, $P_F$, $P_{Xe}$ and $\alpha$. We shall vary the $\ell$ and $k$ parameters and specify the values for $P_F$, $P_{Xe}$, and $\alpha$.

The following is a card by card description of Table I, the sample data set.

Card 1

columns 1-80: The title for this data set. Format (10A8)

Card 2

columns 1-5 (right justified): the number of parameters to be varied.

columns 6-10 (right justified): the maximum number of independent variables.

If the largest molecule in the data set contains $n$ atoms, one may always punch $n$ in this field and usually $n - 1$. 
TABLE I.
SAMPLE DATA FOR PROGRAM ESCHAR

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<td>L(KE) 100.</td>
</tr>
<tr>
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<td>Q(KF) 0.9</td>
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<td>Q(F,KEF6) 0.7</td>
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</tr>
<tr>
<td>5</td>
<td>6</td>
<td></td>
</tr>
<tr>
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<td>3</td>
<td>4</td>
</tr>
<tr>
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<td>5</td>
<td></td>
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<tr>
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<td>8.2</td>
<td>9</td>
</tr>
<tr>
<td>-4.60</td>
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<td>2</td>
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<tr>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
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<td>4</td>
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<tr>
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<td>5</td>
<td>5</td>
</tr>
<tr>
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<td>10</td>
<td>4</td>
</tr>
<tr>
<td>-3.38</td>
<td>1</td>
<td>2</td>
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<td>13</td>
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<tr>
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<td>5</td>
<td>6</td>
</tr>
<tr>
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<td>3</td>
<td>4</td>
</tr>
<tr>
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<td>1.89</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
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<td>12</td>
<td>6</td>
</tr>
<tr>
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<td>1.417</td>
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</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

* THIS LINE REPRESENTS A BLANK CARD IN THE DATA SET.
columns 11-15 (right justified): Maximum number of cycles of least squares analysis. (Default value is 25). Format (3I5)

Card 3

columns 1-5 (right justified): The total number of parameters in the data set. Format (I5).

Cards 4 ...

columns 1-10, (21-30, 41-50, 61-70): The alphabetic names for the parameters.
columns 11-20 (31-40, 51-60, 71-80): The initial values of the parameters to be used in cycle 1 of the least squares analysis.

Format (4(A10, F10.5))

*NOTE* The program assigns indices to the parameters from the order in which they are read in. Thus the first parameter (columns 11-20) is $p_1$, the second parameter is $p_2$, etc. The last parameter must be the $\alpha$ parameter from equation 1.

Cards 5 ...

columns 1-4, (5-8, 9-12, ...; right justified): the atomic number assigned to each parameter. Actually only the charge parameters require atomic numbers and so the first entry on this card is 54, the atomic number of Xe, and this entry is the atomic number for $q_{\text{Xe}}(\text{Xe})$. Because $q_{\text{Xe}}(\text{Xe})$ is the seventh parameter, the atomic number of Xe is placed in the seventh field (columns 25-28) of the card. Format (20I4)

Cards 6 ... (For a free atom binding energy)
columns 3-12: The core binding energy for a free atom in the data set.

In this case $E_B(\text{Xe}) = 0.0$. 
columns 13-15 (right justified): The index of the appropriate $\ell$ parameter. In this case 3 because $p_3 = \ell_{\text{Xe}}$.

columns 17-19 (right justified): The index of the appropriate $k$ parameter. In this case 4 because $p_4 = k_{\text{Xe}}$.

columns 21-23 (right justified): The index of the appropriate $q$ parameter. In this case 7 because $p_7 = q_{\text{Xe}}(\text{Xe})$.

*NOTE* For a free atom binding energy each card six must be followed by a blank card, or, if the number in columns 6-10 of Card 2 is greater than 3, by two blank cards.

Cards 8 ... (For a free atom binding energy)

columns 3-12: The net charge on the free atom (presumably zero).

columns 25-27 (right justified): The index of the $q$ for the free atom. In this case 7 because $p_7 = q_{\text{Xe}}(\text{Xe})$.

columns 29-36: The number 1.0

*NOTE* If the number in columns 6-10 of card 2 is greater than 3, this card must be followed by a blank card.

Cards 6 ... (For a molecular binding energy)

columns 3-12: The first core binding energy for a free molecule in the data set. In this case $E_B(\text{F, XeF}_2) = -5.48$.

columns 13-15 (right justified): The index of the appropriate $\ell$ parameter. In this case 1 because $p_1 = \ell_{\text{F}}$.

columns 17-19 (right justified): The index of the appropriate $k$ parameter. In this case 2 because $p_2 = k_{\text{F}}$.

columns 21-23 (right justified): The index of the appropriate $q$ parameter. In this case 8 because $p_8 = q_{\text{F}}(\text{XeF}_2)$.

columns 25-27 (right justified): The index of a charge for the first atom $B$ in the summation $\sum_{B\neq A} p_8 = q_{\text{F}}(\text{XeF}_2)$ is also the charge for the other F atom in XeF$_2$. 

columns 29-36: The internuclear distance, in Angstroms, between the ionized atoms (specified in columns 21-23) and the atom specified in columns 25-27.

Up to 3 additional atoms and internuclear distances may be punched on card 6 in the following columns.

columns 37-39, 49-51, 61-63 (all right justified): Indices for B₂, B₃, and B₄.


Format (2X, F10.5, 3(I3, 1X), 4(I3, 1X, F8.6), 8X)

*NOTE* If there are more than 4 nonionized atoms in the molecule, the indices Bᵢ and the distances R_ABᵢ for i>4 are punched on a separate card which immediately follows the appropriate Card 6. Use the Format (6(I3, 1X, F8.6), 8X).

*NOTE* If the number punched in columns 6-10 of Card 2 is greater than 3, then each Card 6 must be followed by either a blank card or by the card having Bᵢ and R_ABᵢ for i>4.

Card 7

columns 1-4, (5-8, 9-12, ... , 37-40; all right justified): The indices of the P_B parameters in equation 1 for the atoms B≠A on the previous Card 6. In this case 5 and 6 because the atoms Bᵢ in XeF₂ for the E₉(F) are the nonionized F and the Xe, respectively, and P₅ = P_F while P₆ = P_Xe.

*NOTE* The next 3 cards are the Cards 6 and the Card 7 for E₉(Xe, XeF₂).

After all the binding energies for a molecule have been read into the program (in the case for XeF₂ there are only E₉(F) and E₉(Xe)), the next
card (or two cards) represent the charge neutrality equation for that molecule.

Cards 8 ... (for a molecular binding energy)
columns 3-12: The total charge of the molecule (zero for a free molecule)
columns 25-27 (right justified): The index of the first charge in the molecule. In this case 8 because \( q_8 = q_p(XeF_2) \)
columns 28-36: The number of atoms in the molecule which have that charge. In this case 2 because there are two equivalent fluorine atoms.

The charge neutrality information for up to 3 more atomic charges may be added onto Card 8. The indices, \( i \), of the charges go into columns 37-39, 49-51, 61-63 (all right justified), and the respective number of times these charges occur in the molecule go into columns 40-48, 52-60, 65-72.

Format (2X, I10.5, 12X, 4(I3, I1X, F8.6), 8X)

*NOTE* If there are more than four different charges in a molecule, continue listing the indices and multiplicities on the next card using the format (6 (I3, I1X, 8F.6), 8X) for up to 6 more charges. If the number punched in columns 6-10 of Card 2 is greater than 3, then each Card 8 must be followed with either a blank card or by one of these extra data cards.

The remaining cards in the sample data set, except for the very last card, describe the binding energy equations followed by the charge neutrality equations for \( XeF_4 \), \( XeF_6 \), and \( F_2 \) respectively. Punch a 1 in column 2 of the last charge neutrality equation in the data set in
order to designate the end of the experimental data.

Cards 9 ...
columns 1-4 (right justified): The number of fixed parameters in the data set, i.e. the number of parameters which will not be varied and thus will retain their initial values. In this case 3.
columns 5-8, (9-12, 13-16, ...; right justified): The indices of the fixed parameters. In this case 5, 6, 15 because we are fixing $p_5 (P_F)$, $p_6 (P_{Xe})$, and $p_{15}(a)$.

Format (2014)

This completes the sample data set.
APPENDIX B
A LISTING OF PROGRAM ESCAR

PROGRAM ESCAR = INPUT, OUTPUT, TAPE1 = INPUT, TAPE2 = OUTPUT

PROGRAM ESCAR IS A GENERAL LEAST SQUARES PROGRAM FOR DETERMINING
ATOMIC CHARGES IN MULTICLUS FROM ESCA CORE BINDING ENERGY CHEMICAL
SHIFTS. BINDING ENERGY DATA IS FIT TO A RELAXATION CORRECTED
VERSIBILITY OF THE ELECTROSTATIC POTENTIAL EQUATION, AND THE ATOMIC
CHARGES AND MODEL PARAMETERS ARE VARIED UNTIL BEST LEAST SQUARES
VALUES ARE OBTAINED.

THIS PROGRAM WAS ADAPTED FROM THE OAK RIDGE PROGRAM CRGS BY

***INPUT***
CARD 1
   TITLE FORMAT (10A8)
CARD 2
   NV,NX,NC (DEFAULT = 25) FORMAT (3I5)
CARD 3
   NP FORMAT (15) 
CARD 4
   PNAME(i),P(i),I=1,NP FORMAT (4(A10,F10.5))
CARD 5
   NC(1),NC=25 FORMAT (14I4)
CARD 6
   ISANT,YG,INDEX,X FORMAT (12,F10.5,3(I3,1X),4(I3,1X,F8.6),8X/(6(I3,1X,F8.6),8X)
CARD 7
   IX FORMAT (1014)
CARD 8
   NK,(INDEX(I),I=1,NK)

DIMENSION AM(720),XM(120),YM(120)
DIMENSION PNAME(120),P(120),ROW(120),PNAME(150),INDEX(150)
DIMENSION TITLE(10)

COMMON/ARRAYS/KI(150),KY(150),INDEX(150),DC(150),P(150),
LY(120),XM(120),YM(120),INDEX(150)
WRITE (9,1)
READ TITLE AND CONTROL CARD
READ (10,154) TITLE
READ (9,156) TITLE
IF (NC GT 10) NC=25
WRITE (9,165) NV,NX,NC
WRITE (9,162)
WRITE (9,164)
WRITE (9,170)
READ TRIAL PARAMETERS
READ (10,174) NP,PNAME(I),P(I),I=1,NP
WRITE (9,166)
A 1
A 2
A 3
A 4
A 5
A 6
34 WRITE (9,170) NP
   C
   READ (10,177) (*2(I),I=1,NP)
   C
   READ OBSERVATIONS TO SENTINEL
   J=0
   C
   36 J=J+1
   READ (10,178) ISENT,YC(J),INDEX(I,J),I=1,3),INDEX(I+3,J),X(I,J),
   1 I=1,NX)
   IF (INDEX(I,J)+1 .GT. 1) READ (10,175) (IX(I,J),I=1,NX)
   IF (ISENT) 36,33,31
   C
   38 NW=J
   WRITE (9,180) J
   WRITE (9,178) (*2(INDEX(I,J)),I=1,NP)
   C
   READ KEY INTEGERS AND PARAMETER INCREMENTS IF SPECIFIED
   READ (10,177) NK, (K1(NK(I),I=1,NK)
   C
   DO 40 I=1,NP
      K1(I)=1
   40 CONTINUE
   C
   WRITE (9,183)
   C
   M00=M0
   DO 45 I=1,N00
      IF (INDEX(I+1,J)+1 .EQ. 1) 42,45
      42 J=INDEX(I+1,J)+1
      K1(J)=K1(J)+1
      M0=M0+1
      IYD(IYD)+1
      45 CONTINUE
   DO 50 I=1,NK
      K1(K1(I))=INDEX(I)
      IF (K1(I)-1 .EQ. 1) M0=M0+1
      K1(I)=0
   50 CONTINUE
   C
   WRITE (9,184) K1,P(K1)
   C
   WRITE (9,185) N0,NV
   C
   INITIALIZE PROBLEM AND ENTER SUBROUTINE PRELIM IF PROVIDED
   N0=N0+1
   SAVE=0.2
   10 STOP=1
   C
   PUT OUT TRIAL PARAMETERS, KEY INTEGERS, AND PARAMETER INCREMENTS
   WRITE (9,208)
   DO 54 I=1,NP
   54 WRITE (9,210) I,PNAME(I),P(I)
   C
   START LOOP TO PERFORM NC CYCLES AND ONE FINAL CALCULATION OF Y
   NCY=NC+1
   DO 134 IC=1,NCY
   C
   CLEAR ARRAYS 44 AND V EXCEPT ON LAST CYCLE
   IF (IC-NCY) 56,62,62
   C
C BY-PASS IF DERIVATIVE IS ZERO
C
84 JK=JK+1
G0 TO 93
C
86 DO 98 K=J,NV
  AM(JK)+AM(JK)+TEMP=DV(K)
  JK=JK+1
88 CONTINUE
C
90 CONTINUE
C FIN LOOP TO STORE MATRIX AND VECTOR
C
92 CONTINUE
C END LOOP THROUGH NO OBSERVATIONS
C
93 COMPUTE AND PUT CUT AGREEMENT FACTORS
  FAC=FLMAT*A
  IF (FAC .EQ. 0.0) FAC=1.0
  SOSIG=SIG/FAC
  SAVE=SOSIG
  WRITE (9,181)
  WRITE (9,192) IC,SIG,SOSIG
C
94 BY-PASS MATRIX INVERSION AND PARAMETER OUTPUT ON FINAL CYCLE
  IF (IC=NCY) 94,138,136
96 IF (ISTIP) 95,95,132
C
95 START LOOP TO TEST FOR ZERO DIAGONAL ELEMENT
   II=0
60 IF NT=1,2
   ON 105 II=1,2
   IF (AM(II)) 98,46,98
99 IF (II=II+10)
   II=II-1
100 CONTINUE
C END LOOP TO TEST FOR ZERO DIAGONAL ELEMENT
C
101 TERMINATE JCR IF ZERO DIAGONAL ELEMENT WAS FOUND
   IF (II=1) 144,132,148
C
102 CALL SUBROUTINE TO REPLACE MATRIX WITH INVERSE
       CALL MATINV (AM,NV,ISING)
       IF (ISING) 104,106,104
       IF (II=1) 144,132,148
C TERMINATE JCR IF SINGULAR MATRIX WAS FOUND
104 WRITE (9,198)
   GO TO 148
C
106 START LOOP FOR MATRIX VECTOR MULTIPLICATION FOR
   PARAMETER CHANGES
108 PD1=0.0
CONV<? 0.00 5C 1•1.~~   5C 1-MC  
PIITULIZ:  1 II•'·~  
VCIIcO,0  
PJIT  
CYCLE I AND PUT OUr CAPTION FOR LIST OF Y(CALC)  
START LOOP THROUGH MC OBSERVATIONS  
DO 92 I=1,NOO  
DO 65 J=1,NP  
65 DC(J)=0.0  
ENTER USERS SUBROUTINE TO COMPUTE Y(CALC) AND DERIVATIVES  
CALL CALC(I,KP,NX,YC)  
68 D(Y=0)(I)-YC  
SIG=SIG+DY**2  
PUT OUT Y(CALC) AND OTHER INFORMATION FOR ONE OBSERVATION  
WRITE (9,190) YC(I),YC,DY,(INDEX(J,I),J=1,3),(INDEX(J+3,I),X(J,I),  
1 J=1,NX)  
IF (INDEX(I,J)=*EO. 1) GC TO 92  
IF (IC =EO. 1) WRITE (9,191) (IX(J,I),J=1,NX)  
BY-PASS DERIVATIVE AND MATRIX SET-UP ON FINAL CALC OF Y  
IF (IC-NCY) 73,92,92  
70 IF (ISTOP) 72,72,92  
START LOOP TO STORE AN ARRAY OF NV DERIVATIVES  
72 J=1  
DO 82 K=1,NP  
82 IF (KI(K)) 82,82,74  
OBTAIN DERIVATIVE FROM THOSE PROGRAMMED BY USER  
74 DO(J)=DC(K)  
80 J=J+1  
82 CONTINUE  
END LOOP TO OBTAIN DERIVATIVES  
START LOOP TO STORE MATRIX AND VECTOR.  
1634 OR GLS STORAGE SCHEME IS REVERSE OF 7090 OR GLS  
JK=1  
DO 90 J=1,NV  
90 TEMP=DV(J)  
IF (TEMP) 84,84,86
110 DIAGONAL ELEMENTS OF INVERSE MATRIX

112 J = I * 1
114 CONTINUE

116 CONTINUE. LNO LOOP FOR MATRIX VECTOR MULTIPLICATION

C

RECOMPUTE AGREEMENT FACTOR USING MODIFIED SIG
FAC*FLOAT(IND-INV)
IF (FAC .LE. 0.0) FAC = 1.0
SIG = ABS(SIG)
SIGSIG = SQRT(F(SIG/FAC))

C

PUT OUT CAPTION FOR LIST OF CORRECTED PARAMETERS
WRITE (9,101)
WRITE (9,150) TITLE
WRITE (9,180)
WRITE (9,220) IC

C

START LOOP TO CORRECT AND PUT OUT PARAMETERS

C

J = 1
DO 122 I = 1, NP

C

IF (K(I)) 118, 118, 120

C

118 WRITE (9,222) I, PNAME(I), P(I), P(I)
GO TO 122

C

120 POLDO = P(I)
P(I) = POLDO + PD(J)
SIGSIG = SQRT(F(DIAG(J))*SIGSIG
WRITE (9,204) I, PNAME(I), POLDO, PD(J), P(I), SIG
J = J + 1

C

122 CONTINUE
DO 125 I = 1, NP

C

123 II = KYO(I)
P(I) = Y0(I)/X(1, II)
DO 124 J = 2, NX
IF (INDEX(J+3, 11) + 1 .EQ. 1) GO TO 124
TJ = INDEX(J+3, 11)
P(I) = P(I) - P(I)*X(J, 11)/X(1, II)

C

124 CONTINUE
125 CONTINUE. END LOOP TO CORRECT AND PUT OUT PARAMETERS
C PUT PUT ESTIMATION AGREEMENT FACTORS
WRITE (*,181)
WRITE (*,194) IC,SIG,SUSIG
WRITE (*,181)
C ENTER USERS SUBROUTINE TO TEST AND MODIFY PARAMETERS
C OR END JOB
CALL TEST(SAVE1,SAVE2,ISTOP)
C TERMINATE JOB IF INDICATED BY USERS SUBROUTINE TEST
130 IF (ISTOP) 134,134,62
C 122 WRITE (*,181)
WRITE (*,236) ISTOP
G0 TO 130
C 134 CONTINUE
C END LOOP THROUGH NC CYCLES AND FINAL CALC OF Y
C TERMINATE JOB
136 IF (NC) 132,132,138
C CALCULATE AND PUT GUT CORRELATION MATRIX
138 WRITE (*,156) TITLE
WRITE (*,219)
DO 140 I=1,NI
C DIAG(I)=I/500*DIAG(I)
140 CONTINUE
C I=1
DO 146 J=1,NI
C DO 142 J=1,NI
C ROW(JJ)=3.0
142 CONTINUE
C DO 144 J=1,NI
C DO 144 J=1,NI
C ROW(JJ)=AM(IJJ)*DIAG(I)*DIAG(J)
C 144 CONTINUE
C WRITE (*,220) I,(ROW(JJ),J=1,NI)
146 CONTINUE
C 148 CONTINUE
152 CONTINUE
C STOP
C FORMAT STATEMENTS
C FORMAT 111,111,111,111 /* */ PROGRAM ECHARM /* */ ATOMIC CHARGE
1 DETERMINATIONS FROM CORE BUNDING ENERGY CHEMICAL SHIFTS USING /
2 / 10K,50AU RELAXATION CORRECTED ELECTROSTATIC POTENTIAL EQUATION
3 J I=1,SUM(HH[I]{K+VR)*[12-2I]+SUM(0R/P-128-QD)*[2A+1]*1/(R-6P)
A-1/R))*)L /* */
SUBROUTINE CALC(I,NP,NK,Y)
C SUBROUTINE CALC CALCULATES BINDING ENERGIES USING THE POINT CHARGE
C POTENTIAL EQUATION WRITTEN IN THE FORM EN=K*Q*V VALUES FOR K,L,
C AND THE U'S ARE THE PARAMETERS. THE IV/ TERMS IN V ARE THE
C INDEPENDENT VARIABLES
C
COMM(ARRAYS/K/I(150),K/Y(I(150)),INDEX(I(13,200)),D(150),P(I50)),
1 YV/O,200,X1O,2003),N(1(150),I(10,200))
C
154 FORMAT(10H)
155 FORMAT(1X,1CAH) A 35.
156 FORMAT(15H) A 36.
157 FORMAT (15H) A 36.
158 FORMAT (5X,3H) A 36.
159 FORMAT (5X,3H) A 36.
160 FORMAT (10H) A 36.
161 FORMAT (10H) A 36.
162 FORMAT (5X,3H) A 36.
163 FORMAT (5X,3H) A 36.
164 FORMAT (5X,3H) A 36.
165 FORMAT (5X,3H) A 36.
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218 FORMAT (5X,3H) A 36.
219 FORMAT (5X,3H) A 36.
220 FORMAT (5X,3H) A 36.
221 FORMAT (5X,3H) A 36.
222 FORMAT (5X,3H) A 36.
223 FORMAT (5X,3H) A 36.
D(I,J)=D(I,J)-1.4*X(J,J,K)*X(1,K)/X(1,K)-1.4*X(J,J,K)*X(1,K)*
1*(L(I,J))**2*(1.0/X(J,J,I)-P(NP)*P(NP))-1.0/X(J,J,I)
D(NP)=D(NP)-T**2*(X(J,J,I)-P(NP))*P(NP)**2*(P(NP))
110 CONTINUE
GO TO 130
120 TERM=1.4*(Z(J,J,I)-P(I,J))*Z(1,J)*1.0
Y=1.4*(Z(J,J,I)-T**2*(X(J,J,I)-P(NP)*P(NP))-1.0/X(J,J,I)
D(I,J)=D(I,J)-1.4*X(J,J,I)-1.0*(Z(1,J)+1.0/X(J,J,I)-P(NP))
1*(P(NP))-1.0/X(J,J,I)
D(NP)=D(NP)-T**2*(X(J,J,I)-P(I,J))*P(NP)**2*(P(NP))
130 CONTINUE
RETURN
END

SUBROUTINE MATINV (AM,N,NFALL)
DIMENSION AM(1,1)

C ************ SIGNED 1 OF CHOLESKI INVERSION ************
C ***** FACTOR MATRIX INTO LOWER TRIANGLE X TRANSPOSE *****
K=1
IF (N-1) 16,2,4
2 AM(1)=1.0/N(1)
GO TO 36
C ***** LOOP M OF A(L,M) *****
4 DO 22 M=1,N
[IMAX=M-1]
GO TO 36
C ***** LOOP L OF A(L,M) *****
5 DO 20 L=M,N
SUMA=0,0
KLI=L
KMI=M
IF (IMAX) 10,10,6
6 DO 8 I=1,1,M
SUMA=SUMA+AM(KLI)*AM(KMI)
8 J=N-I
J=N-I
KLI=KLI+J
8 KMI=KMI+J
10 TERM=AM(K)-SUMA
IF (L=M) 12,12,19
12 IF (TERM) 10,10,14
C ***** A(M,M)=SQRT(TERM) *****
14 DENOM=SUMF(TERM)
AM(K)=DENOM
GO TO 20
16 NFALL=K
GO TO 38
C ***** A(L,M)=TERM/AM(M,M) *****
18 AM(K)=TERM/DENOM
20 K=K+1
22 CONTINUE
C ************ SEGMENT 2 OF CHOLESKI INVERSION ************
C ***** INVERSION OF TRIANGULAR MATRIX *****
AM(1)=1.0/AM(1)
123

DO N=1,10

DATA (Z(i,j))=1.0

DATA (Z(i,j))=1.0,0.5,0.0,0.7,0

DATA (Z(i,j))=1.0,0.5,0.0,0.7,0

DATA (V(i,j))=1.0

DATA (V(i,j))=1.1,1.0

DATA (V(i,j))=1.0,0.76,0.735,0.700

DATA (V(i,j))=1.0,0.76,1.178,0.780

Y=0.0

IF (INDEX(1,1)=1.0,0.1) 5,10

5 Y=Y+YP(1)

GO TO 140

10 I=INDEX(1,1)

12=INDEX(1,1)

J=INDEX(1,1)

NZ=INDEX(1,1)

DO 30 J=1,N

30 IF (K(I,J)) 20,30,30

20 IF (I,EQ. J) 40,50

C=CONTINUE

GO TO 60

40 K=KEY(13)

Y=Y+P(I,J)*Z(I,J)*V(K,J)/X(I,J)+P(I,J)*X(I,J)*V(K,J)

10 W=INDEX(1,1)

D(I,J)=0.1

D(I,J)=D(I,J)-Z(I,J)

DO 50 J=2,N.

IF (INDEX(I,K)) .5.0, 1.0 GO TO 50

J=INDEX(J,1)


D(I,J)=D(I,J)+V(I,J)

50 CONTINUE

GO TO 70

60 Y=Y+P(I,J)*Z(I,J)*D(I,J)-P(I,J)*D(I,J)-Z(I,J)*D(I,J)

70 DO 80 J=1,N.

IF (INDEX(J)) .5.0, 1.0 GO TO 80

J=INDEX(J,1)

NZ=INDEX(J,1)

NR=INDEX(J,1)

DO 90 JJ=1,N.

IF (K(I,J,J)) 40,90,90

80 IF (J.EQ. J) GO TO 100

90 CONTINUE

GO TO 120

100 K=KEY(13)

TERM=1.0*Z(I,J)*V(K,J)/X(I,J,J)+Z(I,J)*P(N)*P(N)

Y=Y+4.0*V(K,J)/X(I,J,J,1)-TERM*1.0/X(I,J,J,1)-P(N)*P(N)

J=INDEX(J,1)

D(N)=TERM/X(I,J,J,1)-P(N)*P(N)+2*P(N)

D(N)=TERM/X(I,J,J,1)-P(N)*P(N)+2*P(N)

DO 110 JJ=2,N.

IF (INDEX(J,J)) .5.0, 1.0 GO TO 110

J=INDEX(J,J,1)

TERM=1.0*P(I,J)*X(J,J,J,1)+Z(I,J)*P(N)

Y=Y+1.4*P(I,J)*X(J,J,J,1)+Z(I,J)*P(N)

10 P(N)=1.0/X(I,J,J,1)
SUBROUTINE TEST(SAVE1,SAVE2,ISTOP)

SUBROUTINE TEST TERMINATES THE REFINEMENT IF THE CHANGE IN SQSIG
DIVIDED BY SQSIG IS LESS THAN 0.0001.

IF (ABS(SAVE2) .LE. 1.0D0) 10,20
10 T=(SAVE1-SAVE2)
 GO TO 30
20 T=(SAVE1-SAVE2)/SAVE2
30 IF (ABS(T) .LT. 0.0001) ISTOP=ISTOP+1
 SAVE1=SAVE2
 RETURN
FUNCTION FLOAT
FLOAT=FLOAT
RETURN
END
FUNCTION Sort
SORT=SORT
RETURN
END
IV. VALENCE ELECTRON BINDING ENERGIES OF SOME SILICON COMPOUNDS FROM X-RAY PHOTOELECTRON SPECTROSCOPY

Abstract

X-ray photoelectron spectra in the valence electron region were obtained for gaseous SiH₄, SiH₃CH₃, Si(CH₃)₄, SiH₃Cl, and SiF₄. The experimental ionization potentials and relative peak intensities are consistent with extended Hückel theory MO calculations. The data can be rationalized without assuming substantial participation of silicon d orbitals in the bonding of these compounds.

Introduction

Photoelectron spectroscopy enables one to measure molecular ionization potentials (IP's) which are lower than the energy of the ionizing photon. Koopmans' theorem¹ states that, in the absence of electronic relaxation, IP's are given by the negative of orbital energies. For valence electron IP's, which are below 50 eV, the error introduced by Koopmans' theorem seems to be less than a few electron volts. Thus calculated orbital energies for valence molecular orbitals (MO's) agree fairly well with the experimental IP's, and the ordering of the MO's taken from a photoelectron spectrum almost always agrees with that from a good ab initio MO calculation.²

Most valence electron IP's are measured using ultraviolet photoelectron spectroscopy³ (UPS) because this method has high resolution. However, IP's from MO's of high binding energy are inaccessible in the common form of UPS, and Jahn-Teller distortions during photoemission degrade the spectra of some molecules. Although X-ray photoelectron
spectroscopy\(^2\) (XPS) has poorer resolution than UPS, the higher energy IP's can be measured, and Jahn-Teller distortions have not been observed. Also, the development of a simple method of intensity analysis\(^4\) for XPS makes the MO assignments of the spectral bands more certain.

We have measured the gas-phase XPS valence electron IP's for SiH\(_4\), SiH\(_3\)CH\(_3\), Si(CH\(_3\))\(_4\), SiH\(_3\)Cl, and SiF\(_4\). These spectra have been interpreted with the aid of simple extended Hückel theory (EHT) MO calculations.\(^5\) In all cases the ordering of the MO's by the EHT calculations was consistent with spectral intensities, and there was reasonable agreement between the experimental IP's and the calculated orbital energies.

**Experimental**

Silane,\(^6\) SiH\(_3\)CH\(_3\),\(^7\) SiH\(_3\)Cl,\(^8\) and SiF\(_4\)\(^9\) were prepared using standard methods and purified by vacuum distillation. Practical grade Si(CH\(_3\))\(_4\) was obtained from Matheson, Coleman, and Bell Co. Infrared spectra were taken of all the compounds and compared with literature spectra to ensure purity.\(^10\)

XPS spectra were taken on the Berkeley iron-free double-focussing magnetic photoelectron spectrometer.\(^11\) Sample pressure in the irradiation chamber was approximately 70\(\mu\). Magnesium K\(\alpha\) X-rays (1253.6 eV) were used to obtain the spectra of SiH\(_4\), SiH\(_3\)Cl, and SiF\(_4\). Aluminum K\(\alpha\) X-rays (1486.6 eV) were used to obtain the spectra of SiH\(_3\)CH\(_3\) and Si(CH\(_3\))\(_4\) because the K\(\alpha_3,4\) satellite radiation from aluminum interfered less with the spectra of these molecules than did that from magnesium. Binding energies in this work represent vertical Franck-Condon transitions and were standardized against the neon 2s binding energy (48.42 eV). During referencing, both neon and the sample gas were present in the irradiation chamber.
Calculations

The spectra were deconvoluted to obtain band positions and relative band intensities by least-squares fitting of the data to analytical lineshapes. For the more complex spectra, different initial deconvolutions of the experimental data into individual bands were refined by least-squares analysis to ensure that the reported values represent a true minimum in the least-squares parameter surface. The uncertainties in band positions and in relative band intensities, given in the tables, are statistical uncertainties taken from the response matrices of the converged, least-squares refined deconvolutions. In a few instances, where the statistical uncertainties were very low, we have reported higher values, based upon our experience with the reproducibility of experimental values. Lorentzian or Gaussian lineshapes are normally used to fit XPS data. We have found that Lorentzian lineshapes give better fits for spectra taken with magnesium Kα X-rays, while Gaussian lineshapes give better fits when aluminum Kα X-rays are used. This observed behavior may originate in the greater energy separation of the aluminum Kα1 and Kα2 X-rays. Thus, the SiH₄, SiH₃Cl, and SiF₄ spectra were fit to Lorentzian lineshapes, and the SiH₃CH₃ and Si(CH₃)₄ spectra were fit to Gaussian lineshapes.

The EHT calculations utilized Hoffmann's original method. The diagonal elements of the Hamiltonian matrix were orbital energies from atomic calculations by Clementi rather than empirical values. The off-diagonal elements were calculated using the relation

\[ H_{ij} = 0.875(H_{ii} + H_{jj})S_{ij} \]  \hspace{1cm} (1)
Overlap integrals were calculated from Slater-type orbitals using exponents and principal quantum numbers proposed by Cusachs and Corrington.\textsuperscript{13} The valence basis set included silicon 3d orbitals as parameterized by Corrington.\textsuperscript{14} Partial gross populations for use in intensity analysis were calculated by Mulliken analysis.\textsuperscript{15} Molecular geometries from the literature\textsuperscript{16} were used in the calculations.

A semi-empirical intensity analysis has been developed for XPS valence spectra.\textsuperscript{4} The cross-section for absorption of an X-ray in the one-electron and dipole approximations is\textsuperscript{17}

\[
\sigma_{j,\text{EK}} = \frac{4\pi a_0^2}{3} \hbar \nu |\langle \psi_j | r \rvert \psi_{\text{EK}} \rangle|^2
\]

(2)

where $\psi_j$ is the LCAO-MO from which the photoelectron is ionized and $\psi_{\text{EK}}$ is the photoelectron wave function. After expanding $\psi_j$ in terms of atomic orbitals (AO's), the total cross-section for absorption may be approximated as a sum of atomic subshell photoionization cross-sections.\textsuperscript{4} Each subshell cross-section, $\sigma_{\text{AA}}^{\text{AO}}$, involves a valence AO wavefunction and the plane wave photoelectron wavefunction. For a given subshell ($s, p, d, \ldots$) of a given element, $\sigma_{\text{AA}}^{\text{AO}}$ is a constant, independent of any particular molecular orbital.\textsuperscript{4} Thus, the intensities of two valence electron bands in a spectrum are related as follows:

\[
\frac{I_{1}^{\text{MO}}}{I_{1j}^{\text{MO}}} = \frac{\sigma_{\text{AA}}^{\text{AO}} \Sigma_{\text{AA}}^{\text{AO}}}{\sigma_{\text{AA}}^{\text{AO}} \Sigma_{\text{AA}}^{\text{AO}}}
\]

(3)

where $P_{\text{AA}}^{\text{AO}}$ are partial gross populations and the index $A$ runs over the atoms while the index $\lambda$ runs over the valence atomic subshells. Although calculable in principle, relative values of the $\sigma_{\text{AA}}^{\text{AO}}$ are usually determined empirically using spectra from simple molecules and partial gross populations.
from ab initio MO calculations. These quantities may then be used to predict intensity ratios for the spectra of other molecules. For hydrogen, \( \sigma_{\text{H}1s} \) has been found to be essentially zero, thus simplifying the intensity analysis of hydrides.

Relative intensities are quantitatively given by eqn. (3) if the necessary \( c_{\alpha \lambda}^\text{AO} \) are known and the \( P_{\alpha \lambda \lambda} \) are taken from an ab initio calculation. For most of the molecules discussed in this paper, populations from ab initio calculations are not available, and we have instead used EHT populations. Because EHT calculations for heteroatomic molecules are excessively polarized, eqn. (3) cannot be used quantitatively. However, as we shall show in the section on results, it is often possible, using the relative band intensities, to assign MO's to the bands in a spectrum knowing only the degeneracies and the qualitative AO parentages of the MO's. This gives the experimenter two independent means of evaluating the results of an MO calculation: are the Koopmans' theorem ionization potentials from the calculation consistent with the experimental values, and are the MO assignments based upon Koopmans' theorem identical to those deduced from the relative band intensities of the spectrum? Thus, even when ab initio calculations of high enough quality for quantitative intensity analysis are not available, the use of this qualitative technique provides powerful aid in the interpretation of XPS valence spectra.

Silicon 3d orbitals were included in our EHT basis sets, but for our choice of parameters, the d orbitals did not mix appreciably into the filled MO's. Thus, the EHT orbital energies and AO populations and parentages which we report correspond essentially to s, p valence basis
set calculations, and we shall not consider pπ+dπ bonding in interpreting the spectra. In addition, ω_{Si3d} is expected to be small relative to ω_{Si3s} and ω_{Si3p} because the overlap integral between the Si3d orbitals and the photoelectron would be small. Therefore the d orbitals are expected to have little effect on spectral intensities.

Because the sensitivity of spectrometer is not exactly known, and because the absolute X-ray flux in the irradiation chamber is not well-established, the ordinates in our spectra should be considered to have arbitrary units. Thus only the relative intensities of bands in a single spectrum have physical meaning. Therefore, in both the text and the tables, all the intensity data refer to the relative intensities of the deconvoluted bands, where the area of the most intense of the deconvoluted bands has been defined to be unity.

Results

Silane

The spectrum of SiH₄, shown in Figure 1, consists of two well-separated bands. In the valence electron nomenclature which we shall use in this paper, these are the \((1a_1)^2\) and \((1t_2)^6\) MO's.* The valence IP's, relative intensities of the bands, and the EHT results are listed in Table 1. Although the EHT orbital energies are about 1.6 eV higher than the experimental IP's (because Koopmans' theorem neglects electronic relaxation), the energy difference between the two MO's is close to the experimental value. An extended basis set \textit{ab initio} calculation for SiH₄ has been

* These MO's correspond to the 3a₁ and 2t₂ MO's from \textit{ab initio} calculations.
Table 1

EXPERIMENTAL AND EHT RESULTS FOR SiH₄

<table>
<thead>
<tr>
<th>Orbital</th>
<th>IP (eV)*</th>
<th>$\varepsilon_{\text{EHT}}$ (eV)</th>
<th>Relative Areas</th>
<th>Main AO† Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a₁</td>
<td>18.02(5)</td>
<td>-19.25</td>
<td>1.00(7)</td>
<td>Si 3s</td>
</tr>
<tr>
<td>1t₂</td>
<td>12.67(7)</td>
<td>-14.30</td>
<td>.65(7)</td>
<td>Si 3p</td>
</tr>
</tbody>
</table>

* Error in last significant figure appears parenthetically.
† Hydrogen parentage is omitted.
made by Rothenberg, Young, and Schaefer. They calculated valence orbital energies of \(-19.89\) and \(-13.22\) eV for \(1a_1\) and \(1t_2\) valence MO's, respectively. The simple EHT results are close to those from the \textit{ab initio} calculation, and both sets of energies indicate the magnitude of error associated with the calculation of valence IP's from ground state orbital energies.

Both the \(1a_1\) and \(1t_2\) MO's are bonding orbitals. The \(1a_1\) MO is constructed from the Si3s and \(1s\) AO's, while the \(1t_2\) MO's are constructed from Si3p and \(1s\) AO's. The ratio of the cross sections, \(\sigma_{Si3s}/\sigma_{Si3p}\) was calculated to be 2.7 using the experimental relative band intensities, partial gross populations from the \textit{ab initio} calculation and eqn. (3). Using EHT populations, this ratio was calculated to be 2.8. Although the close agreement of the two ratios is probably fortuitous, it supports the use of EHT populations and orbital parentages for qualitative intensity analysis.

\textbf{Methyilsilane}

The spectrum of SiH3CH3, shown in Figure 2, was deconvoluted into five bands. In order of decreasing binding energy, these were assigned to the \((1a_1)^2(2a_1)^2(1e)^4(2e)^4(3a_1)^2\) valence MO's on the basis of the EHT calculation. The experimental and calculated data for SiH3CH3 appear in Table 2. The IP's were reproduced fairly well by the EHT orbital energies. The \(1a_1\) and \(2a_1\) MO's are carbon-hydrogen and silicon-hydrogen bonding MO's, respectively; their parentages are largely C2s plus \(1s\) and Si3s plus \(1s\) respectively. The \(1e\) and \(2e\) MO's are also carbon-hydrogen and silicon-hydrogen bonding orbitals, but involve the C2p and Si3p AO's.
Table 2

EXPERIMENTAL AND EHT RESULTS FOR SiH$_3$CH$_3$

| Orbital | IP (eV)* | $\epsilon_{\text{EHT}}$ (eV) | Relative Areas* | Main AO [Components]
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1a$_1$</td>
<td>22.8(1)</td>
<td>-23.22</td>
<td>.66(3)</td>
<td>C 2s</td>
</tr>
<tr>
<td>2a$_1$</td>
<td>17.49(6)</td>
<td>-18.59</td>
<td>1.00(3)</td>
<td>Si 3s</td>
</tr>
<tr>
<td>1e</td>
<td>13.1(6)</td>
<td>-15.88</td>
<td>.06(2)</td>
<td>C 2p</td>
</tr>
<tr>
<td>2e</td>
<td>12.1(1)</td>
<td>-14.07</td>
<td>.28(2)</td>
<td>Si 3p</td>
</tr>
<tr>
<td>3a$_1$</td>
<td>11.0(3)</td>
<td>-12.67</td>
<td>.13(2)</td>
<td>C 2p, Si 3p</td>
</tr>
</tbody>
</table>

* Error in last significant figure appears parenthetically.
† Hydrogen parentage is omitted.
respectively, rather than the s orbitals. The 3a1 MO is constructed from both C2p and Si3p AO's and provides most of the carbon-silicon bonding.

The SiH3CH3 IP's are related to those of CH4 and SiH4. The la1 and 1e MO's of SiH3CH3 give IP's at nearly the same energy as the la1 and lt2 valence MO's of CH4. The 2a1 and 2e MO's of SiH3CH3 likewise give IP's of nearly the same energy as the la1 and lt2 MO's of SiH4. There is, of course, no analog of the 3a1, MO of SiH3CH3 in the MO's of CH4 or SiH4.

Liskow and Schaefer have made an extended basis set ab initio calculation for SiH3CH3 which produced the same order for the valence MO's as was obtained from the EHT calculation. The ab initio valence MO orbital energies are (in eV): la1: -25.75; 2a1: -19.00; 1e: -15.34; 2e: -12.72; 3a1: -12.34. These energies are in somewhat poorer agreement with experiment than the EHT results.

The relative intensities of the peaks in the SiH3CH3 spectrum provide additional support for the EHT orbital assignment. Our data indicate that \( \sigma_{Si3s}/\sigma_{Si3p} = 2.7 \) while Gelius found that \( \sigma_{C2s}/\sigma_{C2p} = 13 \); thus, s-type valence MO's for carbon and silicon should be more intense than p-type MO's. From this conclusion, one assigns the two peaks at high binding energy to the la1 and 2a1 MO's. On the basis of this assignment, the ratio \( \sigma_{C2s}/\sigma_{Si3s} \) is estimated to be 0.3 using the relative peak intensities and EHT populations for la1 and 2a1 MO's. This value, however, only represents a lower limit, because the EHT populations are too polarized in favor of carbon. The correct value is probably nearer to unity. Because the value for \( \sigma_{C2p} \) is quite small, the least intense peak should correspond to the 1e MO's. The 2e and 3a1 MO's both have considerable Si3p character. However, the band from the doubly degenerate 2e MO's would be more intense than that from the non-degenerate 3a1 MO. Thus, intensity data confirm the orbital ordering given by the ab initio and EHT calculations.
Tetramethylsilane

There are sixteen filled valence MO's in Si(CH₃)₄. The EHT calculation yields the assignment

\[(1a₁)^2 (1t₂)^6 (2a₁)^2 (2t₂)^6 (1e)^4 (1t₁)^6 (3t₂)^6\]

with binding energies ranging from 12 to 24 eV. Because of the close spacing of the levels, the spectrum, shown in Figure 3, was obtained using one-half the usual channel width. The EHT orbital energies are in fair agreement with IP's from the deconvoluted spectrum. These data for Si(CH₃)₄ are presented in Table 3. The 1a₁ MO is constructed primarily from C₂s and Si₃s AO's. The 1t₂ MO's are carbon-hydrogen bonding MO's constructed from C₂s and Si₃s AO's. The 1t₂ MO's are carbon-hydrogen bonding MO's constructed from C₂s and H₁s AO's. The EHT energies for these MO's are fairly close to experiment. The 2a₁ MO is constructed from the Si₃s AO with additional contributions from the C₂p and H₁s AO's. The 2t₂, 1e, and 1t₁ MO's are primarily carbon-hydrogen bonding MO's, although the 2t₂ MO's include some Si₃p parentage. The EHT binding energies for these levels are more closely spaced than those obtained from the spectrum. The 3t₂ MO's are carbon-silicon bonding MO's of mainly C₂p and Si₃p parentage.

A UPS spectrum of the five low-energy IP's of Si(CH₃)₄, showing considerable Jahn-Teller distortion, has been published; the MO's were assigned using a CNDO/2 calculation. Considerable evidence for d orbital bonding was found by this calculation, with the result that

We made a CNDO/2 calculation for the simpler, related molecule SiH₃CH₃ using Standard Santry and Segal parameters, which include 3d orbitals on silicon. The MO assignments were 1a₁, 1e, 2a₁, 2e, 3a₁. These differ from the ab initio assignments, and are inconsistent with our spectral intensities.
Table 3

EXPERIMENTAL AND EHT RESULTS FOR Si(CH₃)₄

<table>
<thead>
<tr>
<th>Orbital</th>
<th>IP (eV)*</th>
<th>$\epsilon_{\text{EHT}}$ (eV)</th>
<th>Relative*</th>
<th>Main AO† Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a₁</td>
<td>24.0(1)</td>
<td>-23.88</td>
<td>.26(2)</td>
<td>C 2s, Si 3s</td>
</tr>
<tr>
<td>1t₂</td>
<td>21.72(5)</td>
<td>-22.87</td>
<td>1.00(1)</td>
<td>C 2s</td>
</tr>
<tr>
<td>2a₁</td>
<td>15.5(1)</td>
<td>-16.71</td>
<td>.29(1)</td>
<td>Si 3s, C 2p</td>
</tr>
<tr>
<td>2t₂</td>
<td>14.1(1)</td>
<td>-16.32</td>
<td>.10(1)</td>
<td>C 2p, Si 3p</td>
</tr>
<tr>
<td>1e</td>
<td>13.2(4)</td>
<td>-15.78</td>
<td>.03(1)</td>
<td>C 2p</td>
</tr>
<tr>
<td>1t₁</td>
<td>11.5(4)</td>
<td>-15.10</td>
<td>.03(1)</td>
<td>C 2p</td>
</tr>
<tr>
<td>3t₂</td>
<td>10.4(1)</td>
<td>-11.97</td>
<td>.17(1)</td>
<td>C 2p, Si 3p</td>
</tr>
</tbody>
</table>

* Error in last significant figure appears parenthetically.
† Hydrogen percentage is omitted.
the CNDO/2 MO's have a different order than the EHT MO's. However, the intensities from our spectrum are consistent with the EHT assignments and not with the reported CNDO/2 assignments. As in the case of SiH3CH3, the s-type peaks should be significantly more intense than the p-type peaks. The largest peak represents ionization from the triply degenerate 1t2 MO's which are largely constructed from C2s AO's. The 1a1 and 2a1 MO's are then assigned to the 24.0 and 15.5 eV peaks, respectively. The 2t2 and 3t2 MO's, which include Si3p AO parentage, should give more intense peaks than the 1e and 1t1 MO's which include only C2p and Hls AO's. Furthermore, the Si3p AO population in the 3t2 MO's is significantly greater than that in the 2t2 MO's, and thus the peak from the former would be larger. Peaks from the 1e and 1t1 MO's should both be weak, as was the 1e MO peak in SiH3CH3. Except for some ambiguity for the 1e and 1t1 MO's, if the spectrum is assigned on the basis of these intensity criteria alone, the EHT assignment is duplicated.

Silyl chloride

The EHT calculation for SiH3Cl ordered the valence MO's \((1a_1)^2(2a_1)^2(1e)^4(3a_1)^2(2e)^4\). The photoelectron spectrum of SiH3Cl was deconvoluted into five peaks, and is illustrated in Figure 4. The experimental and calculated data appear in Table 4. The 1a1 MO is calculated to be nearly a pure Cl3s AO and may be considered to be nearly a chlorine lone pair orbital. The 2a1 MO is principally constructed from Si3s and Hls AO's and contributes silicon-hydrogen bonding to the SiH3 group. The remaining orbitals, the 1e, 3a1, and 2e MO's, do not include appreciable parentage from the chlorine or silicon 3s AO's. The 1e and 3a1 MO's...
Table 4

EXPERIMENTAL AND EHT RESULTS FOR SiH$_3$Cl

<table>
<thead>
<tr>
<th>Orbital</th>
<th>IP (eV)$^*$</th>
<th>$\epsilon_{EHT}$ (eV)</th>
<th>Relative* Areas</th>
<th>Main AO$^\dagger$ Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1a_1$</td>
<td>23.7(1)</td>
<td>-29.58</td>
<td>1.00(18)</td>
<td>Cl 3s</td>
</tr>
<tr>
<td>$2a_1$</td>
<td>17.97(9)</td>
<td>-18.63</td>
<td>.65(16)</td>
<td>Si 3s</td>
</tr>
<tr>
<td>$1e$</td>
<td>13.8(2)</td>
<td>-14.85</td>
<td>.64(15)</td>
<td>Cl 3p, Si 3p</td>
</tr>
<tr>
<td>$3a_1$</td>
<td>12.9(3)</td>
<td>-13.71</td>
<td>.34(15)</td>
<td>Cl 3p, Si 3p</td>
</tr>
<tr>
<td>$2e$</td>
<td>11.51(8)</td>
<td>-13.12</td>
<td>.72(8)</td>
<td>Cl 3p</td>
</tr>
</tbody>
</table>

$^*$ Error in last significant figure appears parenthetically.

$^\dagger$ Hydrogen parentage is omitted.
include significant Si3p, Cl3p, and Hls AO parentage. The 2e MO's although they do not have much Si3p character, are constructed from both the Cl3p and Hls AO's. This fact suggests that the description of these orbitals as chlorine lone pair orbitals\textsuperscript{24,25} is an oversimplification. The EHT calculation may be interpreted as distributing the p-like chlorine lone pair orbitals among the 2e and 3a_1 MO's. Also, results from the calculation are consistent with pure p silicon-chlorine bonding and s, p hybridized silicon-hydrogen bonding.

Except for the la_1 MO, the EHT orbital energies are in good agreement with the experimental values. The la_1 MO is predicted to have a binding energy several electron volts higher than was observed. This error is probably caused by faulty parameterization. The Cl3s orbital energy, as calculated by Clementi\textsuperscript{12} and used in our EHT program, is several electron volts more negative than an empirical value.\textsuperscript{26} Because the la_1 MO of SiH_3Cl given by the EHT calculation is essentially just the Cl3s AO, the predicted binding energy for this MO might also be expected to be high. Our XPS IP's for SiH_3Cl are in fair agreement with values for the four low-energy IP's reported in earlier UPS studies of this compound.\textsuperscript{24,25}

Intensity analysis again supports the EHT assignment. The most intense peak is assigned to the Cl3s-like la_1 MO. Because the cross-section ratio for argon is low\textsuperscript{4} (\(\sigma_{\text{Ar}3s}/\sigma_{\text{Ar}3p} = 1.4\)), one might expect that bands from MO's including Cl3p AO's would be nearly as intense as those from s-type MO's. Thus, the 17.97 eV peak is assigned to the 2a_1 MO mainly on the basis of the energy considerations mentioned.
previously. The relative intensities of the three remaining peaks closely reflect their respective orbital degeneracies. The slightly greater intensity of the band from the 2e MO's compared to that from the 1e MO's suggests that the ratio $\sigma_{\text{Cl}3p}/\sigma_{\text{Si}3p}$ is greater than one. A corresponding example would be known for first row elements where $\sigma_{\text{F}2p}/\sigma_{\text{C}2p} = 1.5$.

**Silicon tetrafluoride**

The spectrum of SiF$_4$, shown in Figure 5, was deconvoluted into seven bands. The EHT calculation yielded the MO sequence $(1a_1)^2(1t_2)^6 (2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$. Numerical data for SiF$_4$ appear in Table 5. The binding energies taken from the EHT calculation are in good agreement with the experimental values. The $1a_1$ and $1t_2$ MO's are largely constructed from F2s AO's. The $1a_1$ MO does however include some Si3s AO parentage, while the parentage of the $1t_2$ MO's is almost purely F2s. The parentage of the $2a_1$ MO, although largely F2p, includes appreciable Si3s character. The $2t_2$ MO's, although largely constructed from F2p AO's, include some Si3p and a little F2s parentage. The $3t_2$ MO's include both F2p and Si3p parentage while the $1e$ and $1t_1$ MO's are constructed entirely from F2p AO's.

The intensities of the spectral bands are consistent with the EHT MO assignments. The two high binding energy s-like bands are most intense. The band assigned to the $2a_1$ MO is less intense than the pure s-bands, but more intense than would be expected for a pure p-band arising from a non-degenerate MO. The higher intensity of the band from the $2t_2$ MO's compared to bands assigned to the $3t_2$ and $1t_1$ MO's is
Table 5

EXPERIMENTAL AND EHT RESULTS FOR SiF₄

<table>
<thead>
<tr>
<th>Orbital</th>
<th>IP (eV)*</th>
<th>εₑHt (eV)</th>
<th>Relative Areas</th>
<th>Main AO. Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a₁</td>
<td>40.6(2)</td>
<td>-43.70</td>
<td>.60(9)</td>
<td>F 2s, Si 3s</td>
</tr>
<tr>
<td>1t₂</td>
<td>39.27(9)</td>
<td>-42.66</td>
<td>1.00(10)</td>
<td>F 2s</td>
</tr>
<tr>
<td>2a₁</td>
<td>21.4(2)</td>
<td>-21.97</td>
<td>.12(8)</td>
<td>Si 3s, F 2p</td>
</tr>
<tr>
<td>2t₂</td>
<td>19.4(2)</td>
<td>-21.19</td>
<td>.17(6)</td>
<td>F 2p, Si 3p, F 2s</td>
</tr>
<tr>
<td>1e</td>
<td>18.1(4)</td>
<td>-19.86</td>
<td>.09(6)</td>
<td>F 2p</td>
</tr>
<tr>
<td>3t₂</td>
<td>17.4(3)</td>
<td>-19.16</td>
<td>.13(6)</td>
<td>F 2p, Si 3p</td>
</tr>
<tr>
<td>1t₁</td>
<td>16.4(2)</td>
<td>-18.19</td>
<td>.11(3)</td>
<td>F 2p</td>
</tr>
</tbody>
</table>

* Error in last significant figure appears parenthetically.
consistent with the inclusion of F2s parentage in the 2t2 MO's. The band assigned the p-like le MO's has, as expected, the least intensity, and the 3t2 MO's, which includes Si3p parentage, give a more intense band than the pure F2p l1 MO's. (If \( \sigma_{C2s}/\sigma_{Si3s} \equiv 1 \), then one calculates \( \sigma_{F2p}/\sigma_{Si3p} \equiv 0.6 \).

The XPS valence spectrum for CF4 has been published, and is qualitatively very similar to our SiF4 spectra. The SiF4 IP's are not as well separated as those of CF4, but this behavior is expected when silicon is substituted for carbon. An ab initio calculation for CF4 found the same orbital assignments as our EHT calculation found for SiF4. The CF4 assignments, later confirmed by rigorous intensity analysis, and the similarity of the CF4 and SiF4 spectra support the EHT assignments for SiF4.

The four lowest IP's of SiF4 have previously been measured in UPS studies of the compound, and there is good agreement between the XPS and the UPS binding energies. In their study, Bassett and Lloyd propose the same MO assignments for the spectral bands as do we. However, in a later study, Jonas et al. propose alternate assignments based partially upon a CNDO/2 MO calculation which included silicon 3d orbitals in the basis set. These latter assignments, which suggest the stabilization of some MO's by the Si3d AO's, produce a spectrum which is inconsistent with the observed XPS intensities.

Conclusions

A summary of the binding energies from the spectra and the EHT calculations is presented in Figure 6. In this figure, the EHT orbital energies have been adjusted by an additive constant so that the calculated value of the lowest IP matches experiment. This simple adjustment
takes some account of electronic relaxation, at least to the extent that the relaxation energies for all the MO's of a given molecule have the same value. The agreement between experimental and calculated values is good and compares well with ab initio and other SCF correlations. It thus appears that EHT can accurately reproduce the ordering of the MO's in small and symmetric molecules such as those studied in this work, and that valence IP's may be estimated with some confidence from EHT orbital energies. Others have observed that, for less symmetric molecules, EHT calculations may incorrectly order groups of closely-spaced orbitals. (Some hint of this possibility is seen in the Si(CH$_3$)$_4$ results, where the orbital energies for the related $2t_2$, $1e$, and $1t_1$ MO's are too closely spaced.) However, even in such cases, the predicted binding energies are within a few electron volts of the experimental values.

The successful correlation of our EHT results with the spectra suggests that the main features of the chemical bonding in these compounds may be described without recourse to silicon 3d AO's. If d orbitals make important contributions to the parentage of some MO's, then the energies of these MO's should be stabilized sufficiently by $p\pi+d\pi$ bonding to affect the order of the MO's. This was not observed, the MO orderings from the EHT calculations, which had no significant d orbital bonding, matched orderings obtained from the relative band intensities of the spectra. If d orbitals were less important, but still not negligible, the MO ordering might not be affected, but certain MO's would be energetically stabilized relative to the others. The $1e$ MO's in SiF$_4$ and the $1e$ MO's
in SiH₃CH₃ are specific examples of such MO's. However, comparison of the calculated and experimental IP's (Figure 6) for SiF₄ and for SiH₃CH₃ does not indicate such stabilization. However, valence MO binding energies calculated using Koopmans' theorem may differ from measured energies by several electron volts. Thus small differences between experimental and calculated values, or the lack of small differences, may not be significant, and their interpretation in terms of d orbital bonding is of dubious value. We thus conclude that, although we cannot quantify the extent of d orbital bonding in these compounds, the principal features of the spectra (band assignments, approximate IP's and relative band intensities) may be rationalized by considering only s and p orbital bonding.
REFERENCES


Figure Captions

Fig. 1. Valence spectrum of SiH₄. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg Kα₃,₄ satellite radiation.

Fig. 2. Valence spectrum of SiH₃CH₃. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Al Kα₃,₄ satellite radiation.

Fig. 3. Valence spectrum of Si(CH₃)₄. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Al Kα₃,₄ radiation.

Fig. 4. Valence spectrum of SiH₃Cl. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg Kα₃,₄ satellite radiation.

Fig. 5. Valence spectrum of SiF₄. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg Kα₃,₄ satellite radiation.

Fig. 6. Experimental and calculated valence electron binding energies for SiH₄, SiH₃CH₃, Si(CH₃)₄, SiH₃Cl, and SiF₄.
Figure 1

Counts/492 sec ($\times 10^2$) vs Binding Energy (eV)
Figure 3
Figure 4
Figure 5
Figure 6
V. STATIC RELAXATION IN GERMANE
AND THE ESTIMATION OF RELAXATION ENERGY DIFFERENCES
FROM AUGER AND CORE BINDING ENERGIES OF GERMANIUM COMPOUNDS

ABSTRACT

Auger and core electron spectra were measured for several germanium compounds in the gas phase. The \( \text{L}_2\text{M}_{45}\text{M}_{45} \) and \( \text{L}_3\text{M}_{45}\text{M}_{45} \) Auger spectra of GeH\(_4\) were deconvoluted to determine the energies of the individual component peaks. The molecular relaxation energy of the GeH\(_4\) M\(_{45}\) shell was taken to be the average difference between the experimental and calculated energies. Differences in the molecular relaxation energies of the other germanium compounds relative to GeH\(_4\) were calculated using the chemical shifts of the \(^1\text{G}\) components of the \( \text{L}_3\text{M}_{45}\text{M}_{45} \) Auger spectra and of the Ge 3d core electrons.

INTRODUCTION

Recently, Shirley [1-3] refined Assad and Burhop's theory [4] for predicting the kinetic energies of Auger electrons by including additional relaxation effects. An Auger energy is given by the following expression

\[
E(I,J,J) = E_B(I) - 2E_B(J) - J(J,J) + R_J,
\]

where the Auger process involves the core electron subshells I and J, \( E_B \) is the experimental binding energy of subshells I and J as given by X-ray photoelectron spectroscopy, \( J(J,J) \) represents the sum of the final-state coupling terms, and \( R_J \) corrects for static relaxation of the J subshell orbitals. The energies of KLL and LMM Auger processes are successfully predicted by this model [2,3].
We have measured the $L_3M_{45}M_{45}$ Auger spectra and the Ge 3d core electron spectra of several germanium compounds in the gas phase. In the case of GeH$_4$, the $L_2M_{45}M_{45}$ spectra were also measured, and both the $L_2M_{45}M_{45}$ and $L_3M_{45}M_{45}$ Auger spectra were deconvoluted into their component peaks. The molecular relaxation energy for the $M_{45}$ level in GeH$_4$ was taken to be the average difference between the experimental Auger energies and values calculated from eq.(1), neglecting molecular relaxation. Germane was selected for a thorough evaluation of eq.(1) because we believed that its relaxation energies would be approximately the same as those of a free atom of germanium, for which relaxation energies may be readily estimated.

Auger spectra of the other germanium compounds were not analyzed in detail because they closely resemble the GeH$_4$ spectra. However, differences in molecular relaxation energies of the $M_{45}$ shell for these compounds were calculated from the $^1G\, L_3M_{45}M_{45}$ Auger chemical shifts and the Ge 3d core electron chemical shifts using a simple extension of eq.(1). These relaxation energy differences, relative to GeH$_4$, were calculated without the use of approximate, estimated values.

**EXPERIMENTAL**

The spectra and chemical shifts reported in this paper were measured on the Berkeley iron-free, double-focussing magnetic X-ray photoelectron spectrometer [5]. Al K$_\alpha$ (1486.6 eV) radiation was used to obtain the Ge 3d chemical shifts and the GeH$_4$ Auger spectra. The remaining Auger energies were measured using Mg K$_\alpha$ (1253.6 eV) radiation. The samples were introduced into the spectrometer at a pressure of 30-50μ; argon gas was simultaneously introduced at a pressure of 20-30μ; and the
Ar 2p<sub>3/2</sub> line (248.45 eV) was used as the standard. The germanium compounds were prepared using standard methods and checked for purity by infrared spectroscopy and vapor pressure measurements.

**DISCUSSION OF RESULTS**

The L<sub>2</sub>M<sub>45</sub>M<sub>45</sub> and L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger spectra for GeH<sub>4</sub> were deconvoluted and least-squares fitted to lorentzian lineshapes. Each spectrum consists of five components corresponding to the possible J states of the final d<sup>8</sup> cation, namely 1S, 1G, 3P, 1D, and 3F. These are illustrated in figs. 1 and 2. We have also measured the core binding energy of the M<sub>45</sub> shell. Although we were unable to measure the energies of the L<sub>2</sub> and L<sub>3</sub> shells, these values may be accurately estimated using the M<sub>45</sub> energy together with the energies of the germanium L<sub>α1,2</sub> and L<sub>β1</sub> X-rays. These correspond to L<sub>3</sub>M<sub>45</sub> and L<sub>2</sub>M<sub>45</sub> transitions, respectively. Because the energy difference between two atomic core levels is independent of chemical environment [6], the energy of an L level is simply the sum of the M<sub>45</sub> energy and the energy of the appropriate X-ray. The final-state coupling term, J(3d, 3d), was evaluated using atomic, two-electron Slater integrals, and is given for each final state by the expression

\[
J(3d, 3d)_{1A} = \alpha_{1A} F_0(3d, 3d) + \beta_{1A} F_2(3d, 3d) + \gamma_{1A} F_4(3d, 3d) \tag{2}
\]

The coefficients for each state appear in ref. [3]. Theoretical energies for the L<sub>2</sub>M<sub>45</sub>M<sub>45</sub> and L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger spectra of GeH<sub>4</sub> were calculated using eq. (1), except that the static relaxation, R<sub>M45</sub>, was neglected. The experimental and calculated values, the differences between them, and the quantities used in calculating these energies are listed in table 1.
Table I
Energies and Related Quantities for the 
\( L_2 M_{45} M_{45} \) and \( L_3 M_{45} M_{45} \) Auger Spectra of GeH₄

<table>
<thead>
<tr>
<th>State</th>
<th>( 1S )</th>
<th>( 1G )</th>
<th>( 3P )</th>
<th>( 1D )</th>
<th>( 3P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_2 M_{45} M_{45} ) exp.</td>
<td>1154.5(2)</td>
<td>1160.3(1)</td>
<td>1161.1(2)</td>
<td>1162.2(1)</td>
<td>1164.4(1)</td>
</tr>
<tr>
<td>( L_2 M_{45} M_{45} ) calc.</td>
<td>1138.9</td>
<td>1145.1</td>
<td>1146.1</td>
<td>1146.6</td>
<td>1149.4</td>
</tr>
<tr>
<td>( \Delta E )</td>
<td>15.6</td>
<td>15.2</td>
<td>15.0</td>
<td>15.6</td>
<td>15.0</td>
</tr>
<tr>
<td>( L_3 M_{45} M_{45} ) exp.</td>
<td>1123.6(1)</td>
<td>1129.3(1)</td>
<td>1130.7(1)</td>
<td>1132.7(2)</td>
<td>1133.6(1)</td>
</tr>
<tr>
<td>( L_3 M_{45} M_{45} ) calc.</td>
<td>1108.4</td>
<td>1114.6</td>
<td>1115.6</td>
<td>1116.1</td>
<td>1118.9</td>
</tr>
<tr>
<td>( \Delta E )</td>
<td>15.2</td>
<td>14.7</td>
<td>15.1</td>
<td>16.6</td>
<td>14.7</td>
</tr>
<tr>
<td>( J(3d,3d)^b )</td>
<td>42.4</td>
<td>36.2</td>
<td>35.2</td>
<td>34.7</td>
<td>31.9</td>
</tr>
<tr>
<td>( E_B(3d) )</td>
<td></td>
<td></td>
<td></td>
<td>37.2(1)</td>
<td></td>
</tr>
<tr>
<td>( E_{hv}(L_{\alpha 1,2})^c )</td>
<td></td>
<td></td>
<td></td>
<td>1188.0</td>
<td></td>
</tr>
<tr>
<td>( E_{hv}(L_{\beta 1})^c )</td>
<td></td>
<td></td>
<td></td>
<td>1218.5</td>
<td></td>
</tr>
</tbody>
</table>

a) All values in eV. Uncertainty in tenths for experimental values appears parenthetically.

b) Values calculated using Slater integrals from Mann's tables, ref. [7].

c) X-ray energies from Beardon's table, ref. [8].
The energy difference between experimental and calculated values for each state corresponds to the total static relaxation \( R_{45} \). Because this term depends only on the final state, it should have essentially the same value for all the \( d^8 \) states. The differences between calculated and experimental values are reasonably constant, with an average value of 15.3 eV.

The static relaxation\(^*\), \( R_J \), may be subdivided into three components: inner-shell, intra-shell, and outer-shell [3]. The outer-shell relaxation may be easily estimated [9] for a free atom using a polarization potential of Hedin and Johannson [11] together with the principle of equivalent cores [12]. Using Slater integrals from Mann's tables [7], the \( M_{45} \) outer-shell relaxation for a germanium atom is calculated to be 5.6 eV for the valence electron configuration \( s^2p^2 \) and 5.7 eV for the configuration \( sp^3 \). For a molecule, the outer shells are the valence molecular orbitals, and thus, the outer-shell relaxation (which we shall refer to as the molecular relaxation) is not easily estimated.

The \( M_{45} \) relaxation energy has been calculated by Rosen and Lindgren [10] to be 10.6 eV for copper. The outer-shell relaxation for the single 4s electron is calculated, using the method previously outlined, to be 1.4 eV. Thus, the inner-shell plus intra-shell relaxation energy for the copper \( M_{45} \) level is 9.2 eV. Because the electronic configuration

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* The static relaxation energies calculated in refs. [9, 10] are for photoelectric ionizations. As shown in ref. [1], the static relaxation energy for an Auger ionization is twice that for a photoelectric ionization.
of a germanium core is the same as that of a copper core, the inner-shell plus intra-shell relaxation energies for the M45 levels should be nearly the same for both elements. We estimate the inner-shell plus intra-shell relaxation energy for the germanium M45 shell to be about 10 eV because the core levels of germanium have somewhat higher binding energies than those of copper, leading one to expect a greater relaxation energy for germanium than for copper.

The molecular relaxation energy for GeH4 is the difference between the total static relaxation energy, 15.3 eV, and the estimated inner-shell plus intra-shell relaxation energy, 10 eV, or approximately 5.3 eV. This value, for a germanium atom in an sp3 molecular environment, is close to the estimated free-atom value. This result is plausible because the 4a1 and 3t2 valence molecular orbitals of GeH4 are closely related to the 4s and 4p valence atomic orbitals of germanium.

Differences in the M45 molecular relaxation energies of a series of compounds may be easily calculated from eq.(1) by making the approximation that core-electron chemical shifts do not depend upon the level measured [6]. We rewrite eq.(1) for energy differences:

\[ \Delta \varepsilon(L,J,J) = \Delta \varepsilon_{B}(L) - 2\Delta \varepsilon_{B}(J) + \Delta \varepsilon_{J} = -2\Delta \varepsilon_{B} + \Delta \varepsilon_{J} \]  

(3)

The inner-shell and intra-shell relaxation for a difference should be zero, leaving only a difference in molecular relaxation energy. This is given by rearranging eq.(3):

\[ \Delta \varepsilon_{J}^{mol} = \Delta \varepsilon(L,J,J) + \Delta \varepsilon_{B} \]  

(4)
Experimental values of the chemical shifts for the Ge 3d core level and the $^{1}G \text{L}_{3}\text{M}_{4.5}\text{M}_{4.5}$ Auger line of some volatile germanium compounds are listed in Table 2 together with the corresponding $\Delta R_{45}^{\text{mol}}$ values. These energy differences do not depend upon our estimate of the inner-shell plus intra-shell relaxation energy for germanium. However, the approximate magnitude of the molecular relaxation energy, $R_{45}^{\text{mol}}$, for each compound may be obtained by adding 5.3 eV to each difference. A comparison of these energies with atomic outer-shell relaxation energy shows that molecular relaxation energies may deviate by several electron volts from the free-atom value. For GeF$_4$, the molecular relaxation energy is significantly lower than the atomic value despite the increased number of valence electrons. This result is undoubtedly a consequence of the high electronegativity and low polarizability of fluorine.

In calculating the differences in molecular relaxation, we have used GeH$_4$ as our reference compound for making comparisons. Because all of the compounds are covalent and tetrahedral one would expect that $R_{j}^{\text{mol}}$ might be a simple function of the substituents. In accord with this expectation, the ratio $\Delta R_{45}^{\text{mol}}\text{(GeX}_4)/\Delta R_{45}^{\text{mol}}\text{(GeH}_3X)$ is approximately 3 for X = CH$_3$, Cl, and Br. It appears that $R_{45}^{\text{mol}}$, for a given substituent, is somewhat less than linearly proportional to the degree of substitution. Relaxation terms arise primarily from charge polarization during photo-emission. Because $R_{j}^{\text{mol}}$ measures a substituent effect, one should be able to correlate the relative polarizabilities of functional groups with $\Delta R_{j}^{\text{mol}}$. One would expect a larger $\Delta R_{j}^{\text{mol}}$ to correspond to a greater polarizability. For GeX$_4$ compounds, the $\Delta R_{j}^{\text{mol}}$ values suggest that the
Table II

Ge 3d Binding Energy, Ge L3M45M45 Auger Chemical Shift, and the Difference in Molecular Relaxation Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_b$ (3d)</th>
<th>$\Delta E$ (L3M45M45)</th>
<th>$\Delta R_{mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH$_4$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>GeH$_3$CH$_3$</td>
<td>-0.46</td>
<td>1.05</td>
<td>0.6</td>
</tr>
<tr>
<td>Ge(CH$_3$)$_4$</td>
<td>-1.27</td>
<td>3.14</td>
<td>1.9</td>
</tr>
<tr>
<td>GeF$_4$</td>
<td>4.65</td>
<td>-5.22</td>
<td>-0.6</td>
</tr>
<tr>
<td>GeH$_3$Cl</td>
<td>0.87</td>
<td>-0.10</td>
<td>0.8</td>
</tr>
<tr>
<td>GeCl$_4$</td>
<td>2.70</td>
<td>-0.49</td>
<td>2.2</td>
</tr>
<tr>
<td>GeH$_3$Br</td>
<td>0.75</td>
<td>0.31</td>
<td>1.1</td>
</tr>
<tr>
<td>GeBr$_4$</td>
<td>2.05</td>
<td>0.82</td>
<td>2.9</td>
</tr>
</tbody>
</table>

a) All values in eV. Uncertainty in experimental values ± 0.05.
polarizability of the substituents increases in the order 
F < H < CH₃ < Cl < Br. This order is consistent with optically 
determined polarizabilities [13].

These relaxation energy differences can be helpful in explaining 
ESCA chemical shifts. The binding energy differences \( E_B(HX) - E_B(X_2) \) 
for \( X = F, Cl, Br \) are -2.7 (\( F_2: \text{ref.}[14]; \) HF: ref.[15]), -0.4[16], 
-0.1 eV [16], respectively. The small chemical shifts for chlorine 
and bromine compared to fluorine are difficult to explain on the basis 
of ground-state charge distributions. The \( R_{mol}^{mol} \) values in table 2, 
however, suggest that the molecular relaxation energy of \( X_2 \) is large 
compared to that of \( HX \) for \( X = Cl, Br \) and small for \( X = F \). It is 
therefore reasonable that the observed \( HX, X_2 \) shifts for chlorine and 
bromine are much smaller than that for fluorine.
REFERENCES

Figure Captions

Fig. 1. GeH₄ L₂M₄5M₄5 Auger spectrum. The components listed in order of increasing kinetic energy are \( ^1S, ^1G, ^3P, ^1D \), and \(^3F\).

Fig. 2. GeH₄ L₃M₄5M₄5 Auger spectrum. The components listed in order of increasing kinetic energy are \( ^1S, ^1G, ^3P, ^1D \), and \(^3F\).
VI. THE CALCULATION OF LATTICE POTENTIALS FOR IONIC SOLIDS

1. Introduction

Judging from the number of articles that have appeared in the literature, the use of X-ray photoelectron spectroscopy (ESCA) to investigate electron distributions in solid-phase samples has become almost routine. Despite this fact, the interpretation of these core binding energies from solids, and especially from ionic solids, has lagged far behind that of gas phase ESCA in sophistication. The ESCA chemical shifts measured for solid samples are commonly correlated with just the oxidation states of the ionized atoms, or perhaps with charges on the ionized atoms calculated using extremely simple, empirical models.

The principal reason for this lack of sophistication is doubtless due to the number and complexity of the factors which affect solid state core binding energies. A thorough analysis of solid state core binding energies would involve an expression such as the following:

\[ E_{B}(A)_{\text{solid}} = E_{B}(A)_{\text{free ion}} + \phi_{L} + \Phi_{F} + \Phi_{A} + \phi_{\text{sp}} + \phi_{C} \] (1)

In this expression, \( E_{B}(A)_{\text{solid}} \) is the measured, solid state core binding energy, for some core level of atom A which is part of some complex ion, e.g. the V atom in V(CN)\( _{7}^{4-} \). The \( E_{B}(A)_{\text{free ion}} \) is the binding energy that would be measured for the core in the gaseous complex ion at low pressure, free from associative and solid state effects. This free ion binding energy could be interpreted using models developed to interpret gas phase binding energies, such as the electrostatic potential equation. \( \phi_{L} \) is
the lattice potential, and is defined as the electrostatic potential felt at the core hole in the ionized atom due to the charges on all the ions in the sample except the ion containing the ionized atom. \( E_F \) is the Fermi level of the solid; \( \Phi_A \) is the work function of the sample; \( \Phi_{sp} \) is the work function of the spectrometer; \( \Phi_C \) is a charging potential which arises when the sample material is an insulator. The use of a known core level in a noble metal such as gold, lightly evaporated upon the sample surface for a reference, can to some extent eliminate \( E_F, \Phi_e \) and \( \Phi_{sp} \) as variables; \( \Phi_A \) is optimistically assumed to have about the same value for a wide variety of substances. Thus, only \( \Phi_L \), the lattice potential, remains unaccounted for.

This paper will present a method of calculating \( \Phi_L \) in the point charge approximation when the crystal structure of the ionic substance under investigation has been determined. Also, the results of this method for nineteen ionic compounds will be presented together with several, largely unsuccessful, attempts at using these data to develop a simple model to estimate lattice potentials when the crystal structure is not known.

2. Method of Calculation

The lattice potential, as defined here, is quite similar to the Madelung potential, and for substances having structures for which a Madelung constant is known, \( \Phi_L \) can be easily calculated. Most interesting compounds however, do not fall into this fortunate but limited class. For example, in a general ternary salt, \( A_{\text{B}_m\text{C}_n} \), where \( A, B, \) and \( C \) are point charge ions of charge \( q_A, q_B, \) and \( q_C \), respectively, the lattice
potential felt at ion $A_0$ is given by the expression:

$$\Phi_L(A_0) = e^2 \sum_{i=1}^{\infty} \left( \frac{q_A}{R_{A_0A_i}} \right) + \sum_{i=1}^{\infty} \left( \frac{q_B}{R_{A_0B_i}} \right) + \sum_{i=1}^{\infty} \left( \frac{q_C}{R_{A_0C_i}} \right)$$

(2)

where $R_{A_0X_i}$ is the distance between ion $X_i$ and $A_0$, the particular ion $A$ chosen as the test point, or origin. Monatomic ions, such as Na$^+$ and Ca$^{2+}$, should be quite well described by the point charge approximation. Complex ions, which are more or less spherical, such as N(CH$_3$)$_4^+$ or AsF$_6^-$, should also be fairly well described by point charges located at the central atom of the ion. Some error is probably introduced by describing the XeF$_5^+$ ion, for example, as a positive unit point charge centered on xenon, but we feel that the error should be small. A bridged ion, such as Xe$_2$F$_{11}^+$, was described, in this work, as a unipositive point charge half way between the two xenons along the Xe-Xe axis. An alternate, and perhaps superior description, would be to assign a charge of $+1/2$ to each Xe.

Finally, a cyclic ion, such as (R$_6$P$_3$N$_3$H)$_2^+$, was represented by a charge of +1 located at the center of P$_3$N$_3$ ring.

The infinite summations in equation 2, taken separately, do not converge. However, lattice potentials have finite values. In order to reduce the number of $q/R$ terms that we must calculate, we have partitioned the infinite lattice into regions of zero net charge, specifically into unit cells. Thus, to calculate the potential felt at ion $A_0$, we first find the potential felt at $A_0$ due to all the other ions in the unit cell in which $A_0$ is located. Then, we add to this the potential felt at $A_0$ due to all the ions in the "layer" of unit cells surrounding $A_0$'s unit cell. This constitutes a "cubic" assembly of unit cells with an edge
dimension of 3 unit cells and forms a "partial lattice". This procedure is repeated for "cubes" of edge dimension 5 and 7. In order to have zero net charge in such a partial lattice, it is necessary to divide the charges of any ion located on a corner, an edge, or a face of the completed assembly by 8, 4, and 2, respectively. Although we have not proven mathematically that this procedure gives fully converged lattice potentials, an examination of figure 1, where the absolute value of $\Phi_L$ is plotted against the length, in unit cells, of the cubic partial lattice, gives us confidence in this method.

3. Results and Discussion

The results of these calculations for nineteen ionic substances are given in Table I. A lattice potential was calculated for each structurally unique ion in all nineteen substances. For a few complex ions, lattice potentials were calculated for more than one atom in the ion. For example, lattice potentials were calculated for both the central and terminal Mn atoms in the $[\text{Mn}_3(\text{CO})_{14}]^-$ ion of $[\text{Ph}_4\text{As}][\text{Mn}(\text{CO})_{14}]$. Table I also includes the cell volume per formula unit for each substance. The literature sources for the structural data necessary for these calculations are given in the references at the end of Table I.

There is quite a variation in the magnitudes of the lattice potentials, even for this small sample. For cations, the lattice potentials range from $-0.35 \text{ eV}$ felt at the center of the $\text{R}_6\text{P}_3\text{N}_3\text{H}^+$ ring of $[\text{HN}_3\text{P}_3(\text{NMe}_2)_6]_2[\text{Mo}_6\text{O}_{19}]$ to $-13.39 \text{ eV}$ felt at the Ca$^{2+}$ ions of Ca[Pt$20_4$]. For anions, the potentials varied from $-0.32 \text{ eV}$ for the Cu$^{2-}$ site in $[(\text{n-C}_4\text{H}_9)_4\text{N}][\text{Cu}(\text{S}_2\text{C}_4\text{N}_2)]$ to $+22.64 \text{ eV}$ for the $\gamma^4\gamma^-$ site in $\text{K}_4\text{V}(\text{CN})_7\cdot2\text{H}_2\text{O}$. The potential measured for $I^-$ in $[\text{Fe}(\text{C}_16\text{H}_{32}\text{N}_4)\text{Cl}]I$ has little physical
Figure 1
Plot of Lattice Potential against the Cube Dimension (See Text).
<table>
<thead>
<tr>
<th>Complex</th>
<th>Coordination</th>
<th>$\phi^+(eV)$</th>
<th>$\phi^-(eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>44.85 Å³/f.u.</td>
<td>Na⁺ -8.92(0)</td>
<td>Cl⁻ +8.92(0)</td>
</tr>
<tr>
<td>[(n-C₄H₉)₄N][Cu(S₂C₄N₂)₂]</td>
<td>751.30 Å³/f.u.</td>
<td>N⁺ -2.77(2)</td>
<td>Cu⁻ -0.32(2)</td>
</tr>
<tr>
<td>Cs[Co(B₉C₁₁H₁₁)₂]</td>
<td>448.20 Å³/f.u.</td>
<td>Cs⁺ -2.28(2)</td>
<td>Co⁻ +3.91(2)</td>
</tr>
<tr>
<td>Perchlorato Tetrapheny1-</td>
<td>865.04 Å³/f.u.</td>
<td>Zn⁺ -4.66(1)</td>
<td>Cl⁻ +4.54(2)</td>
</tr>
<tr>
<td>porphinato Zinc(II)</td>
<td>448.20 Å³/f.u.</td>
<td>N⁺ -2.63(2)</td>
<td>Sb⁻ +6.07(1)</td>
</tr>
<tr>
<td>[(C₉H₇NH)₂Sb(Br₆)][Br]</td>
<td>689.70 Å³/f.u.</td>
<td>N⁺ -2.90(1)</td>
<td>Br⁻ +5.87(2)</td>
</tr>
<tr>
<td>[Fe(C₁₆H₃₂N₄)Cl]I</td>
<td>538.24 Å³/f.u.</td>
<td>Fe⁺ -4.65(1)</td>
<td>(½I)⁻¹/₂ -1.20(2) [disordered]</td>
</tr>
<tr>
<td>[Me₄N]₃[Pt(GeCl₃)₅]</td>
<td>1065.54 Å³/f.u.</td>
<td>N₁⁺ -2.90(1)</td>
<td>Pt³⁻ +9.79(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂⁺ -2.86(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₃⁺ -4.23(2)</td>
<td></td>
</tr>
<tr>
<td>[HN₃P₃(NMe₂)₆][Mo₆O₁₉]²⁻</td>
<td>1487.67 Å³/f.u.</td>
<td>P₁⁰ -0.57</td>
<td>Mo₁₀ 8.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₁⁰ -1.10</td>
<td>Mo₂⁰ 8.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(PN)₃⁺ -0.35(2)</td>
<td>Mo₃⁰ 7.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Mo₆]²⁻ +8.18(2)</td>
</tr>
<tr>
<td>[Ph₄As]⁺[Mn₃(CO)₁₄]⁻</td>
<td>983.82 Å³/f.u.</td>
<td>As⁺ -0.55(4)</td>
<td>Mn₁⁺ +5.27(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn₂⁻ +5.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn₃⁺ +5.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn₄⁻ +5.10(2)</td>
</tr>
</tbody>
</table>
# Lattice Potentials (cont'd)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Volume ($\text{A}^3$/f.u.)</th>
<th>K$^+$</th>
<th>K$_2^+$</th>
<th>K$_3^+$</th>
<th>K$^4^+$</th>
<th>V$^{4-}$</th>
<th>V$^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_4\text{V(CN)}_7\cdot\text{2H}_2\text{O}$</td>
<td>391.74</td>
<td>-1.30(6)</td>
<td>-0.91(8)</td>
<td>-0.91(8)</td>
<td>-1.23(8)</td>
<td>+22.64(9)</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4\text{Sm(SO}_4)_2\cdot\text{4H}_2\text{O}$</td>
<td>269.53</td>
<td>N$^+$</td>
<td>-3.22(4)</td>
<td>Sm$^-$</td>
<td>+5.70(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Fe(}\text{SANE})_2\text{Cl}$</td>
<td>650.29</td>
<td>Fe$^+$</td>
<td>-5.94(1)</td>
<td>Cl$^-$</td>
<td>+6.79(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ti}^+[\text{Co(CO)}_4]^{-}$</td>
<td>174.41</td>
<td>Ti$^+$</td>
<td>-6.29(1)</td>
<td>Co$^-$</td>
<td>+6.20(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}^{2+}[\text{Pt}2\text{O}_4]^{-}$</td>
<td>93.48</td>
<td>Ca$^{2+}$</td>
<td>-13.39(2)</td>
<td>Pt$^-$</td>
<td>+7.79(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{[(C}_6\text{H}_5)_3\text{P}_2\text{N][Fe(CO)}_4\text{CN]}$</td>
<td>920.71</td>
<td>N$^+$</td>
<td>-2.75(2)</td>
<td>Fe$^-$</td>
<td>+2.21(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{trans [CH}_3\text{(CH}_3\text{CN)[CH}_3\text{]}_2\text{Pt(P[CH}_3\text{]}_2\text{C}_6\text{H}_5\text{][PF}_6]}$</td>
<td>662.93</td>
<td>Pt$^+$</td>
<td>-5.66(2)</td>
<td>P$^-$</td>
<td>+6.65(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{[Xe}<em>2\text{F}</em>{11}\text{][AuF}_6]}$</td>
<td>306.11</td>
<td>Xe$_1^0$</td>
<td>-4.38</td>
<td>Au$^-$</td>
<td>+5.10(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{[XeF}_5\text{][AsF}_6]}$</td>
<td>196.16</td>
<td>Xe$^+$</td>
<td>-6.05(3)</td>
<td>As$^-$</td>
<td>+4.61(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{[Xe}_2\text{F}_3\text{][AsF}_6]}$</td>
<td>233.27</td>
<td>Xe$_1^0$</td>
<td>-4.62</td>
<td>As$_1^-$</td>
<td>+4.77</td>
<td>As$_2^-$</td>
<td>+4.81</td>
</tr>
</tbody>
</table>
LATTICE POTENTIALS (cont'd, page 3)

(from last page)

\[ \begin{array}{c|c}
   \text{Xe}_2^0 & -4.89 \\
   \text{Xe}_3^0 & -4.66 \\
   \text{F}_4^+ & -4.66 \\
\end{array} \]
Lattice Potentials, contd.

a The estimated uncertainty in the last significant figure appears parenthetically.  

b For NaCl, a = 5.64 Å.  


e Perchlorate TPP Zn.  


meaning as this structure is disordered with two sites for $I^-$, and the potential was calculated with an $I^{-1/2}$ ion in both sites. Several attempts were made to systematize these potentials in the hope of being able to devise a simple model to estimate lattice potentials for substances where structural data is unavailable and these results are summarized in Table II.

The first column in Table II gives the potential per unit charge, $-\Phi_L(A)/q_A$. Although this reduces the larger potentials so that no term in the column has a magnitude greater than 9 eV, the variations remaining in the potentials are still large compared to ESCA chemical shifts. The next column of figures shows an extension of this idea. In addition to dividing $\Phi_L(A)$ by $-q_A$, the potential is multiplied by the $V^{-2/3}$, where $V$ is the volume per formula unit. This approach was motivated by the simple idea that, as the volume per formula unit is decreased, the ions are forced closer together and the potential increases. The cube root of $V$ was used, rather than $V$ itself, so that the product would be unitless, and thus be sort of a Madelung constant. However, little was gained by this decision. If, out of 39 potentials in the table, one discards the three values under 1.0 and the two values over 4.0, as somehow freaks of nature, these pseudo-Madelung "constants" still vary by a factor of four. In addition, such an approach cannot compensate for the following two types of behavior. In $[(n-C_4H_9)4N][Cu(S_2C_4N_2)2]$, the $[Cu(S_2C_4N_2)2]^{-}$ ion feels a small negative potential, despite its being an anion. An examination of the packing in the unit cell explains this: The relatively flat anions are packed in stacks, and thus the anions are not shielded from each other very well by the cations. For most of these substances, the potentials
<table>
<thead>
<tr>
<th>A SUMMARY OF THE ATTEMPTS TO SYSTEMATIZE THE LATTICE POTENTIALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\phi_L(A)/q_A(eV)$</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td><strong>NaCl</strong></td>
</tr>
<tr>
<td>Na$^+$</td>
</tr>
<tr>
<td>Cl$^-$</td>
</tr>
<tr>
<td>[(n-C$_4$H$_9$)$_4$N][Cu(S$_2$C$_4$N$_2$)]</td>
</tr>
<tr>
<td>N$^+$</td>
</tr>
<tr>
<td>Cu$^-$</td>
</tr>
<tr>
<td>Cs[Co(B$_9$C$<em>2$H$</em>{11}$)]</td>
</tr>
<tr>
<td>Cs$^+$</td>
</tr>
<tr>
<td>Co$^-$</td>
</tr>
<tr>
<td>Perchlorato TPP Zn(II)</td>
</tr>
<tr>
<td>Zn$^+$</td>
</tr>
<tr>
<td>Cl$^-$</td>
</tr>
<tr>
<td>[C$_9$H$_7$NH$_2$][SbBr$_6$][Br$_3$]</td>
</tr>
<tr>
<td>N$^+$</td>
</tr>
<tr>
<td>Sb$^-$</td>
</tr>
<tr>
<td>Br$^-$</td>
</tr>
<tr>
<td>[Fe(C$<em>{16}$H$</em>{32}$N$_4$)Cl]I</td>
</tr>
<tr>
<td>Fe$^+$</td>
</tr>
<tr>
<td>I$^-$</td>
</tr>
<tr>
<td>[((CH$_3$)$_4$N)$_3$[Pt(GeCl$_3$)$_5$]</td>
</tr>
<tr>
<td>N$_1^+$</td>
</tr>
<tr>
<td>N$_2^+$</td>
</tr>
<tr>
<td>Pt$^{3-}$</td>
</tr>
<tr>
<td>Table II contd.</td>
</tr>
<tr>
<td>------------------</td>
</tr>
</tbody>
</table>

**[HN₃P₃(N(CH₃)₂)₆]₂[Mo₆O₁₉]**

<table>
<thead>
<tr>
<th>Ion</th>
<th>P₃N₃⁺</th>
<th>Mo₆²⁻</th>
<th>Mo₆²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.35</td>
<td>0.28</td>
<td>0.73</td>
</tr>
</tbody>
</table>

**[Ph₄As][Mn₃(CO)₁₄]**

<table>
<thead>
<tr>
<th>Ion</th>
<th>As⁺</th>
<th>Mn⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.55</td>
<td>5.07</td>
</tr>
</tbody>
</table>

**K₄[V(CN)₇]·2H₂O**

<table>
<thead>
<tr>
<th>Ion</th>
<th>K⁺</th>
<th>V⁴⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.09</td>
<td>5.66</td>
</tr>
</tbody>
</table>

**NH₄[Sm(SO₄)₂]·4H₂O**

<table>
<thead>
<tr>
<th>Ion</th>
<th>N⁺</th>
<th>Sm⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.22</td>
<td>5.70</td>
</tr>
</tbody>
</table>

**Fe(SANE)₂Cl**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Fe⁺</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.94</td>
<td>6.79</td>
</tr>
</tbody>
</table>

**Tl[Co(CO)₄]**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Tl⁺</th>
<th>Co⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.29</td>
<td>6.20</td>
</tr>
</tbody>
</table>

**Ca[Pt₂O₄]**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ca²⁺</th>
<th>Pt⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.70</td>
<td>7.79</td>
</tr>
</tbody>
</table>

**[(((C₆H₅)₃P)₂N] [Fe(CO)₄CN]**

<table>
<thead>
<tr>
<th>Ion</th>
<th>N⁺</th>
<th>Fe⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.75</td>
<td>2.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion</th>
<th>N⁺</th>
<th>Fe⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.96</td>
<td>1.49</td>
</tr>
<tr>
<td>Compounds</td>
<td>Pt</td>
<td>P</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>trans-([\text{CH}_3{\text{CH}_2\text{CN(\text{CH}_3)}_2}\text{Pt}{\text{P(\text{CH}_3)}_2\text{C}_6\text{H}_5}_2]\text{PF}_6)</td>
<td>5.66</td>
<td>3.43</td>
</tr>
<tr>
<td>([\text{Xe}_2\text{F}_11])[\text{AuF}_6])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Xe-F-Xe})^+)</td>
<td>5.12</td>
<td>2.40</td>
</tr>
<tr>
<td>(\text{Au}^-)</td>
<td>5.10</td>
<td>2.39</td>
</tr>
<tr>
<td>([\text{XeF}_5])[\text{AsF}_6])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Xe}^+)</td>
<td>6.05</td>
<td>2.44</td>
</tr>
<tr>
<td>(\text{As}^-)</td>
<td>4.61</td>
<td>1.86</td>
</tr>
<tr>
<td>([\text{Xe}_2\text{F}_3])[\text{AsF}_6])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{Xe-F-Xe})^+)</td>
<td>4.37</td>
<td>1.87</td>
</tr>
<tr>
<td>(\text{As}^-)</td>
<td>4.77</td>
<td>2.04</td>
</tr>
</tbody>
</table>

\(a\) See text  
\(b\) Disordered  
\(c\) Not calculated
felt at the anion and at the cation do not have equal or nearly equal magnitudes, even when both ions have charges of the same magnitude. Thus, dividing both potentials $\sqrt{3} \cdot 2$ will not, in any meaningful sense, reduce the difference between the two values. To try to account for these two kinds of behavior, a third approach at systematizing the potentials was tried. In this approach, which was restricted to binary salts with singly charged ions, the following procedure was followed:

For the cation, $\Phi_L$ is divided by $e^2 (q_c/R_{cc}^{\text{min}} + q_a/R_{ac}^{\text{min}})$, while for the anion, $\Phi_L$ is divided by $e^2 (q_a/R_{aa}^{\text{min}} + q_c/R_{ac}^{\text{min}})$. $R_{aa}^{\text{min}}$ and $R_{cc}^{\text{min}}$ are the minimum distances between two anions and two cations, respectively, in the unit cell; $R_{ac}^{\text{min}}$ is the minimum distance between the anion and the cation; $q_a$ and $q_c$ are the charges on the anion and cation, respectively, and are equal to $\pm 1.0$ for all of the cases considered here. Again, the quantity obtained is unitless. The results of this approach are listed in the third column of Table II. In short, this approach failed completely.

Thus, although we have a good method for determining lattice potentials for ionic solids of known structure, and although the calculated potentials for a substance can be understood by considering the packing of the specific structure, we have as yet devised no general procedure for estimating lattice potentials. If this goal is to be realized, it is probably necessary to include more substances in our sample, and to more carefully consider the individual packing features of each structure.
References

(1) D. M. Hercules, Analytical Chemistry, 44, 1068 (1972).

(2) W. L. Jolly, Coordination Chemistry Reviews, 13, 47 (1974).


APPENDIX A

A Brief Description of Program POTENT

Program POTENT, a computer program which contains a mixture of Fortran II and Fortran IV statements, calculates lattice potentials in the point charge approximation for ionic crystals using structural information obtained from X-ray diffraction studies of crystals. The program requires 52,200 (octal) core to load and 42,000 (octal) core to run using the RUN76 Fortran compiler at the Lawrence Berkeley Laboratory computing center. This program was developed from Program MODEL, written by University of California Professor, Kenneth N. Raymond.

The procedure used by the program to calculate the lattice potentials is shown in the flow chart, figure 2. Briefly, the cell constants $a$, $b$, $c \cos(\alpha)$, $\cos(\beta)$, $\cos(\gamma)$, and $Z$ are read into the program together with the symmetry operations for the appropriate space group. Then the positions and charges of the crystallographically unique ions are read into the program in the (usually) non-orthogonal unit cell coordinate system. From this information a unit cell is constructed, and ions in this cell are selected as origin points for the potential calculations. Then cubic "layers" of unit cells are constructed around this central unit cell. The potentials are evaluated using the relation:

$$\phi(A_0) = e^2 \sum_i \left( q_i / R_{iA_0} \right)$$

(1)

where $q_i$ is the charge on ion $i$, and $R_{iA_0}$ is the distance between ion $i$ and the origin $A_0$ which is the position of an ion in the central unit cell. $R_{iA_0}$ is evaluated by converting the positions of ion $i$ and of the origin ion, $A_0$, into rectangular coordinates and then using the usual expression for the distance norm in $\mathbb{R}^3$. There is a separate origin
Figure 2

A Flow Chart describing the Operation of Program POTENT
in the central unit cell for each crystallographically unique ion which was included in the unit cell.

The program also calculates the volume of the unit cell, and the distances between the origin ions.
Appendix B

Input instructions for Program POTENT

Card 1

Columns 1-5 (right-justified): number of data sets in this job (NC)

Format (15)

Card 2

Columns 1-80: title card for first data set. Any combination of alphameric characters may be punched on this card (TITLE)

Format (8A10)

Card 3

Unit cell parameter card for first data set

Columns 1-10: a (in Å)
Columns 11-20: b (in Å)
Columns 21-30: c (in Å)
Columns 31-40: cos α
Columns 41-50: cos β
Columns 51-60: cos γ

Reminder: cosθ is a negative number for 90° < θ < 180°

Format (6F10.5)

Card 4

Program parameter card for the first data set.

Columns 1-5 (right-justified): the number of unit cells in the edge of the "cubic" array of unit cells. This number must be an odd number if there is to be a unit cell at the center of the cube. Thus n = 1, 3, 5, 7, ... (NCUBE)

* Restriction * For most lattices, the program is only dimensioned large enough for NCUBE ≤ 7.
Column 6-10 (right-justified): the number of crystallographically unique ions (or atoms) to be placed in the unit cell. Usually only centers of charge are included, e.g. for XeF$_5$(AsF$_6$), only points representing Xe$^+$ and As$^-$ are located in the lattice (NATOMS)

* Restriction * NATOMS < 9

Columns 11-15 (right-justified): the number of general symmetry cards for the specific space group (see below) (NS)

* Restriction * NS < 48 (which is hardly a restriction)

Columns 16-20 (right-justified): the number of translational symmetry cards for the specific space group. (See below) (NT)

* Restriction * NT < 8 (which is likewise no restriction)

Column 25: Punch a 1 in this column if the unit cell is centrosymmetric; otherwise leave blank. (!CENT)

Columns 26-30 (right-justified): The number of formula units per unit cell (NUNITS)

Format (6I5)

NOTE: The number of symmetry cards (of both types), as well as the values which go on these cards may be found by looking up the lattice space group, e.g. P2$_1$/c, in: Norman F. M. Henry and Kathleen Lonsdale, eds., *International Tables for X-Ray Crystallography, Volume I: Symmetry Tables*, Kynock Press, Birmingham 1969. If a unit cell is centrosymmetric, then only one-half of the general symmetry operations found in the tables are read into the program since the remainder are generated by the center of symmetry operation. Talk with any crystallographer to learn which of the symmetry operations are superfluous.
Cards 5...

Translational symmetry cards for the first data set. Translational symmetry operations involve a translation from an original position \( x_0, y_0, z_0 \) to a new position \( x_0 + x, y_0 + y, z_0 + z \), where \( x, y, \) and \( z \) are in the non-orthogonal cell coordinate system.

\[
columns 1-10: x \\
columns 11-20: y (\text{ANT}) \\
columns 21-30: z
\]

Primitive cells, e.g. \( P2_1/c \), have no non-trivial translational symmetry operations (\( NT = 0 \)), and this card may be omitted if \( NT \) was set to zero.

Format (3F10.8)

Cards 6...

General symmetry cards for the first data set. General symmetry operations involves a more complex translation from \( x_0, y_0, z_0 \) to

\[
\begin{align*}
x + (a_x x_0 + b_x y_0 + c_x z_0), \\
y + (a_y x_0 + b_y y_0 + c_y z_0), \\
z + (a_z x_0 + b_z y_0 + c_z z_0)
\end{align*}
\]

All of the coefficients \( (x, y, z, a_x, b_x, c_x) \) can, and often do, have the value 0.0.

\[
columns 1-15: x \\
columns 16-18: a_x, \text{ columns 19-21: } b_x, \text{ columns 22-24: } c_x \\
columns 25-39: y \\
columns 40-42: a_y, \text{ columns 43-45: } b_y, \text{ columns 46-48: } c_y \\
columns 49-63: z \\
columns 64-66: a_z, \text{ columns 67-69: } b_z, \text{ columns 70-72: } c_z
\]

Users of this program at the University of California, Berkeley, who are confused by the instructions should see Prof. Raymond or one of his students as these cards use his SADIAN format.
Ion position cards for the first data set. Positions are given in the non-orthogonal cell coordinate system, and are taken from the table of atom positions in a structure report. Negative numbers are acceptable, but the magnitude of the number should be less than 1.0. Only one atom position card is necessary for each crystallographically unique ion (or atom) being placed in the unit cell.

columns 1-8: a table for the ion or atom represented by this position (ATOM)

columns 31-40: x₀  
columns 41-50: y₀  (COORDS)

columns 51-60: z₀

columns 61-70: The charge assigned to that atom or group (zero is a permissible charge.) (Q)

Format (A8, 22X, 4F10.6)

This completes the cards necessary to describe the first data set. Other data sets, either other crystals, or the same crystal but a different value for NCUBE, are treated in exactly the same manner.

A sample input consisting of four data sets follows.
### Sample Data for Program POTLAT

<table>
<thead>
<tr>
<th>Name</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS+(C9H8C2H11)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.698</td>
<td>7.331</td>
<td>21.207</td>
<td>0.0</td>
<td>-0.20336 0.0</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS+(C7H10C2H11)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.698</td>
<td>7.331</td>
<td>21.207</td>
<td>0.0</td>
<td>-0.20336 0.0</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QUINOLINUM HEXABROMOCINNAMONATE(VI) TRIFluORAC TETRACHLOROC (C9H5C=HN)2583P9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.518</td>
<td>11.316</td>
<td>11.351</td>
<td>0.0</td>
<td>-0.12908 0.0</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1+</td>
<td>0.397</td>
<td>-0.2209</td>
<td>0.2937</td>
<td>1.0</td>
</tr>
<tr>
<td>SR1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>BR4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>(MN3(CO)14)-(P=4451+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.614</td>
<td>9.648</td>
<td>18.022</td>
<td>-0.18895</td>
<td>-0.11609</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS+</td>
<td>0.4274</td>
<td>0.4856</td>
<td>-0.2341</td>
<td>1.0</td>
</tr>
<tr>
<td>MN1(0)</td>
<td>-0.0965</td>
<td>0.1565</td>
<td>-0.1139</td>
<td>0.0</td>
</tr>
<tr>
<td>MN2(-)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>MN3(0)</td>
<td>-0.2370</td>
<td>0.0855</td>
<td>0.4867</td>
<td>0.0</td>
</tr>
<tr>
<td>MN4(-)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>-1.0</td>
</tr>
</tbody>
</table>
This data set consists of two calculations for Cs[Co(B$_9$C$_2$H$_{11}$)$_2$], one having NCUBE = 5, the other having NCUBE = 7, a calculation for (C$_9$H$_7$NH)$_2$(SbBr$_6$)(Br$_3$), a ternary salt, and a calculation for [Mn$_3$(CO)$_{14}$][Ph$_4$As]. The charge centers for all of these ions were taken to be the most central atom in each ion. One should note that the last two data sets have no translational symmetry cards (NT = 0). In addition, the first general symmetry card for all these data sets and for any data set, is the identity operation

$$(x + lx_0, y + ly_0, z + lz_0)$$

The last data set shows several features deserving of comment. There were two crystallographically different Mn$_3$(CO)$_{14}$ ions in the unit cell, and thus it was necessary to include both of these positions. (As the calculations later showed, both types of Mn$_3$(CO)$_{14}$ have nearly identical lattice potentials.) Although the charge on an Mn$_3$(CO)$_{14}$ ion was located on the central Mn atom, the terminal Mn atoms were also included in constructing the unit cell, but were assigned zero charge. Thus, one can also determine the potential felt at other atoms in an ion besides the potential felt at the charge center. To obtain the correct value, however, it is necessary to subtract the quantity $14.4 \times q/R$ from the calculated potential where $q$ is the charge assigned to the charge center of the ion, and $R$ is the distance, in Å, from the ion's charge center to the other atom for which the calculation was also made.
APPENDIX C

A LISTING OF PROGRAM PENT

PROGRAM PENT CALCULATES CRYSTAL LATTICE POTENTIALS FOR USE IN
SOLID STATE ESCA ALIGNING CORRELATIONS

INPUT

1. CARD 1. NUMBER OF DATA SETS FORMAT (15)
2. CARD 2. NAME OF CRYSTAL, ETC. FOR FIRST DATA SET FORMAT (8A10)
3. CARD 3. LATTICE PARAMETERS A, B, C, COS(LAMDA1), COS(LAMDA2),
   COS(LAMDA3) FORMAT (6F10.5)
4. CARD 4. PARAMETERS ACUC, NATMS, NSYMMETRY, NTRANSLATIONS,
   CENTROSYMTRIC, UNITS FORMAT (C15)
5. CARD 5...6...7... ATOMIC CARDS (ATOM, X0, Y0, Z0, CHARGE)
   FORMAT (4F12.6)
   MAXIMUM NUMBER OF ATOMS IS 9.

OTHER CRYSTALS PUNCHED IN THE SAME MANNER

PROGRAM MODIFIED FROM ONE BY K.RAYMOND BY W.B.PERRY, U.C.BERKELEY
NOVEMBER 1973

DIMENSION TITLE(8),GCP(6),U1(3),U2(3),OM1(3),OM2(3),XY1(3)
DIMENSION U1(9),U2(9)
COMMON/COM/UMT(3,3),UT1(3,3),UT2(3,3),I,CENT,NT,NS,IPUNCH
COMMON/COM2/UT1(3,3),V(3,3)
COMMON/SPACE/UNIT(9,9),NATATOMS
COMMON/ORIGIN/X(9),Y(9),Z(9)
COMMON/CO/COORDINATES
DATA U1/U10.0,0,0,0/U2/U20.0,0,0,0/U3/U30.0,0,0,0/

1 FORMAT (15)
2 FORMAT (4F12.6)
3 FORMAT (6F10.5)
4 FORMAT (//3X,*CELL CONSTANTS* 20X,*CH*, 16X,*CH*, 14X,*CH*, 10X
   1,*COSALPHA*, 8X,*COSBETA*, 7X,*COSGAMMA*, 15X,F15.6)
5 FORMAT (15)
6 FORMAT (6F10.5)
9 FORMAT (//38X,*X*1, *X*1, *Y*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
1. *=X*1, *X*1, *Y*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
2. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
3. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
4. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
5. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
6. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
7. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
8. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
9. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
10. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
11. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
12. *=X*1, *X*1, *X*1, *3F10.5,*1X)/2 38X,*1X)/2 38X,*1X)/2 38X,*1X)
45 FORMAT (//10X,*POTENTIAL AT ID*,A8,3H,*F10.5,3H EV )
46 FORMAT (///,20X,*VOLUME OF THE UNIT CELL IS *F10.4)
1. cubic Angstroms.
2. Format (/ 25x, 2d, the unit cell contains 15, 1d, formula units).
3. Format (/ 20x, 3d, mass volume per formula unit is 15, f0/4).
4. Format (/ 15x, 3d, lattice distances /).
5. Format (/ 10x, 3d, 13x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
6. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
7. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
8. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
9. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
10. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
11. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
12. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
13. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
14. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
15. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
16. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
17. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
18. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
19. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
20. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
21. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
22. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
23. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
24. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
25. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
26. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
27. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
28. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
29. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
30. Format (/ 15x, 3d, 15x, 2d, (4, 4, 21, 21, 14, 14, 4, 4, 5, 5)).
SUBROUTINE CROSS (A, B, C)
DIMENSION HA(3), R(3), C(3), E(6), B(6), CI(3), B9(3,3)
DOLL15=1.3
A1(I)=A(I)
A1(I+3)=A(I)
B1(I)=B(I)
DOLL9=1.3
115 B1(I+3)=B(I)
DOLL9=1.3
119 CI(I)=AI(I+2)-A(I+2)*BI(I+1)
CALL MVIRS, CI, CI
RETURN
END

SUBROUTINE GETSYM
COMMON/COM/ANT(3,8), TS(3,3,48), TTS(3,48), ICENT, NT, NS, IPUNCH
1106 FORMAT(3(F15.9,4F3.0))
1107 FORMAT(26H0SYMMETRY POSITIONS /5SM / 1
1108 FORMAT(40HTRANSLATIONS X Y Z / (1X, I3, 10X, 3F1
10.4))
1109 TFINT 2000, 2001, 2002
2000 ON 1902 13=1.3
2002 ANT(13,1)=3.0
NT=1
GO TO 2004
2001 READ 1108, (ANT(I,1), I=1,3, J=1,3), I=1, NT}
SUBROUTINE MATSET(OMP,OM,PHI,UL,U2,V,NT)

   DIMENSION U(3,3),OMP(6),UM(3,3),U(3,3),UL(3),U2(3),U3(3),U4(3)

   CALL STOPAF(OMP,PHI)
   CALL M13(OM,OM,OM,OM,UL,U2,U3,U4)
   CALL NXTPFP(OMP,PHI)
   CALL C05SFP(UL,U2,U3)
   CALL C05SSL(OMP,OM)
   CALL C05SSS(UL,U2,U3,U4)
   DO 11 J=1,3
      U(1,J)=0
   11 CONTINUE
   DO 12 J=1,3
      U(1,J)=U(2,J)
   12 CONTINUE
   CALL M13(U,V,NT)
   RETURN
END

SUBROUTINE M13(AI,C)

   DIMENSION A(3,3),AI(3,3)

   DO31=1,3
   DO 31 J=1,3
      K=1+ MOD (J+1,3)
      M=1+ MOD (K+2,3)
      N=1+ MOD (J+2,3)
      L=1+ MOD (J+1,3)
 31 AI(J,J)=A(L,K)*A(K,M)-A(L,M)*A(N,K)

   D=0
   DO11=1,3
   DO 11 J=1,3
      I=J+1
      AO=AI(I,J)*AI(J,I)
   11 CONTINUE
   DO21=1,3
   DO 21 J=1,3
      AO*=AI(I,J)*AI(J,I)/O
   21 CONTINUE
   RETURN
END

SUBROUTINE MTXYZ(ICK,X)

   DIMENSION X(3)
   COMMON/COMZ/XMAX,XXDA(3),XALL(3,4000)
COMMON/COM3/ U(3,3), V(3,3)
INTEGER NRGY, XM, X
DO 1 J=1,3
X(J)=0
DO 1 I=1,3
1 X(I)=X(I)+V(I,J)*XALL(J,1)
RETURN
END

SUBROUTINE NCV(A, R, C)
DIMENSION A(1:3), R(1:3)
C(I)=1.0
DO 2 I=1,3
2 C(I)=A(I,J)*R(J)+C(I)
RETURN
END

SUBROUTINE NORM(A, U)
DIMENSION A(1:3), U(3)
DO 1 I=1,3
1 U(I)=A(I)*1
RETURN
END

SUBROUTINE SAME(NXALL, INS, INT, IC, IPUNCH, IFID, ATOM, Q, INDX)
COMMON/COM2/ RGY, XM, XDA(3), XALL(3,4CGO)
COMMON/SPACE/VLINE
COMMON/ORIGIN/XYO(9,3), V(19), NAGMS
INTEGER RGY, XM
FORMAT(10X, 9A2, 1X, 9F10.5, 1X, 10X, 3P10.5)
IF (NXALL .EQ. 0) GO TO 21
DO 5 S=1, NXALL
5 CONTINUE
GO TO 1
6 CONTINUE
21 NXALL=NXALL+1
DO 6 S=1,3
6 XALL(S,NXALL)=XDA(S)
CALL MXY2 (NXALL, XM)
IF (IC .GT. 237) GO TO 1
7 CENTRO=1M
GO TO 10
8 CENTRO=1M
10 IF (IPUNCH .EQ. 1) PRINT 11, ATOM, XDA, INS, INT, CENTRO, XM

11 FORMAT(10X, 9A2, 1X, 9F10.5, 1X, 10X, 3P10.5)
NLINES=NLINES+1
INPNTS=INPNTS+1
IF (PUNCH .EQ. 1) GO TO 20
20 DO 30 I=1,NATOMS
**
30 CONTINUE
RETURN
END

SUBROUTINE SEARCH(ATOM1,X21,X22,X23,INDX,0)
DIMENSION XD(3),XH(3),0(9)
COMMON/COM/0(3),TS(3,3),R(TS(3,3),8),TS(3,48),CENT,NT,NS,PUNCH
COMMON/CMY/CMY,XMAX,XMIN,XALL(3),XALL(3),XYMAX
COMMON/SPAC/NT,NS
INTEGER NY,NSX
201 FORMAT(1X,4X,ATM,N,9X,CELL COORDINATES,9X,NS NT C,
1 11N, MODEL COORDINATES, 9X, 2 2X, 2 ( 14X, 9X, 9X, 9X, 9X, 9X, 15X, 1 )
202 FORMAT(1/
203 FORMAT(12X,AB, 15 NGT WITHIN THE CELL BOUNDARIES *)
IF FIND=0
NALL=0
IF (NLINES. EQ. 0) AND PUNCH .EQ. 1) PRINT 201
C
C
ENTP SYMMETRY LOOP
C
30 D0 999 J=1,NS
40 D0 990 JJ=1,13
50 XD(JJ)=TS(S,1,J)+*X21*TS(1,JJ,J)+*X22*TS(2,JJ,J)
*/X23*TS(3,JJ,J)
C
C
ENTER TRANSLATION LOOP
C
60 D0 999 IA=1,NT
70 D0 70 JJ=1,13
70 XDA(JJ)=XDA(JJ)+ANT(JJ,IA)
C
C
ENTER LOOP FOR CENTROSYMMETRIC CASES
C
NICE=1
IF (CENT .NE. 0) NICE=2
DO 998 INICE=1,NICE
IF ((INICE .EQ. 1) GO TO 80
71 DO 74 JJ=1,13
74 XDA(JJ)=XDA(JJ)
80 D0 81 JJ=1,13
IF (XDA(JJ) .LT. 0.0) XDA(JJ)=XDA(JJ)+1.0
IF (XDA(JJ) .GT. 1.0) XDA(JJ)=XDA(JJ)-1.0
C
C
81 CONTINUE
START LOOPS FOR BOUNDARY CONDITIONS.

DO 120 J=1:MAX,Y,IXMAX
XXDA(I)=XXDA(I)+FLOAT(J-1)
END

DO 120 J=1:MAX,Y,IXMAX
XXDA(J)=XXDA(J)+FLOAT(J-1)
END

DO 105 J=1,3
IF (XXD(J) .GT. FLOAT(MAX)) GO TO 120
105 CONTINUE

110 QFAC=1.0

DO 111 J=1:3
IF (XXD(J) .GE. 0.3 .OR. XXDA(J) .GT. FLOAT(MAX)) QFAC=QFAC*2.5
111 CONTINUE

CALL SAMPLE(INPLIT,J,J,TA,IICE,IPUNCH,IFIND,ATOM,QI,INULX)

120 CONTINUE

998 CONTINUE

999 CONTINUE

IF (IFIND .NE. 0) GO TO 9999
PRINT 201
IF (NLIN .GE. 40) NLIN=0
RETURN
END

SUBROUTINE STAA(A,AA)
DIMENSION(A(1,3)),AA(3,3)
AA(1,1)=A(1,1)*A(1,1)
AA(2,2)=A(2,2)*A(2,2)
AA(3,3)=A(3,3)*A(3,3)
AA(1,2)=A(1,1)*A(2,2)*A(3,3)
AA(2,3)=A(1,1)*A(2,2)*A(3,3)
AA(3,1)=A(1,1)*A(2,2)*A(3,3)
AA(1,3)=A(1,1)*A(2,2)*A(3,3)
AA(2,1)=A(1,1)*A(2,2)*A(3,3)
RETURN
END

FUNCTION VMV(A,B,C)
DIMENSION(A(3),B(3),C(3))
VMV=0.0
DO 111=1,3
DO 111=1,3
VMV=VMV+A(I,J)*B(I,J)*C(I)
RETURN
END
VII. THE CALCULATION OF ATOMIC CHARGES IN MOLECULES
BY AN ELECTRONEGATIVITY EQUALIZATION PROCEDURE:
A DESCRIPTION OF PROGRAM CHELEQ

Abstract

Program CHELEQ is a Fortran IV computer program which calculates atomic charges in molecules containing up to 60 atoms by an electronegativity equalization procedure. In addition, the calculated charges may be correlated with experimentally determined ESCA core binding energies using the electrostatic potential equation: \( E_B = kQ + V + \lambda \), or using a relaxation corrected potential equation: \( E_B = kQ + V + \lambda + E_R \). The program determines the parameters \( k \) and \( \lambda \) by linear least squares analysis.

Introduction

Program CHELEQ is a Fortran IV computer program which requires approximately 64,400 (octal) core memory to load and 55,000 (octal) core to execute using the RUN76 Fortran compiler for the CDC 7600 computer at the Lawrence Berkeley Laboratory.* The program, as dimensioned in this write-up, can calculate charges on molecules containing up to 60 atoms, and each atom may be bonded to up to 6 other atoms. A further restriction is that the total number of bonds (a multiple bond equals only one bond) may not exceed 60.

The electronegativity equalization procedure used by program CHELEQ to calculate atomic charges in molecules is based upon a

*The amount of required core memory can be significantly reduced if the dimensions of certain arrays are reduced. This possibility is discussed in Appendix A.
definition of electronegativity by Iczkowski and Margrave.\(^2\) To calculate the atomic charges in a molecule using this method, the molecule is first represented by a valence bond structure, which may be the average of several resonance structures. Charge-dependent, orbital electronegativities are then defined for each of the hybrid, bonding orbitals represented in the valence bond structure. Charge is then transferred through the bonds until the electronegativities of each pair of mutually bonded orbitals are equalized. More specifically, one must solve one of the following equations for each bond in the molecule:

\[
\frac{7.3(h_m + h_n)}{(N_{nm})^{0.7}} q_{nm} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} = \]

\[
x(p)_n - x(p)_m + \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}} \left[ x(s)_n - x(p)_n \right] \]

\[
- \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}} \left[ x(s)_m - x(p)_m \right] + c_{n} F_{n} - c_{m} F_{m}
\]

The \(q_{ij}\) are the unknown quantities, and one obtains \(n\) equations and \(n\) unknown \(q_{ij}\)'s for a molecule containing \(n\) bonds. The charge on an atom \(i\) is given by:

\[
Q_i = F_i + \sum_{j} q_{ij}
\]
The rationale for these formulae and definitions of the quantities appearing in the formulae appear in references 1 and 3. In Ref. 1, results are presented for molecules containing primarily first row atoms whereas Ref. 3 also includes molecules containing heavier atoms. The program described in this work includes the revisions presented in Ref. 3 together with value for x(s), x(p) and h for the elements from hydrogen through radon.

The interpretation of ESCA core binding energies by the electrostatic potential equation\textsuperscript{4} provides a simple method of evaluating atomic charges. This equation has the form:

$$E_B(A) = kQ_A + V + \ell$$

(3)

where $E_B$ is a core binding energy, $k$ and $\ell$ are parameters, $Q_A$ is the charge on atom A, and $V$ is the potential due to the other atoms in the molecule and is equal to

$$e^2 \sum_{B \neq A} Q_B/R_{AB}.$$ 

A better description of ESCA chemical shifts should be given by a modification of this equation which includes the effects of the electronic rearrangement, or relaxation, which takes place during photo-emission. This equation\textsuperscript{3} has the form:

$$E_B(A) = kQ_A + V + \ell + E_R$$

(4)

$E_B$, $k$, and $\ell$ are defined as before. In order to calculate the relaxation energy, $E_R$, two charge calculations must be made: one for the neutral molecule, and one for the isoelectronic cation which is obtained by substituting the core of the next heavier atom on the periodic
Program CHELEQ includes the option of using the calculated charges to correlate ESCA binding energies by means of either Eqs. 3 or 4. In the latter case, the calculation for the isoelectronic cation is automatically carried out by the program.

Program Description

The topology of the valence bond structure, that is, which atoms are bonded to which other atoms, bond orders and formal charges, are read into the program atom by atom together with the atomic numbers of the atoms. The program then determines the hybridization of each atom from the topological data and calculates the right-hand side of Eq. 1, which is the charge independent part of the equation, for each bond. Then, the system of Eq. 1 is written in matrix form:

$$AX = B$$

where \( A \) is an \( n \times n \) matrix of coefficients from the left-hand sides of Eq. 1, \( X \) is an \( n \times 1 \) matrix of the \( q_{ij} \) and \( B \) is an \( n \times 1 \) matrix of the right-hand sides of Eq. 1. The values of the \( q_i \) are determined by the Gauss-Seidel procedure for solving systems of linear equations. Atomic charges are then calculated by summing the appropriate \( q_{ij} \) for an atom and adding this sum to the formal charge of the atom.

If an ESCA core binding energy correlation including electronic relaxation effects is being made, the program increases the atomic number of the ionized atom, together with its formal charge, by one.
unit, and the calculation is repeated for the isoelectronic cation. It is possible to specify a different topology for the isoelectronic cation than for the neutral molecule. The \( Q \) or \( Q^* \) and \( V \) or \( V^* \) terms are stored and/or calculated and then stored for each molecule in the data set which is being correlated. After all the charge calculations have been made, the program fits the data to the electrostatic potential equation by determining the parameters \( k \) and \( \ell \) through least squares analysis. After printing the experimental and calculated binding energies, their difference, and the relaxation energy (if Eq. 4 was used for the correlation), the standard deviation and two correlation coefficients are calculated. Finally, a rough plot of the correlation is printed.

A simplified flow chart of the program is presented in Fig. 1.
Fig. 1. A flow chart describing the operation of program CHELEQ.
Data Input for Program

The first operation in supplying input data to the program is to numerically order the atoms in the molecules. For example:

\[
\begin{array}{c}
F_3 \\
F_4 \quad C_2 \quad H_1 \\
F_5
\end{array}
\]

These numbers will be used by the program as indices, and will specify which atoms are bonded to which other atoms.

**Card 1: Data Set Card**

columns 6-10 (right justified): The number of molecules in the data set (NC)

columns 16-20: punch NOFIT in these columns if just atomic charges are desired, i.e., no binding energy correlation. Leave these columns blank for a ground state correlation (equation 3). Punch RELAX into these columns for a correlation including relaxation effects (equation 4). (FIT).

columns 21-80: The title of the data set. Any combination of alphabetic characters may be used (LABEL)

*Restriction* NC < 75

Format (5X, I5, 5X, A5, 6A10)

**Card 2: Title card for the (first) molecule**

columns 1-80: Name, etc. of the first molecule. Any combination of alphabetic characters may be used (CNAME)

FORMAT (10A8)
Card 3: General information about the molecule

columns 6-10 (right justified): the number of atoms in the molecule (NA)

columns 16-20 (right justified): the index of the (i.e. the number assigned to) the core ionized atom (MESCA). This may be left blank if no ESCA correlation is desired.

columns 26-35: the core binding energy of the ionized atom in electron volts (BEX). This also may be left blank if no ESCA correlation is desired.

*Restriction* NA ≤ 60

Format (5X, I5, 5X, I5, 5X, F10.0)

Cards 4 •••: Atom data cards. One card for each atom in the molecule. The order of these cards is important. The first card must contain the information about the atom which was assigned the index 1, the second card must be for the atom assigned index 2, etc.

columns 6-10 (right-justified): The atomic number of the atom represented by this card (NZ).

columns 16-20: The formal charge of the atom (C).

The next data on the card are for the bonds between the atom represented by this card and other atoms in the molecule. BNDSTO is the index previously assigned to an atom in the molecule, and N is a bond order.

columns 22, 23 (right justified): BNDSTO for the 1st bond, that is, the index of an atom which is bonded to the atom represented by this card. Any bond may be used for the "first" bond.
columns 25-28: N for the first bond

columns 30,31 (right justified): BNDSTO for the 2nd bond (if any).

columns 33-36: N for the second bond (if any).

columns 38,39 (right justified): BNDSTO • • •

columns 41-44: N • • •

columns 46,47 (right justified): BNDSTO • • •

columns 49-52: N • • •

columns 54,55 (right justified): BNDSTO • • •

columns 57-60: N • • •

columns 62,63: (right justified): BNDSTO • • •

columns 65-68: N • • •

columns 70-80: The distance from the atom represented by this card to the ESCA ionized atom, in Angstroms. (If this card represents the ionized atom, R = 0.0). This datum may be omitted if no ESCA correlation is desired (R).

*Restrictions* NZ ≤ 86; an atom may be bonded to no more than 6 other atoms.

*Default Value* If, for any bond, the field for N is left blank, the program will assume N = 1 (a single bond).

Format (5X, I5, 5X, F5.0, 6(1X, I2, 1X, F4.0), 1X, F11.0)

Calculations made for the isoelectronic cations used in relaxation correlations sometimes have different bond orders than do the neutral molecules. For example, we believe that the ground state of a carboxylic acid is well represented by the structure:

\[ R \overset{\cdots}{\underset{\text{O}}{\text{C}}} \overset{\text{O}}{\text{H}} \]
The isoelectronic cation for a carbonyl core-ionized oxygen should, however, be represented as an intermediate between the two structures:

![Diagram of isoelectronic cation]

To use different bond orders and formal charges in the calculation for the isoelectronic cation than were used for the neutral molecule, the following procedure is followed. Punch a 1 in column 1 of each atom data card where there will be a change in the bond orders or the formal charge. Immediately following such an atom data card is another card with C, BNDSTO, and N information punched in columns 16-68 using the same format as the atom data card. When this procedure is used for the card representing the ionized atom, the formal charge on that atom, for the isoelectronic cation, is the charged punched onto the second card, not $F_c + 1$, as is the case for "normal" molecules. Cards which represent atoms with the same bond orders and formal charges in both the ion and the neutral molecule, for example the atoms in the R group of the carboxylic acid, need not be altered.

Format (15X, F5.0, 6(I1, I2, I1, F4.0))

Card 5: The title card for the second molecule in the data set. The second and subsequent molecules are treated exactly the same as the first molecule.

Sample input data for three molecules is given below. Carbon monoxide, a molecule which has multiple bonding and non-zero formal charges, is represented by the structure
where the atom indices are written as subscripts, the bond order is written above the bond and the formal charges are written above the appropriate atoms. Formic acid has different structure representing the neutral molecule and the isoelectronic cation for the carbonyl oxygen. The structure for the neutral molecule is:

The structure for the carbonyl oxygen isoelectronic cation is:

Finally the structure for SiF$_4$ is simply:
**SAMPLE DATA FOR PROGRAM CHELEQ**

**CARBON MONOXIDE**

<table>
<thead>
<tr>
<th>C IS BINDING ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>1.128</td>
</tr>
</tbody>
</table>

**FORMIC ACID**

<table>
<thead>
<tr>
<th>C HI5, CARBONYL BINDING ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1.113</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>2.27</td>
</tr>
<tr>
<td>2.64</td>
</tr>
<tr>
<td>1.98</td>
</tr>
</tbody>
</table>

**SILICON TETRAFLUORIDE**

<table>
<thead>
<tr>
<th>SI 2Ω 3/2 BINDING ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>14</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>1.54</td>
</tr>
<tr>
<td>1.54</td>
</tr>
<tr>
<td>1.54</td>
</tr>
<tr>
<td>1.54</td>
</tr>
<tr>
<td>0.0</td>
</tr>
</tbody>
</table>
References

Reducing the Core Memory Required by Program CHELEQ

As listed in this write-up, program CHELEQ can handle molecules containing up to 60 atoms. This limit may be larger than is necessary for many users. If this dimension is reduced, considerable savings of core memory will result. The following arrays, may be redimensioned from 60 to some other number, n.

- **CON (60,60)** → **CON(n,n)**
- **LAB (60,60)** → **LAB(n,n)**
- **S(60,60)** → **S(n,n)**
- **BNDSTO (60,12)** → **BNDSTO(n,12)**
- **N(60,12)** → **N(n,12)**
- **B(60)** → **B(n)**
- **C(60)** → **C(n)**
- **Cl(60)** → **Cl(n)**
- **NZ(60)** → **NZ(n)**
- **RAD(60)** → **RAD(n)**
- **SQ(60)** → **SQ(n)**
- **X(60)** → **X(n)**
- **COMMON/ARRAYS/V(60,61)** → **V(n,n+1)**
- **COMMON/ARRAYS/A(60,61)** → **A(n,n+1)**

The array PLOT(60,60) in subroutine ESCAL should not be redimensioned.

---

*a* appears in the main program  
*b* appears in subroutine CONST  
*c* appears in subroutine LINEQ  
*d* appears in subroutine ESCAL
APPENDIX B
A LISTING OF PROGRAM CHELEQ

PROGRAM CHELEQ (INPUT,OUTPUT,TAPES+INPUT,TAPES+OUTPUT)

PROGRAM CHELEQ CALCULATES SET ATOMIC CHARGES USING AN ORBITAL
ELECTRONEGATIVITY EQUALIZATION METHOD DEVELOPED BY W.L. JOLLY

PROGRAM IS PARAMETERIZED FOR THE ELEMENTS H THROUGH P
MAXIMUM NUMBER OF ATOMS IS 60, MAXIMUM NUMBER OF (SIGMA) BONDS IS 60

THIS VERSION CONTAINS A LEAST SQUARES FIT OF THE CHARGE DISTRIBUTIONS
TO EXPERIMENTAL BONDING ENERGIES USING THE ESCLA POTENTIAL MODEL

TO OBTAIN A FIT OF BONDING ENERGY AGAINST CHARGE (I.E. TO IGNORE
THE POTENTIAL TERM) WITH THE BOND DISTANCES ON THE DATA CARDS
MAXIMUM NUMBER OF COMPOUNDS IN BONDING ENERGY CORRELATION IS 75

INPUT
CARD 1 NUMBER OF COMPOUNDS IN THE RUN
FOR A RELAXATION CORRECTED FIT OF CHARGES TO BINDING
ENERGIES, PUNCH RELAX IN COLUMNS 16-20.
IF NO FIT OF CHARGES TO BINDING ENERGIES IS WANTED,
PUNCH NOFIT IN COLUMNS 16-20. GENERAL ALPHABERIC
INFORMATION ABOUT THE DATA SET MAY BE PUNCHED IN
COLUMNS 21-80. FORMAT (5X,15,5A,5,A10)
CARD 2 NAME, ETC. FORMAT (10A8)
CARD 3 NUMBER OF ATOMS IN COMPOUND, NUMBER OF THE IONIZED ATOM,
EXPERIMENTAL BONDING ENERGY FORMAT (5X,15,5X,15,5X,F10.6)
IF NO FIT IS WANTED, BINDING ENERGIES AND IONIZED ATOM
NUMBER MAY BE OMITTED
CARDS 4,.... (ONE PER ATOM) ATOMIC NUMBER, FORMAL CHARGE, (NEXT
INFO LISTED PAIRWISE FOR EACH BOND) NUMBER OF
ATOM BONDED TO, BOND ORDER OF THAT BOND (UP TO SIX
BONDS PER ATOM), DISTANCE TO IONIZED ATOM (ANGSTROMS)
FORMAT (11X,4X,15,5X,F5.0,6(X,12,1X,F4.0),1X,F11.0)
**NOTE**
TO USE DIFFERENT H-BONDERS IN THE ISOLELECTRONIC CATION (IN
RELAXATION CORRECTED EB FITS), SEE PROGRAM WRITEUP (LAL REPORT).

ADDITIONAL COMPOUNDS PUNCHED IN SAME MANNER

PROGRAMMED BY W.B. PERRY AT U.C.B.

DIMENSION CM(12,75),NZ(60),BNDSTO(60,12),N(60,12),LAB(60,60)
DIMENSION CN(60,60),C(60,5,60),*OR(60),C1(60)
DIMENSION LBL(60),BEX(75),RAD(60),VA(75),QESCA(75)
DIMENSION S16(60)
REAL N
INTEGER BNSTO
COMMON/C0,C0F7T/P(100),CK,A
COMMON/ÄôPAYS/V(60,61)
COMMON/ÄôFEX/071751,0V1731
DATA AFIT/5HOFIT/
DATA RELAX/5HRELAX/
READ (5,5) NIX,WPD,FIT,LABLE
WRITE (6,6) LABLE
DO 40 J=1,NK
DO 60 I=1,60
BNOSTO(I,J)=0
15 N(I,J)=0.0
READ (5,10) (C(NC), NC=1,NC)
READ (5,20) NA, NESC, BSE(NC)
DO 40 I=1,NA
READ (5,30) N(NT(I),NZ(I)),C(I),((BNOSTO(I,J),N(I,J),J=1,6),RAD(I)
IF (NTH(I)) .EQ. 2, 32, 34
31 READ (5,32) C(I),(BNOSTO(I,J),N(I,J),J=7,12)
34 CONTINUE
40 CONTINUE
42 DO 4d N(I,J)=1.2
IF (NT .EQ. 2 .AND. FIT .NE. RELAX) GO TO 400
IF (NT .EQ. 2) N(I,NESC)*N(I,NESC)+1
IF (NT .EQ. 2) C(NESC)+C(NESC)+1.0
IF (NT .EQ. 2) 22, 4d
40 CONTINUE
CALL CONST(NA,NB,NSTO,NZ,C,N,CON) do 50 I=1,NA
DO 50 J=1,6
K = BNOSTO(I,J)
IF (K .GT. 1.0) GO TO 50
NB = NB+1
50 CONTINUE
NB = NBT/2
NB1 = NB+1
DO 55 I = 1,60
DO 55 J=1,61
55 VI,J=0.0
L=0
DO 60 I=1,NA
DO 60 J=1,6
K = BNOSTO(I,J)
IF (K .LT. .EQ. 1.0) GO TO 60
IF (I .GT. K) GO TO 60
L = L+1
LAR1,K = L
VING1,1 = CON(I,K)
60 CONTINUE
L=0
DO 200 I=1,NA
DO 200 J=1,6
NZI = NZ(I)
DO 200 J=1,6
K = BNOSTO(I,J)
IF (K .LT. J) GO TO 200
IF (I .GT. K) GO TO 200
NZK = NZ(K)

L = L+1
DO 110 JJ=1,6
CA=1.0
KK = RANDST(J, JJ)
IF (KK .EQ. 0.1) GO TO 110
IF (I .GT. KK) 70, 90, 20
70 DO 90 LA=1,98
IF (KK .EQ. K) CA = CK/(N(1,J)**A)
IF (LARI(KK,1), EQ. LA) V(L,LA) = V(L,LA)+B(NZI)*CA
80 CONTINUE
GO TO 110
90 DO 100 LA=1,99
IF (KK .EQ. K) CA = CK/(N(1,J)**A)
IF (LARI(KK,1), EQ. LA) V(L,LA) = V(L,LA)-B(NZI)*CA
100 CONTINUE
GO TO 160
110 CONTINUE
DO 160 JJ=1,6
CA=1.0
KK = RANDST(K, JJ)
IF (KK .EQ. 0.1) GO TO 160
IF (K .GT. KK) 120, 140, 200
120 DO 130 LA=1,98
IF (KK .EQ. K) CA = CK/(N(1,J)**A)
IF (LARI(KK,1), EQ. LA) V(L,LA) = V(L,LA)-B(NZI)*CA
130 CONTINUE
GO TO 160
140 DO 150 LA=1,99
IF (KK .EQ. K) CA = CK/(N(1,J)**A)
IF (LARI(KK,1), EQ. LA) V(L,LA) = V(L,LA)+B(NZI)*CA
150 CONTINUE
160 CONTINUE
200 CONTINUE
IF (N8 .EQ. 1) 202, 204
202 NZI = NZ(1)
NZK = NZ(2)
V1(NBI) = -CUM(1,2)/((B(NZI)+B(NZK))*CK/(N(1,1)**A))
GO TO 206
204 CALL LINEQ (N8)
206 CONTINUE
DO 210 I=1,14
215 S0(I) = G(I)
WRITE (6, 2500) (CAAME(I,NC), I=1,10)
20 DO 230 L=1,NN
DO 230 I=1,NN
DO 233 J=1,6
K = RANDST(1,1)
IF (K+1 .EQ. 1) GO TO 230
IF (I .GT. K) GO TO 230
IF (LARI(K,1), EQ. LA) 210, 230, 230
210 WRITE (6, 2200) I, K, V(L,NBI), I, K, S(I,K), K, I, S(K,I)
S0(I) = S0(I)+V(L,NBI)
S0(K) = S0(K)-V(L,NBI)
GO TO 240
230 CONTINUE
240 CONTINUE
TOTCHG=0.0
VA(NC)=0.0
DO 270 I=1,14
TOTCHG = TOTCHG+S0(I)
IF (RAD(I)+1.0) =0.0, 1.0) 243, 244
243 VA(NC) = VA(NC) + 14.4*S0(I)/RAD(I)
246 CONTINUE
SUBROUTINE CONST(NA, RNDO, NC, CN, CON, S)

SUBROUTINE CALCULATES THE CONSTANT TERMS IN THE ELECTRONEGATIVITY

EQUALIZATION EQUATIONS

DIMENSION RNDO(0:12), NC(0:1), CON(0:60), XS(1001), XP(1001)

COMMON(C007FF(101), CK, A)

REAL N, NIJ, NMIN

INTEGER RNDO

DATA (XS(I), I=1,100) / 2.21,0.0,2.0,0.3,2.25,1.0,4.6,6.0/6.2,6.26,7.35,0.77,1.36,1.20,
1 1.32,1.45,1.56,1.0,1.64,1.70,1.75,1.75,1.06,1.18,4.00,1.86,
2 3.4,3.5,4.4,6.0,0.0,0.5,2.26,1.11,1.22,1.22,1.3,1.20,1.36,4.21,4.5,1.35,
4 1.21,1.34,2.88,3.60,4.24,4.12,4.12,5.30,2.40,1.08,1.06,0.12,3.23,
5 1.33,1.40,1.40,1.40,1.55,1.44,1.44,1.44,1.44,2.44,2.44,2.58,3.06,3.49,
6 4.7,3.45,0.1

DATA (XS(I), I=1,100) / 2.21,0.0,2.0,0.3,2.25,1.0,4.6,6.0/6.2,6.26,7.35,0.77,1.36,1.20,
1 1.32,1.45,1.56,1.0,1.64,1.70,1.75,1.75,1.06,1.18,4.00,1.86,
2 3.4,3.5,4.4,6.0,0.0,0.5,2.26,1.11,1.22,1.22,1.3,1.20,1.36,4.21,4.5,1.35,
4 1.21,1.34,2.88,3.60,4.24,4.12,4.12,5.30,2.40,1.08,1.06,0.12,3.23,
5 1.33,1.40,1.40,1.40,1.55,1.44,1.44,1.44,1.44,2.44,2.44,2.58,3.06,3.49,
6 4.7,3.45,0.1

DATA XS(2), XS(3), XS(4) / 2.75, 0.84, 2.15 /

DATA XS(5), XS(5) / 0.4, 1.15 /

DATA (XP(I), I=1,20) / 4.00, 0.12, 1.75, 2.65, 3.49, 3.90, 4.00, 0.32,
1 0.56, 1.11, 1.82, 2.23, 2.62, 2.95, 3.60, 0.38, 0.62, 1.20, 1.32, 1.45,
```
1.60, 1.40, 1.44, 1.49, 1.51, 1.55, 1.60, 2.00, 2.40, 2.80, 2.82, 3.00, 3.60, 4.00, 4.40, 4.80, 4.80, 5.20, 5.60, 6.00, 6.40, 6.80, 7.20, 7.60, 8.00, 8.40, 8.80, 9.20, 9.60, 10.00, 10.40, 10.80, 11.20, 11.60, 12.00, 12.40, 12.80, 13.20, 13.60, 14.00, 14.40, 14.80, 15.20, 15.60, 16.00, 16.40, 16.80, 17.20, 17.60, 18.00, 18.40, 18.80, 19.20, 19.60, 20.00, 20.40, 20.80, 21.20, 21.60, 22.00, 22.40, 22.80, 23.20, 23.60, 24.00, 24.40, 24.80, 25.20, 25.60, 26.00, 26.40, 26.80, 27.20, 27.60, 28.00, 28.40, 28.80, 29.20, 29.60, 30.00, 30.40, 30.80, 31.20, 31.60, 32.00, 32.40, 32.80, 33.20, 33.60, 34.00, 34.40, 34.80, 35.20, 35.60, 36.00, 36.40, 36.80, 37.20, 37.60, 38.00, 38.40, 38.80, 39.20, 39.60, 40.00, 40.40, 40.80, 41.20, 41.60, 42.00, 42.40, 42.80, 43.20, 43.60, 44.00, 44.40, 44.80, 45.20, 45.60, 46.00, 46.40, 46.80, 47.20, 47.60, 48.00, 48.40, 48.80, 49.20, 49.60, 50.00, 50.40, 50.80, 51.20, 51.60, 52.00, 52.40, 52.80, 53.20, 53.60, 54.00, 54.40, 54.80, 55.20, 55.60, 56.00, 56.40, 56.80, 57.20, 57.60, 58.00, 58.40, 58.80, 59.20, 59.60, 60.00, 60.40, 60.80, 61.20, 61.60, 62.00, 62.40, 62.80, 63.20, 63.60, 64.00, 64.40, 64.80, 65.20, 65.60, 66.00, 66.40, 66.80, 67.20, 67.60, 68.00, 68.40, 68.80, 69.20, 69.60, 70.00, 70.40, 70.80, 71.20, 71.60, 72.00, 72.40, 72.80, 73.20, 73.60, 74.00, 74.40, 74.80, 75.20, 75.60, 76.00, 76.40, 76.80, 77.20, 77.60, 78.00, 78.40, 78.80, 79.20, 79.60, 80.00, 80.40, 80.80, 81.20, 81.60, 82.00, 82.40, 82.80, 83.20, 83.60, 84.00, 84.40, 84.80, 85.20, 85.60, 86.00, 86.40, 86.80, 87.20, 87.60, 88.00, 88.40, 88.80, 89.20, 89.60, 90.00, 90.40, 90.80, 91.20, 91.60, 92.00, 92.40, 92.80, 93.20, 93.60, 94.00, 94.40, 94.80, 95.20, 95.60, 96.00, 96.40, 96.80, 97.20, 97.60, 98.00, 98.40, 98.80, 99.20, 99.60, 100.00, 100.40, 100.80, 101.20, 101.60, 102.00, 102.40, 102.80, 103.20, 103.60, 104.00, 104.40, 104.80, 105.20, 105.60, 106.00, 106.40, 106.80, 107.20, 107.60, 108.00, 108.40, 108.80, 109.20, 109.60, 110.00, 110.40, 110.80, 111.20, 111.60, 112.00, 112.40, 112.80, 113.20, 113.60, 114.00, 114.40
```

SUBROUTINE LINER (N)

SUBROUTINE LINER SOLVES K SIMULTANEOUS EQUATIONS IN N UNKNOWNS

BY THE METHOD OF GAUSS-SEIDEL

DIMENSION (160), X(60)
COMMON/ARAYS/A(I,J)
DATA EPS / 0.0001 /
DATA MAX / 1000/ 
ITER=1 
N=1
1 1=1,N
B(I)=A(I,N)
1 X(I)=0.0
10 B(I)=0.0
20 DO 20 I=1,N
20 SUM=0.0
IF (I .EQ. 1) GO TO 40
LAST=I-1
DO 30 J=1,LAST
20 SUM=SUM+A(I,J)*X(I)
30 IF (I .EQ. M) GO TO 60
40 INITL=I+1
50 DO 50 J=INITL,N
60 TEMP=(SUM-A(I,J)*X(I))/SUM
70 IF (ABS(TEMP-X(I)) .GT. BIG) BIG=ABS(TEMP-X(I))
80 X(I)=TEMP
90 IF (T(IX) .GE. MAX) GC TO 10
100 A(I,J)=X(I)
END

SUBROUTINE FAIL
WRITE (6,1)
1 FORMAT ("//I0.X,18=GAUSS-SEIDEL SOLUTION DID NOT CONVERGE //")
RETURN
END

SUBROUTINE ESCAL (NC,BEX,CN,QE,V)
DIMENSION PLOT(100,60),CN(10,75),BE(75),BEX(75),QE(75),V(75)
COMMON/ARRAYS/(CN,60,BE,75,BEX,75,QE,75,V,75)
COMMON/RELAX/MM(75),DV(75)
EQUIVALENCE (411,PLCT(11))
DATA DOT,O,X,Y,Blank / 1H.,1M2,1MX,1MY,1M / SUMX = 0.0
SUMY = 0.0
XSQ = 0.0
YSQ = 0.0
XYPROD = 0.0
OFF 10 M=1,NC
SUMX = SUMX + QE(M)
SUMY = SUMY + (BE(X(M))-V(M))
XSQ = XSQ + (QE(M)**2)
YSQ = YSQ + (BE(X(M))-V(M))**2
XYPROD = XYPROD + QE(M)*(BE(X(M))-V(M))
CONTINUE
SLOPE = (NC*XYPROD-SUMX*SUMY)/(NC*YSQ-SUMX**2)
CEPT = (XSQ*SUMY-SUMX*XYPROD)/(NC*XSQ-SUMX**2)
WRITE (6,1)
WRITE (6,20)
WRITE (6,30) SLOPE, CEPT
WRITE (6,20)
WRITE (6,40)
DEVSQ = 0.0
DO 50 M = 1, NC
   WRITE (6, 80) (C(I, K), I = 1, 10)
   WRITE (6, 75) Q, (X(I), Y(I))
   RE(I) = SLR(I) - SQ(I) + V(I) + CHPT
   ER = SLR(I) - SQ(I) + V(I)
   WRITE (6, 15) Q, PLX(M), FR
   DEV = RE(I) - Q * X(M)
   WRITE (6, 9) Q, Y
   DEVSQ = Y**2 + DEVSQ
50 CONTINUE
STODEV = SQRT (DEVSQ / (NC - 1))
CCOFFT = (NC * XYPD(7D) - SUMX * SUMY) / SUM(T(1) (NC * XSU - SUMX)**2) * (NC * YSO - 1)
   SUMX**2)
   SUMY = 0.0
   YSO = 0.0
   XYPD = 0.0
   N = NC
   SUMX = SUMX + X(I)
   SUMY = SUMY + Y(I)
   XSO = XSU + (BE(M))**2
   YSO = YSU + (FX(M))**2
   XYPD = XYPD + X(I) + Y(I)
55 CONTINUE
CCOFFF = (NC * XYPD - SUMX * SUMY) / (NC * XSO - SUMX)**2) * (NC * YSO - 1)
   SUMX**2)
   WRITE (6, 10) N
   WRITE (6, 11) STODEV
   WRITE (6, 11) CCOFFT
   WRITE (6, 11) CCOFFF
   WRITE (6, 11)
   WRITE (6, 40)
   DO 120 M = 1, NC
   IF (M = 1, NC)
      DO 140 M = 1, NC
         IF (BE(M) .LE. REMIN) REMIN = BE(M)
         IF (BE(M) .GE. REMAX) REMAX = BE(M)
         IF (FX(M) .LE. REMIN) REMIN = FX(M)
         IF (FX(M) .GE. REMAX) REMAX = FX(M)
      140 CONTINUE
         FACTR = (50.0 / (REMAX - REMIN))
         DO 150 M = 1, NC
            IX = IFIX(FACTR * (RE(M) - REMIN)) + 3
            IV = IV + (IV * (FACTR * (RE(M) - REMIN))
            SYMX
            IF (PLT(I, J) .EQ. X .OR. PLT(I, J) .EQ. Y) SYM = Y
            PLOT(I, J) = SYM
150 CONTINUE
WRITE (6,1)
WRITE (6,10)
WRITE (6,17) PLOT
WRITE (6,18)
WRITE (6,27)
WRITE (6,28) RCMMX=RMMN=2.0/FACTR
WRITE (6,27) RMMX, RMMN
WRITE (6,21) RMMX, RMMN

C FORMAT STATEMENTS
C
1 FORMAT (1H)
20 FORMAT (5X, 5DH)
30 FORMAT (5X, 2H)
40 FORMAT (2H)
60 FORMAT (5X, 12BH)
70 FORMAT (5X, -H) = , FIG.5, 15H PASTENTIAL = , F10.5, 3H EV/)
80 FORMAT (5X, 15H CALC = ,F10.5, 3H EV, 5X, 15H EXP = ,F10.5, 3H EV,
1 5X, 15H LAX = ,F10.5, 3H EV/)
90 FORMAT (10X, 12H OVLATION = , F10.5, 3H EV/)
100 FORMAT (5X, 2DH)
110 FORMAT (5X, 23H STANDARD DEVIATION = ,F10.5, 3H EV .)
115 FORMAT (5X, 28H CORRELATION COEFFICIENT = ,F8.5, 2H 5X, 13H VS. V
15, KOM) 
116 FORMAT (5X, 28H CORRELATION COEFFICIENT = ,F8.5, 2H 5X, 13H VS.
19, KOM)
160 FORMAT (1X, 62H LEAST SQUARES PLOT OF OBSERVED VS. CALCULATED BIND
11ING ENERGIES )
170 FORMAT (62D2)
180 FORMAT (// 17X, KOM END //)
190 FORMAT (5X, 30H -AXIS IS THE CALCULATED BINDING ENERGY /)
200 FORMAT (5X, 30H -AXIS IS THE OBSERVED BINDING ENERGY/)
210 FORMAT (5X, 10S4AN X INDICATES ONE DATA POINT ASSIGNED THAT POSIT
10N. A Y INDICATES THAT (OR MORE) POINTS AT THE POSITION//)
220 FORMAT (5X, 15H ORIGIN IS AT (, F10.5, 1H, F10.5, 4H)
230 FORMAT (5X, 21H (XMAX, YMAX) IS AT (, F10.5, 1H, F10.5, 4H)
1 // //
RETURN
END
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