RESEARCH PROJECT INITIATION

Project Title: Anions and Cations of Metalloporphyrins and Some Derivatives

Project No: B-1583

Project Director: Dr. R. H. Felton

Sponsor: National Science Foundation

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Dr. Arthur F. Findeis
Program Director
Chemical Instrumentation and Analysis Program
National Science Foundation
Washington, D.C. 20550

Reports Required

Annual - Short informal letter report.

Final - Comprehensive report. See Appendix V of "Grants for Scientific Research" (NSF 69-23) for items to be included in Final Report.

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RESEARCH PROJECT TERMINATION

Date: June 4, 1975

Project Title: Actions & Cations of Metalloporphyrins and Some Derivatives

Project No: 0-33-623 (Formerly B-1501)

Principal Investigator: Dr. R. H. Felten

Sponsor: National Science Foundation

Effective Termination Date: Nov. 30. 1974 (Grant Expiration)

Clearance of Accounting Charges: by 11/30/74 (Final Fiscal Rpt. 4/15/75/
Final Tech. 5/19/75)

Grant/Contract Closeout Actions Remaining: None

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Dr. R.S. Nicholson  
Program Director for  
Chemical Instrument and Analysis  
National Science Foundation  
Washington, D.C. 20550  

Dear Dr. Nicholson:

This letter constitutes an interim report on the research progress funded under NSF grant no. GP 17061. I have enclosed three reprints of a recently published article and a preprint of a Communication to appear in the June issue of J. Amer. Chem. Soc. Since earlier aspects of our metalloporphyrin research are described in these articles, I will discuss current research.

Our objective is to oxidize model ferric porphyrins, isolate the products if possible, and relate these to the enzymatically active compounds I of catalase and horse radish peroxidase.

Cyclic voltammetry of ferric (Fe$^{III}$) tetraphenylporphyrin (TPP) chloride and the μ-oxo dimer of ferric tetraphenylporphyrin (TPPFe-O-FeTPP) showed a reversible, one-electron wave for FeTPPCl ($E_1 = 1.13$ vs sce(aq)) and two, reversible one-electron waves ($E_1 = 0.84V$ and $1.09V$) for the dimer. Controlled potential electrolyses at the first wave plateau gave products whose optical spectra differed slightly from the parent compounds. Coulometric data indicated that 1.0±0.1 electron was removed from FeTPPCl and 1.0±0.1 electron was removed per dimer in the electrochemical oxidation of TPPFe-O-FeTPP. Parent material was recovered by iodide reduction or electrochemical reduction.

The stability of the oxidized dimer is consonant with its low oxidation potential. It may be isolated in pure crystalline form as a perchlorate salt by (1) preparing a CH$_3$Cl$_2$/tetra-n-propylammonium perchlorate (TPAP) solution of [TPPFe-O-FeTPP]$^{+1}$ by electrochemical oxidation, (2) taking the solution to dryness, (3) removing TPAP in boiling water (which amazingly does not react with the oxidized dimer), (4) dissolving parent dimer in benzene to leave (5) pure [TPPFe-O-FeTPP]$^{+1}$. A moving boundary experiment verifies the presence of a positive charge.

At 77°K an epr signal at $g = 2.00$ is observed from the oxidized dimer. Finally, a pmr spectrum of the oxidized species shows three resonances at 11 ppm, 10 ppm, and 4 ppm downfield of TMS. As the ratio of [OX]/[Red] in solution is decreased the 11 ppm + 13 ppm; and 10 ppm + 7.5 ppm + 4 ppm. The values for the parent dimer [Red] are 13 ppm and 7.5 ppm.

The interpretation of the pmr results is that the exchange rate

$$\text{Eq.(1) } (\text{FeTPP})_2O^{1+} + (\text{FeTPP})_2O \not\equiv (\text{FeTPP})_2O^+ + (\text{FeTPP})_2O^{1+}$$
is very fast, and we are observing the time averaged (ensemble average) pmr spectrum. The fact that there is exchange as in Eq.(1), rules out the remote possibility that one porphyrin ring is oxidized, and intramolecular exchange between rings is slow. The only conclusion possible is that oxidation is occurring in the Fe-O-Fe region. In turn this means that quadrivalent iron is stable in porphyrins. The importance of this finding and its relation to biophysical processes may be seen in the articles by D. Busch, H. Gray, and H. Dunford in Bioinorganic Chemistry, Adv. in Chemistry, Vol. 100, 1971, ACS. This result is of immediate interest to workers in the fields of peroxidase, cytochrome, and catalase function.

We are preparing these results for submission as a communication to J. Amer. Chem. Soc.; I will send a preprint when one is available. For the present please consider these results as confidential.

Yours truly,

R.H. Felton
Principal Investigator
GP 17061
Final Report Submitted to the National Science Foundation

by the

Georgia Institute of Technology
Atlanta, Georgia 30332

THE ELECTRONIC STRUCTURE OF METALLOPORPHYRINS AND METALLOENZYMES.

Principal Investigator
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Introduction

Arising from early work upon the hemes a considerable emphasis had been placed upon the role of the central metal in metalloporphyrin redox reactions. It was our belief, however, that the porphinato moiety played an important role in the various in vivo enzymatic, transport, and charge-transfer functions. Various aspects of the biochemical importance of the oxidized and reduced porphyrin ring have recently been discussed. Important results are as follows:

1) Electrochemical studies\(^1,2\) demonstrated that metalloporphyrins could undergo two successive, reversible one-electron oxidations. In many instances the oxidized species were obtained by chemical oxidation\(^3\).

2) Analyses of the epr spectra of the radicals confirmed the notion that π-electron abstraction from the porphinato moiety occurs\(^4\).

3) Comparison of optical and epr spectra of the cation radical of magnesium octaethylporphyrin (MgOEP\(^{+}\)) with that of magnesium tetraphenylporphyrin (MgTPP\(^{+}\)) suggested that two different electronic ground states were being observed\(^5\). Theoretical calculations tended to confirm this interpretation: removal of an electron from either of the nearly degenerate highest filled orbitals would lead to a \(^2\)A\(_{2u}\) or \(^2\)A\(_{1u}\) state separated by 2000-3000 \(\text{cm}^{-1}\). Spin density distribution calculations were nicely confirmed experimentally for the \(^2\)A\(_{2u}\) state\(^4\).

4) Sequential oxidation of Co(II)OEP by Br\(_2\) led to the π-cation radical\(^6\):

\[
\begin{align*}
\frac{1}{2}\text{Br}_2 & \quad \rightarrow \quad \text{Co(III)OEP}^+ \text{Br}^- \\
\text{Co(II)OEP} & \quad \rightarrow \quad \text{Co(II)OEP}^{2+} \quad 2\text{Br}^- 
\end{align*}
\]
which upon addition of AgClO₄ formed the ClO₄⁻ salt, viz.,

\[
\text{Co(III)OEP}^{2+} + 2\text{Br}^- \xrightarrow{\text{AgClO}_4} \text{Co(III)OEP}^{2+}, 2\text{ClO}_4^-.
\]

The associated spectral changes upon anion exchange followed the alternations encountered with the \( ^2A_{2u} \) and \( ^2A_{1u} \) ground state switching. Comparison of these spectral with those of the enzymatically active Compounds I of catalase and horseradish peroxidase led us to offer a new formulation for these formally Fe(V) hemeproteins, namely, that \( \pi \)-cation radicals of Fe(IV) porphyrin were present. This suggestion seems to have the approval of workers in the field of peroxidase function.

5) It was incumbent upon us to offer further evidence of the unusual Fe(IV) state, so electrochemical oxidations of model ferric porphyrin were undertaken with a view to establishing their structure. Examination of pmr spectra of the one-electron oxidation products was interpreted as evidence for these complexes being Fe(IV) porphyrins. This interpretation is not fully agreed to by others who prefer a Fe(III)P⁺⁺ assignment.

6) Application of the electrochemical technique to chlorophyll a (Chl) permitted characterization of its oxidized form as Chl⁺⁺ or oxidized P700. The stabler bacteriochlorophyll positive ion was prepared chemically by I₂ oxidation. Electrochemical preparation of the anion radical, \( \text{BChl}^- \), led to the proposal that its role in photosynthesis is at best transitory; most likely, charge separation of the BChl dimer proceeds via the anion,

\[
\text{hv} \quad (\text{BChl})_2 \rightarrow \text{BChl}^{++} + \text{BChl}^-.
\]
A number of other workers have examined metalloporphyrin or metallochlorin redox properties. A recent review by Fuhrhop summarizes that work.\(^\text{11}\)

**Progress Report (5/1/72 to 8/1/74)**

1) **MCD Spectroscopy**

A major objective of the last 1.5 years has been the construction and utilization of an MCD spectrometer. The first has been accomplished and the latter is being implemented. Our design (Fig. 1) is conventional by modern standards\(^\text{19}\), and the instrument has a sensitivity of \(\Delta \text{OD}<10^{-5}\). The spectral range is 220-1100 nm which is accomplished by two light sources, a Xe arc to 800 nm and a 100 watt tungsten-halogen lamp to 100 nm. Switching between two photomultipliers is performed by a totally reflecting prism following the sample. The 0.5 meter monochromator can be fitted with various gratings to cover the spectrum. A Morvue acoustic modulator provides alternately left and right circularly polarized light at 50 KHz. A turning fork chopper at 200 Hz yields a signal for adjusting the PM dynode voltage to maintain a constant photocurrent during transversal of an absorption band. The 50 KHz and 200 Hz photocurrent signals are converted to voltages with a tuned LC circuit. The MCD component is amplified and phase detected while the 200 Hz signal is fed into a controller of the PM high voltage.

A magnetic field of 1.7T is generated by a 7" electromagnet bored axially to an 8 mm diameter. The pole gap of 1" permits use of a variable temperature dewar (10-300°k).

One design feature which has proven useful is incorporation of a current stabilized\(^\text{16}\) power supply for the Xe arc. The noise from the
Block Diagram of MCD Spectrometer

1 Power Supply
2 Light Source
3 Condenser Lens
4 Slit of Monochromator
5 Monochromator
6 Scanning device
7 Slit program
8 Light Chopper
9 Power Supply
10 Collimator Lens
11 Field Stop
12 Polarizer
13 Circular polarization Modulator
14 Power Supply
15 Modulator Program
16 Electric Magnet
17 Power Supply
18 Photomultiplier
19 Diode Voltage Controller
20 Power Supply
21 Preamplifier
22 Lock-In Amplifier
23 Signal Conditioner
24 X-Y Recorder
25 Temperature Controller
26 Cryostat
arc is reduced and resultant MCD spectra display good S/N rations (Fig. 2).

MCD spectra of a large number of metalloporphyrins\textsuperscript{17,18} have been recorded. In the neutral porphyrins both MOEP and MTPP (M = H\textsubscript{2}, Mg, Zn, Cu, Ni, Co(II,III), Fe(III), Mn(III), Pd, and Pt) were examined in CH\textsubscript{2}Cl\textsubscript{2}, benzene or n-hexane. In the last solvent enhanced vibrational resolution is obtained. At -90°C the Pd complex shows splitting of the 0-0 band (not previously reported). We are currently fitting the closed shell metal spectra with a rigid shift model using only A terms in an effort to identify vibrational progressions. We question the validity of Bunnenberg et al's fitting technique in which a harmonic progression is forced\textsuperscript{19}. Their 500 and 600 cm\textsuperscript{-1} vibrations are not observed in our resonance Raman work (\textit{vide infra}) and those frequencies are below the C=C stretching vibrations which should make the dominate contribution to MCD coupling.

Our original motivation for pursuing MCD spectroscopy was assignment of electronic transition in the π-cation radicals. Spectra of MgTPP and MgTPP\textsuperscript{+} are shown in Fig. 3. Unlike MgTPP, the cation evidences no clear A terms in the visible region, although the 410 nm term is an A term. Although excited states are \textsuperscript{2}E\textsubscript{g}, the appearance of B terms is understandable in light of a theoretical prediction\textsuperscript{1} of four electronic states in the visible, instead of the single Q term found with the parent molecules and in the reduced angular momentum of the excited states. The cations of ZnTPP, CuTPP, Co(III)TPP, Ni(II)TPP, ZnOEP, MgOEP, CuOEP, and Co(III)OEP display similar features. Upon cooling MgOEP\textsuperscript{+} dimerizes\textsuperscript{1,20} and the MCD spectrum of the dimer (-80°C) suggests a face-to-face structure since the absorption band at 950 nm shows not a trace of MCD signal; the absorption is considered to be an out-of-plane charge transfer band.
Figure 2. MCD Spectrum of ZnOEP in benzene, 25°
Figure 3. (A) Absorption Spectrum of MgTPP, MgTPP$^+$
(B) MCD Spectrum of MgTPP, MgTPP$^+$
Spectra of the monanions of ZnTPP, CuTPP, CuTPC, and ZnTPC (TPC = tetraphenychlorin) have aided in interpretation of the electronic structure. In 2-methyltetrahydrofuran, the ion-pair NaZnTPP is the dominant species at room temperature, but at -80°C free ZnTPP⁻ is along present. The longest wavelength band of ZnTPP⁻ is predominantly a C term (from the 1/T dependence). This observation settles a mild controversy on assignment of the ground state which must be $^2E_g$. No evidence of spin-orbit coupling is seen in the preliminary experiments. The chlorin anions display two B terms of opposite sign at ca. 780-800 nm, agreeing with the theoretical predictions. The results obtained to date demonstrate the great utility of MCD spectroscopy in aiding spectral assignments of the oxidized and reduced porphyrins.

One problem we are running into is that of finding suitable glasses in which the oxidized porphyrins are stable. For some a 1:1 MeOH/CH₂Cl₂ glass is usable, but excess carrier electrolyte (the ions are prepared electrolytically) precipitates, causing scattering. By reducing the concentration and using the more soluble tetrabutylammonium salts we obtain reasonable spectra. "Inert" plastics react with the cations. We are testing the possibility of photolysis in a boric acid glass.

Spectra of the Fe(IV) porphyrins at room temperature show no strong Q(0-0) A term. There is some similarity between these spectra, HRP I and II, which are oxidized hematin enzymes, and the π-cations. Apparently $d_{π} - p_{π}$ mixing is greatly enhanced in the Fe(IV) systems. At present, we do not understand the Fe(IV) systems and must await the results of low-temperature experiments with a suitable glass.

Also in a systematic study of high and low-spin ferrihemoproteins,
results similar to Vickery\textsuperscript{22} are obtained with myoglobin, i.e., it is possible to distinguish qualitatively high and low-spin forms by the two C terms in the Soret region. A similar result is found with the resting form of HRP. The combination of MCD and resonance Raman should prove quite powerful in correlating the structural changes accompanying the movement of Fe(III) relative to the mean porphyrin plane. Comparison of the visible MCD spectra with various ligands (CN\textsuperscript{−}, N\textsubscript{3}\textsuperscript{−}, OH\textsuperscript{−}, imidazole) added to different ferriheme proteins suggests, quite tentatively, that MCD spectra might be able to distinguish among ligands bound to the sixth position.

Excepting qualitative comparisons we have postponed theoretical interpretations pending availability of low temperature data. It is now clear from Briat's\textsuperscript{23} and Vickery's studies that confusion of A and C terms must be avoided in the partially filled d-shell metals.

**Resonance Raman Spectroscopy**

A new technique which promises to aid in spectral interpretations is resonance Raman (RR) spectroscopy\textsuperscript{24}. The RR experiment consists of irradiating a chromatophore with a laser line at a wavelength absorbed by the sample. Radiation scattered at 90° is then passed through a double monochromator and measured with a photomultiplier and photon counting system. A polarizer placed in front of the PM selects out parallel and perpendicular components of the scattered radiation. As in nonresonant Raman spectra, Stokes lines corresponding to fundamental vibrations dominate the spectrum. Unlike the non-resonant process, however, there is strong wavelength dependence
of the depolarization ratio, \( \rho = \frac{I_\perp}{I_\parallel} = \frac{(3\gamma_s^2 + 5\gamma_{as}^2)}{(45a^2 + 4\gamma_s^2)} \), where \( I_\perp \) and \( I_\parallel \) are the intensities at different polarizer orientations, \( \gamma_s \) is the antisotropic component of the antisymmetric scattering tensor, and \( a \) is the isotropic part of the symmetric tensor. For non-resonant processes \( 0 \leq \rho \leq 3/4 \), while for the resonant processes found in metalloporphyrins, certain nontotally symmetric vibrations will have \( a = \gamma_s \) and \( \rho \to 0 \). The third order perturbation theory of Peticolas\(^{25,26} \) shows that vibronic coupling between Q and B bands of porphyrin permits the antisymmetric scattering tensor to dominate in the \( a_{2g} \) skeletal vibrations. This theory also predicts the dispersion (wavelength dependence) found in heme proteins.

In collaboration with N. T. Yu (Georgia Tech) we have initiated a systematic study of RR spectroscopy applied to metalloporphyrins. Preliminary results are published\(^{27} \) and suggest that the position of an \( a_{2g} \) vibration correlates with the metal to porphyrin plane distance. Recent work has proven quite exciting: the two crystal forms of NiOEP(D\(_{2d}\) and D\(_{4h}\)) suffer displacement of the structure sensitive bands at 1660, 1609 and 1520 cm\(^{-1}\) as large as that found in the in-plane and out-of-plane correlations (Fig. 4). Upon deuteration at the meso carbons two new anomalously polarized bands (ap) appear and the relative intensities of the old ap bands change. This is clear evidence for a mass effect both in energy and in intensities. These results also raise serious doubts as to Spiro's\(^{28} \) correlation between oxidation state and the position of the 1624 to 1640 cm\(^{-1}\) depolarized line. Certainly, with a number of model iron (II) and iron (III) species (Fig. 5) this band remains unchanged.

Results of the dependence of \( I_\parallel \) and \( I_\perp \) upon incident frequency are shown for Mn(III)EtioI(Cl)Etio = Etio porphyrin I) in Fig. 6. Since the
sample is supported in KBr, approximately 30 wt% $\text{Na}_2\text{WO}_4$ is employed as an internal standard to monitor the dye laser power. The data are interpreted as indicating that the band at 585 nm is a Q band component while the 560 nm is probably a charge-transfer process. The apparent increase in intensity of the depolarized bands at 600 nm has now been shown to maximize at 600 nm. There is a real shift in the maxima between the anomalously polarized lines and the depolarized lines. Not shown in the figure is a shoulder at 505 nm on the high energy side of the split "Soret" band of Mn(III) which appears to be a distinct $\pi+\pi^*$ transition coupled via an $a_{2g}$ vibration to this Soret absorption.

**Xα Theory of Electronic Structure**

A major block to progress on a quantitative theory of metalloporphyrin spectra (electronic, MCD, and epr) is inclusion of the metal orbitals to the porphyrin moiety. Gouterman$^{29}$ has utilized the extended Huckel method quite effectively and gained remarkable insight into ground state properties; however, it is important to develop more sophisticated theories. Our approach has been to use the $X\alpha$-SCF theory of Slater$^{30}$. Slater's suggestion is to replace the non-local exchange operator in the Fock hamiltonian by a local potential, viz.

$$V_{X\alpha} = 6 \left(\frac{3}{8} \pi\right) \rho(r)^{1/3}$$

One method of solution is to assume a muffin-tin potential in which molecules are segregated into non-overlapping atomic regions of radius equal to the covalent radius, regions of constant potential in between, and an outer boundary surrounding the entire molecule. Self-consistent solutions are generated by assuming plane wave solutions in the $V = \text{constant}$ region and joining these to numerically generated solutions in the atomic region.
K. Johnson and J. D. Connolly\textsuperscript{31} have shown the resultant orbital energies and charge density distributions agree well with available experimental data. They have recently extended these techniques to transition metal complexes with impressive results. One drawback is the high degree of symmetry required to obtain solutions in a reasonable amount of computer time, another is the rather poor potential curves due to the muffin-tin potential.

Our approach is to discard the scattered wave (SW) technique and substitute an LCAO basis for solution. An immediate advantage is the obtainment of orbital wavefunctions which are absent in the SW version and thereby obtain excited state configurations. It is also possible to support a more reasonable potential between atoms. To incorporate some of the simplifications introduced by Johnson and Connolly we divide the atom into a core region whose initial charge density is that of the Hartree-Fock atom. We also employ a gaussian basis similar to that used by Pople. A floating gaussian set is used to fit $\rho^{1/3}$ in a least squares sense. We find that only two center integrals need be calculated and these are in closed form. No outer boundary is needed.

Trial calculations on $N_2$, $O_2$, $F_2$, and $H_2O$ demonstrate that the LCAO method provides good geometry (not obtained in the SW method) as well as ionization energies. The inclusion of anisotropic potentials in the present calculation is important if accurate separations between ionization energies are desired; the SW version groups the energies together, in distinction to the experimental and LCAO results.

We have now extended the computations to $NH_3$ and $O_3$. Accurate bond
Figure 4
Anomalously Polarized ($A_{2g}$) - Depolarized ($B_{1g} + B_{2g}$) - Polarized ($A_{1g}$)

- Fe(II)Etio·21m
- Fe(II)OEP(CO)Py
- Fe(II)OEP·2Py
- Fe(III)OEP·21m
- Fe(III)Etio·21m
- Fe(II)PPIX·21m (in H₂O)
- Fe(II)PPIX·2Py (in H₂O)
- Fe(II)PPIX·2(CN) (in H₂O)
- Fe(II)PPIX·2(CN) (in H₂O)

Wavenumbers (cm⁻¹):
- 1644, 1593, 1510
- 1636, 1590, 1503
- 1642, 1595, 1504
- 1642, 1590, 1509
- 1623, 1587, 1495
- 1624, 1587, 1497
- 1623, 1590, 1498
- 1639, 1585, 1509

Figure 5
Mn(III)OEP·Cl
(h.s., in-plane)

Integrated Intensities (relative to an internal standard)

Figure 6
distances are found in NH\textsubscript{3}, but with only N s and p functions and H s functions the molecule is planar by .01 au. Inclusion of d functions on N yields the pyrimidal NH\textsubscript{3}, but bond lengths are now 1.96 a\textsubscript{o} (cf. 1.91 a\textsubscript{o}, experimental). The inversion barrier ranges from 0.006 to 0.04 a.u. (two sets of d functions) as compared with the experimental value of 0.009 au. We feel the problem lies in the "basis" functions used to expand $\rho^{\text{1/3}}$ and $\rho$; a function located in the bond is probably required to follow accurately the single-particle density.

Extension to O\textsubscript{3} has produced the first calculation in which the correct ionization energy ordering is obtained. All other calculations (including near Hartree-Fock) predict the $1a_2$ level to be highest; recent photoelectron spectroscopy identifies the $6a_1$ level as highest. Fig. 7 displays the ozone results. This level order is identical to that of SO\textsubscript{2}.

The results to date are quite encouraging, and it is our opinion that the LCAO-X\textalpha{} method will be an important contribution to the theory of transition metal complexes.

Other Work

In an X-ray crystallographic study of the cation radical, ZnTPPC1O\textsubscript{4}, the C1O\textsubscript{4}\textsuperscript{−} was found to be strongly coordinated to Zn\textsuperscript{32}. To ascertain charge distributions we asked Prof. N. Winograd (Purdue) to examine the ESCA spectra of some metalloporphyrins. Upon comparison of N, C, and Zn inner shell binding energies no change was noted between the oxidized and unoxidized forms. This is perplexing for if spin and electron density are directly correlated a 1eV shift in the meso C 1s binding energy is anticipated. A resolution to the paradox is that spin density does not
Figure 7
accurately measure charge density in these systems.

The ESCA results are tabulated below to show binding energies in selected systems. Note that the technique is not particularly sensitive to the oxidation state in hemes; a result which parallels our resonance Raman observations. It is concluded that electron density about the metal in a porphyrin changes only slightly as a metal progresses through its (formal) oxidation states.

### Binding Energies (eV)

<table>
<thead>
<tr>
<th>Metalloporphyrin</th>
<th>Metal</th>
<th>$N_{1s}$</th>
<th>$C_{1s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)Etio'2py</td>
<td>709.6</td>
<td>397.8</td>
<td>284.2</td>
</tr>
<tr>
<td>Fe(III)TPPCl</td>
<td>711.0</td>
<td>398.3</td>
<td>284.5</td>
</tr>
<tr>
<td>(Fe(III)TPP)$_2$O</td>
<td>709.8</td>
<td>398.0</td>
<td>284.3</td>
</tr>
<tr>
<td>(FeTPP)$_2$O$^1+$ClO$_4^-$</td>
<td>710.8</td>
<td>398.3</td>
<td>284.7</td>
</tr>
<tr>
<td>Fe(III)OEPCh</td>
<td>711.0</td>
<td>398.3</td>
<td>284.7</td>
</tr>
<tr>
<td>Fe(III)EtioCl</td>
<td>710.8</td>
<td>398.3</td>
<td>284.7</td>
</tr>
<tr>
<td>Co(II)TPP</td>
<td>795.1</td>
<td>779.5</td>
<td>398.0</td>
</tr>
<tr>
<td>Co(III)TPPBr</td>
<td>795.0</td>
<td>779.8</td>
<td>397.8</td>
</tr>
<tr>
<td>Co(III)TPPBr.2py</td>
<td>795.5</td>
<td>779.8</td>
<td>398.3</td>
</tr>
</tbody>
</table>

We have obtained other crystals suitable for diffractometry and the structure of one of these, free-base tetraphenylchlorin, is being determined by G. Eller at Los Alamos. Preliminary attempts to obtain bacteriochlorophyll cation crystals did not prove successful; this work is being pursued by a new student. Also, as crystals of the Fe(III)TPP-O-Fe(IV)TPP complex were disordered along one axis, we are changing the
counterion in hopes of obtaining a good specimen. Recently, we noted that the Fe(IV)OEP\(\text{C}^{10}_4\) monomer is quite stable and are attempting to crystallize it.

In collaboration with J. Fajer and D. C. Borg we have examined the optical spectra of cation and anion radicals of bacteriochlorophyll, bacteriophaeophytin, and zinc tetraphenylbacteriochlorin. The results indicate little spectral difference between the metallated and demetalled forms. Theoretical calculations of spin density have aided the above workers and G. Feher in assignment of the endor spectra\(^{33}\).
References


Calculation of the ionization potentials of ozone and ammonia by a LCAO-\(X\alpha\) method*

Hideo Sambe and Ronald H. Felton

Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

(Received 29 July 1974)

Recently high resolution photoelectron spectra of ozone were reported.\(^1,2\) Experimental results are in agreement for the first three ionization potentials (I.P.\(^{\prime}s\)), and the first I.P. has been convincingly assigned as \(6\alpha_1\). For the lower I.P.\(^{\prime}s\), however, there are disagreements in the identification of impurity bands and the assignment of orbitals. Since the LCAO-\(X\alpha\) method predicted the I.P.\(^{\prime}s\) of several molecules well without exceptions,\(^3\) we have computed ionization potentials of ozone by this method hoping to clarify discrepancies.

The LCAO-\(X\alpha\) method is one of several computational procedures which yield approximate solutions to Slater’s\(^4\) SCF-\(X\alpha\) equations. The salient distinctions between the present technique\(^3\) and the scattered wave version\(^5\) are (1) the removal of the muffin-tin approximation and (2) expansion of the charge density, \(\rho\), and \(\rho^{1/2}\) by least squares. \(X\alpha\) ionization potentials are found by the transition-state procedure,\(^4\) which appears more reliable than Koopmans’ theorem applied to Hartree–Fock results. It is observed that vertical I.P.\(^{\prime}s\) computed by the LCAO-\(X\alpha\) method are correctly ordered and that differences between I.P.\(^{\prime}s\) are accurate for \(N_2\), \(F_2\), \(CO\), and \(H_2O\).\(^3\) There is, however, a uniform shift upon comparison with experiment. The experimental equilibrium

![Graph](image1)

**FIG. 1.** Experimental and theoretical ionization potentials of the \(O_3\) molecule. \(H–F\) and LCAO-\(X\alpha\) results obtained by Koopmans’ theorem and transition state procedure, respectively. Shadowed band indicates a possible range of vertical ionization potentials. Broken lines are estimated vertical ionization potentials.

![Graph](image2)

**FIG. 2.** Experimental and theoretical ionization potentials of the \(NH_3\) molecule. \(H–F\) and LCAO-\(X\alpha\) results obtained by Koopmans’ theorem and transition state procedure, respectively. Broken line is the estimated vertical ionization potential.
geometry of ozone was utilized as an input datum.

Figures 1 and 2 permit comparison among the theoretical and experimental results. Dotted lines included in the experimental data represent estimated positions of, as yet, unresolved or unobserved vertical I.P.’s. For O₃ the 3b₂, 5a₁, and 1b₁ levels are centered at 20.1 eV which is the position observed in the experiments¹²; by doing so, the 4a₁ I.P. now falls at 24.5 eV which is under the He⁺ band.² The calculation suggests, additionally, in agreement with Frost et al.,¹ that spectral features between 16.5 and 18.5 eV are probably due to an O₂ impurity.

Most importantly, the present computation predicts that the 6a₁ orbital is the highest filled level, in agreement with experiment but in contradiction to Hartree–Fock results.⁶ The new assignments for O₃ are remarkably similar to those¹ found for SO₂: not only the grouping of molecular orbitals but also the ordering within groups are the same.

For NH₃ agreement between the first two Hartree–Fock and LCAO-Xα I.P.’s is shown in Fig. 2. Displacement of the 2a₁ level parallel to the 3a₁ and 1e levels suggests the third vertical I.P. should appear at 26.6 eV, thereby implying that Turner et al.’s⁹ assignment of the 2a₁ level to 21.22 eV is incorrect.

Additionally we have calculated the equilibrium geometry of NH₃ and find the NH bond length to be 1.91 a.u. (cf. 1.91 a.u., experimental). However, computation of the equilibrium HNH angle yields a planar molecule with a = 0.01 a.u. inversion barrier. Upon inclusion of d functions centered at N, the pyramidal geometry is recovered with an inversion barrier of 0.006 a.u. with one set of d functions, and 0.04 a.u. with two sets of d functions (cf., 0.0092, experimental). We suspect that additional expansion functions for ρ and ρ¹/³ will improve the computed NH₃ geometry.

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Calculation of the ionization potentials of ozone and ammonia by a LCAO-Xα method

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(Received 29 July 1974)

Recently high resolution photoelectron spectra of ozone were reported. Experimental results are in agreement for the first three ionization potentials (I.P.'s), and the first I.P. has been convincingly assigned as 6a₁. For the lower I.P.'s, however, there are disagreements in the identification of impurity bands and the assignment of orbitals. Since the LCAO-Xα method predicted the I.P.'s of several molecules well without exceptions, we have computed ionization potentials of ozone by this method hoping to clarify discrepancies.

The LCAO-Xα method is one of several computational procedures which yield approximate solutions to Slater's SCF-Xα equations. The salient distinctions between the present technique and the scattered wave versions are (1) the removal of the muffin-tin approximation and (2) expansion of the charge density, ρ, and ρ₁/₂ by least squares. Xα ionization potentials are found by the transition-state procedure, which appears more reliable than Koopmans' theorem applied to Hartree-Fock results. It is observed that vertical I.P.'s computed by the LCAO-Xα method are correctly ordered and that differences between I.P.'s are accurate for N₂, F₂, CO, and H₂O. There is, however, a uniform shift upon comparison with experiment. The experimental equilibrium
The geometry of ozone was utilized as an input datum.

Figures 1 and 2 permit comparison among the theoretical and experimental results. Dotted lines included in the experimental data represent estimated positions of, as yet, unresolved or unobserved vertical I.P.'s. For O$_3$, the 3$b_2$, 5$a_1$, and 1$b_1$ levels are centered at 20.1 eV which is the position observed in the experiments$^{1,2}$; by doing so, the 4$a_1$ I.P. now falls at 24.5 eV which is under the He$^+$ band.$^5$ The calculation suggests, additionally, in agreement with Frost et al.$^1$ that spectral features between 16.5 and 18.5 eV are probably due to an O$_2$ impurity.

Most importantly, the present computation predicts that the 6$a_1$ orbital is the highest filled level, in agreement with experiment but in contradiction to Hartree-Fock results.$^5$ The new assignments for O$_3$ are remarkably similar to those$^7$ found for SO$_2$: not only the grouping of molecular orbitals but also the ordering within groups are the same.

For NH$_3$, agreement between the first two Hartree-Fock$^8$ and LCAO-Xa I.P.'s is shown in Fig. 2. Displacement of the 2$a_1$ level parallel to the 3$a_1$ and 1*e levels suggests the third vertical I.P. should appear at 26.6 eV, thereby implying that Turner et al.$^9$'s assignment of the 2$a_1$ level to 21.22 eV is incorrect.

Additionally we have calculated the equilibrium geometry of NH$_3$ and find the NH bond length to be 1.91 a.u. (cf. 1.91 a.u., experimental). However, computation of the equilibrium HNH angle yields a planar molecule with a $\sim 0.01$ a.u. inversion barrier. Upon inclusion of $d$ functions centered at N, the pyramidal geometry is recovered with an inversion barrier of 0.006 a.u. with one set of $d$ functions, and 0.04 a.u. with two sets of $d$ functions (cf., 0.0092, experimental). We suspect that additional expansion functions for $\rho$ and $\rho^{1/3}$ will improve the computed NH$_3$ geometry.

*We gratefully acknowledge support from the National Science Foundation (GP-17061).

Calculation of the ionization potentials of ozone and ammonia by a LCAO-\(X\alpha\) method*

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Recently high resolution photoelectron spectra of ozone were reported.\(^1,2\) Experimental results are in agreement for the first three ionization potentials (I.P.'s), and the first I.P. has been convincingly assigned as 6a\(_1\). For the lower I.P.'s, however, there are disagreements in the identification of impurity bands and the assignment of orbitals. Since the LCAO-\(X\alpha\) method predicted the I.P.'s of several molecules well without exceptions,\(^3\) we have computed ionization potentials of ozone by this method hoping to clarify discrepancies.

The LCAO-\(X\alpha\) method is one of several computational procedures which yield approximate solutions to Slater's\(^4\) SCF-\(X\alpha\) equations. The salient distinctions between the present technique\(^3\) and the scattered wave version\(^5\) are (1) the removal of the muffin-tin approximation and (2) expansion of the charge density, \(\rho\), and \(\rho^{1/3}\) by least squares. \(X\alpha\) ionization potentials are found by the transition-state procedure,\(^4\) which appears more reliable than Koopmans' theorem applied to Hartree-Fock results. It is observed that vertical I.P.'s computed by the LCAO-\(X\alpha\) method are correctly ordered and that differences between I.P.'s are accurate for \(N_2\), \(F_2\), \(CO\), and \(H_2O\).\(^3\) There is, however, a uniform shift upon comparison with experiment. The experimental equilibrium

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**FIG. 1.** Experimental and theoretical ionization potentials of the \(O_3\) molecule. H-F and LCAO-\(X\alpha\) results obtained by Koopmans' theorem and transition state procedure, respectively. Shadowed band indicates a possible range of vertical ionization potentials. Broken lines are estimated vertical ionization potentials.

**FIG. 2.** Experimental and theoretical ionization potentials of the \(NH_3\) molecule. H-F and LCAO-\(X\alpha\) results obtained by Koopmans' theorem and transition state procedure, respectively. Broken line is the estimated vertical ionization potential.
geometry of ozone was utilized as an input datum.

Figures 1 and 2 permit comparison among the theoretical and experimental results. Dotted lines included in the experimental data represent estimated positions of, as yet, unresolved or unobserved vertical I.P.'s. For O$_3$ the 3$b_2$, 5$a_1$, and 1$h_1$ levels are centered at 20.1 eV which is the position observed in the experiments$^{11,12}$; by doing so, the 4$a_1$ I.P. now falls at 24.5 eV which is under the He$^+$ band.$^3$ The calculation suggests, additionally, in agreement with Frost et al.$^1$ that spectral features between 16.5 and 18.5 eV are probably due to an O$_2$ impurity.

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*We gratefully acknowledge support from the National Science Foundation (GP-17081).

A new computational approach to Slater's SCF-\(X\alpha\) equation

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(Received 16 September 1974)

A new computational scheme is presented for the performance of LCAO-MO calculations in the SCF-\(X\alpha\) model. The scheme is intended to be applicable for large systems and to be more accurate than the scattered-wave SCF-\(X\alpha\) method. The \(X\alpha\) potential is fitted by least-squares to a linear combination of Gaussians, and the approximated SCF-\(X\alpha\) equation is solved by the conventional Rayleigh-Ritz variational method. The muffin-tin approximation is avoided, and matrix elements are calculated analytically in contrast to the discrete variational scheme. Some illustrative results are given for the ionization energies and equilibrium geometries of small molecules. It is found that overall performance of the method is satisfactory for both ionization energies and equilibrium geometries.

I. INTRODUCTION

A major virtue of the discrete-variational scheme developed for HF-\(X\alpha\) (DV-\(X\alpha\)) applied to Hartree-Fock-Slater (or SCF-\(X\alpha\)) theory is removal of the muffin-tin approximation which is inherent to the scattered-wave \(X\alpha\) method. The \(X\alpha\) method is quite flexible with respect to the choice of basis functions; for example, a numerical basis set can be much smaller than an analytic basis set and yet yield molecular properties with comparable accuracy. However, the number of sample points per atom required to obtain reasonable accuracy in the total energy may become large and thus equilibrium geometries require generous amounts of computation time.

An obstacle in solving the SCF-\(X\alpha\) equation occurs with the \(\rho^{1/3}\) dependence of the \(X\alpha\) potential, where \(\rho\) is the electron density. In a straightforward application of the Rayleigh-Ritz variational method with analytic basis functions, cumbersome integrals arise from the \(X\alpha\) potential. The discrete variational method overcomes this difficulty by numerical evaluation of the relevant integrals. The computational method we now present circumvents this problem by expanding the \(X\alpha\) potential by a least-squares fit to auxiliary functions, chosen so as to yield simple integrals. To reduce the number of two-electron integrals arising from Coulomb interaction, we also expand the electron density appearing in the \(X\alpha\) potential with auxiliary functions. The matrix elements of the one-electron Hamiltonian are then calculated analytically. In Sec. II the computational method is described and in Sec. III results on illustrative examples are presented and discussed.

II. THE LCAO-SCF-\(X\alpha\) METHOD

A. The SCF-\(X\alpha\) model

References to earlier works on the SCF-\(X\alpha\) theory are discussed in recent reviews, and we display here equations germane to the subsequent development of the computational method. In the SCF-\(X\alpha\) model, the one-electron Hamiltonian (in atomic units) is given by

\[
H = -\frac{1}{2} \nabla^2 (1) + \sum_n (-Z_n/r_n) + V_C(1) + V_{X\alpha}(1)
\]

\[
V_C(1) = \int \rho(r)/r_1 dV_1
\]

\[
V_{X\alpha}(1) = -3\alpha [(3/8\pi)\rho(1)]^{1/3}
\]

and

\[
\rho = \sum_k n_k \phi_k^* \phi_k,
\]

where \(\alpha\) is the exchange parameter, \(n_k\) are orbital occupation numbers, and \(\rho\) is the total electron density. The orbitals \(\phi_k\) satisfy the one-electron equation

\[
H \phi_k = \epsilon_k \phi_k,
\]

and Eqs. (1)-(3) are solved self-consistently. The (statistical) total energy \(E\) is given by

\[
E = \sum_k n_k (\epsilon_k, H - \frac{1}{2} V_C - \frac{1}{2} V_{X\alpha}) \phi_k.
\]

The one-electron equation (3) can be derived by applying the variational principle to the total energy (4). The transition-state procedure of Slater simplifies the determination of excitation and ionization energies and appears to be more accurate than Koopmans' theorem applied to Hartree-Fock results, from a computational point of view, replacement of the nonlocal exchange operator of Hartree-Fock theory by the local \(X\alpha\) potential is the key feature which permits rapid calculations for moderately large molecular systems.

B. The LCAO-\(X\alpha\) method

The \(X\alpha\) potential \(V_{X\alpha}\) and the electron density appearing in the Coulomb potential \(V_C\) are least-squares fitted to auxiliary functions centered at the nuclei, viz.,

\[
\rho(r) = \sum_i a_i \phi_i(r),
\]

\[
-3\alpha [(3/8\pi)\rho(r)]^{1/3} = \sum_i b_i \phi_i(r).
\]

The one-electron Hamiltonian becomes

\[
\tilde{H} = -\frac{1}{2} \nabla^2 (1) + \sum_n (-Z_n/r_n) + \tilde{V}_C(1) + \tilde{V}_{X\alpha}(1),
\]

\[
\tilde{V}_C(1) = \sum_i a_i \int f_i(1)/r_1 dV_1,
\]

\[
\tilde{V}_{X\alpha}(1) = \sum_i b_i \phi_i(1).
\]

To solve the corresponding one-electron equation,

\[
\tilde{H} \phi_k = \epsilon_k \phi_k,
\]

we employ the Rayleigh-Ritz variational method with linear variational functions for \(\phi_k\),

\[
\phi_k = \sum_i x_i C_{ik},
\]
where \( \chi_i \) are analytic functions centered at nuclei. This leads to the familiar secular equation,

\[
\sum_x (\langle \chi_i, \hat{H} \chi_x \rangle - \epsilon_x \langle \chi_i, \chi_x \rangle) C_{ix} = 0.
\] (10)

In terms of the solutions of Eq. (10), the electron density is given by

\[
\rho = \sum_{ij} \sum_k n_k C_{ik} C_{jk} x_i^* x_j.
\] (11)

In solving the SCF equations (5)–(11), we start from the expansion coefficients \( a_i \) and \( b_i \) which are found from a least-squares fit to a superposition of atomic Hartree–Fock potentials. The coefficients \( a_i \) and \( b_i \) uniquely determine the starting Hamiltonian \( \hat{H} \). Upon solving the eigenvalue equation (10), a new electron density (11) and, correspondingly, a new \( \alpha \) potential are obtained. Expansion coefficients \( a_i \) and \( b_i \) are recalculated by least-squares fitting. The iteration is
TABLE I. Bond lengths (a. u.) and bond angles (degrees).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Coordinate</th>
<th>Near HF a</th>
<th>LCAO-Xα</th>
<th>DV-Xα b</th>
<th>SW-Xα e</th>
<th>Expt. d</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>R e</td>
<td>2.01</td>
<td>2.07</td>
<td>2.48</td>
<td>4.1</td>
<td>2.07</td>
</tr>
<tr>
<td>F2</td>
<td>R e</td>
<td>2.51</td>
<td>-6.0</td>
<td>⋯</td>
<td>4.3</td>
<td>2.68</td>
</tr>
<tr>
<td>CO</td>
<td>R e</td>
<td>2.08</td>
<td>2.10</td>
<td>2.32</td>
<td>⋯</td>
<td>2.13</td>
</tr>
<tr>
<td>H2O</td>
<td>R OH</td>
<td>1.779</td>
<td>1.846</td>
<td>⋯</td>
<td>1.860</td>
<td>1.809</td>
</tr>
<tr>
<td></td>
<td>b OH</td>
<td>106.1</td>
<td>105.0</td>
<td>⋯</td>
<td>180.0</td>
<td>104.5</td>
</tr>
</tbody>
</table>


b Reference 1.

c Reference 12.


The total energy is then calculated from

\[ E = \sum_{ij} \sum_{k} n_k C_{ik}^* C_{jk} \langle \chi_i | H - \frac{1}{2} \vec{V}_c - \frac{1}{2} \vec{V}_{Xα} | \chi_j \rangle, \]

(12)

where \( \vec{H} \), \( \vec{V}_c \), and \( \vec{V}_{Xα} \) are given by Eq. (7).

Note that the one-electron Hamiltonian \( \vec{H} \) does not employ the muffin-tin approximation and can be as close as desired to the true SCF-Xα Hamiltonian by employing increased numbers of auxiliary and basis functions. Determination of the Coulomb potential from a least-squares analytic fit to the electron density has been employed by several authors\(^5\) and our approach is similar to that of Baerends et al.\(^1\)

C. Auxiliary and basis functions

The auxiliary fitting functions \( f_i \) and \( g_i \) for \( \rho \) and \( V_{Xα} \), respectively, are chosen to be linear combinations of 1s Gaussians centered at nuclei. Since \( \rho \) and \( V_{Xα} \) differ considerably in their spatial shape, we employ different sets for the functions \( f_i \) and \( g_i \). First, the Hartree-Fock atomic electron density \( \rho \) and the corresponding \( \rho^{1/3} \) are fitted as linear combinations of primitive 1s Gaussians. Then the functions \( f_i \) and \( g_i \) are obtained by contracting the 1s Gaussians and are fixed for each atom. (This procedure is similar to that to obtain contracted Gaussian basis for orbitals, such as 4-31G basis.\(^6\) The contracted atomic functions are combined further to give symmetry-adapted auxiliary functions which, unlike orbital basis functions, are always totally symmetric. We have used two or three symmetry-adapted functions for the core region of \( \rho \) and \( V_{Xα} \) and two for the bonding region.

Basis functions \( \chi_i \) appearing in the expansion of the molecular orbitals are the contracted atomic Gaussian basis functions (4-31G) obtained by Pople.\(^6\) There is no advantage in using a larger basis set without, at the same time, enlarging the number of auxiliary and basis functions. Employment of the same, well-defined, atomic basis sets has been shown to be advantageous in predicting physical properties of molecular systems.\(^7\) For all calculations presented in this paper, the same atomic auxiliary and basis functions have been employed and no attempt has been made to optimize them in molecular calculations.

With these choices of auxiliary and basis functions, the matrix elements of Eq. (10) are calculated analytically. It is gratifying to note that the most time-consuming integral in the scheme is the nuclear attraction integral and computation times are not particularly

<table>
<thead>
<tr>
<th>Energy parameter</th>
<th>Near HF a</th>
<th>LCAO-Xα</th>
<th>SW-Xα b</th>
<th>Expt. d</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>2.86</td>
<td>8.60</td>
<td>7.88</td>
<td>8.35</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>-16.31</td>
<td>-16.09</td>
<td>⋯</td>
<td>-9.87</td>
</tr>
</tbody>
</table>

\(^b\) Reference 12.
\(^c\) Reference 14.
sensitive to the number of functions \( f_i \) and \( g_i \) used to expand the potentials. Two minutes (18 iterations in double precision for a calculation of the water molecule on an UNIVAC 1106) reflects the computational speed of the method.

There is only one parameter in the model, namely, the exchange scaling parameter \( \alpha \), which is chosen to be weighted average \( \left[ e.g., \frac{1}{2} (2\alpha R + \alpha_0) \right] \) of the atomic \( \alpha \)'s obtained by Schwars.

**D. Electron density and Xα potential fit**

Expansion coefficients \( a_i \) and \( b_i \) in Eqs. (5) and (6) are determined by minimizing, respectively,

\[
\int \left[ \rho(r) - \sum_i a_i f_i(r) \right]^2 \, dr \tag{13}
\]

\[
\sum_i \int r_i \left[ c \rho_i^{1/3} - \sum_j b_j g_j(r) \right]^2 \, dr + \sum_a W(r_a) \left[ c \rho(r_a)^{1/3} - \sum_j b_j g_j(r_a) \right]^2 \tag{14}
\]

where \( c = -3\alpha(3/8\pi)^{1/3}, \) \( V_1 \) is the spherical core volume around nucleus \( I, \) \( \rho_1^{1/3} \) is the spherically averaged \( \rho^{1/3} \) within \( V_1, \) \( W(r) \) is a weight function, and the summation is over a discrete set of sample points \( r_a. \) Minimization leads to simultaneous equations for \( a_i \) and \( b_j, \) respectively.

For \( \rho, \) all matrix and vector elements of the simultaneous equation are calculated analytically; however, for \( \rho^{1/3} \) the sample point distribution remains to be specified. Care must be exercised in choosing the sample points for potential curve calculations, since the total energy is sensitive to this choice and will yield, on occasions, small discontinuities in the potential curve. To avoid this undesirable feature, the distribution of sample points is set to change continuously during changes of the nuclear configuration keeping the total number of points constant. Sample points are chosen about each nucleus in the space exterior to core volumes \( V_1, \) and along the three Cartesian axes and diagonals of each octant. The radial distribution \( r_0, r_1, \ldots, r_n \)

\[
r_n = D_i (R/R_e) \left[ 1 + A \left( 1 + B + \cdots + B^6 \right) \right] \tag{15}
\]

where \( D_i \) is the radius of \( V_I \) and is one-half of Slater's \( ^* \) atomic radius, \( A \) and \( B \) are 0.2 and 1.2, respectively. The radial distribution changes as the intermolecular distance \( R \) is altered from its equilibrium value \( R_e. \) With this modification the present program produces smooth potential curves. The number of sample points used is a maximum of 120 for \( H_2O \) and thus is one to two orders of magnitude less than that of the DV-Xα method.

**III. RESULTS AND DISCUSSION**

Theoretical and experimental ionization energies are compared in Fig. 1. Hartree–Fock (HF) ionization energies result from Koopmans's theorem applied to near HF calculations, \(^*\) and Xα ionization energies are calculated at the experimental equilibrium geometry by the transition-state procedure. As seen in Fig. 1, the Xα methods yield the correct ordering of ionized states for \( N_2 \) and \( F_2, \) in contrast to HF calculations. Avoidance of the muffin-tin approximation in the LCAO–Xα scheme yields accurate energy level differences, but the levels are displaced uniformly from the experimental data. The discrepancy between the DV–Xα results, \(^1\) which are in excellent agreement with the experiment data, and the LCAO–Xα results are not caused by a computational deficiency in the latter method, but is due to a different treatment of valence electrons. In the DV–Xα calculations \(^1\) core electrons are "frozen" and \( \alpha \) is chosen to describe valence electrons; the present calculation includes both core and valence electrons and employs an exchange scaling parameter appropriate to both core and valence electrons. Finally, we have observed that the ionization energies are quite insensitive to the distribution of sample points used to fit \( V_{xα}, \) a finding similar to that of the DV–Xα scheme.

It is generally recognized that the SCF–Xα model provides a rapid computational route to ionization energies, but its reliability in predicting equilibrium molecular conformations is an open question. The present computational method with its analytic bases permits easy access to potential curves, and it is found that good equilibrium geometries can be calculated for \( N_2, \) \( CO, \) and \( H_2O. \) These results are presented in Table I. The symmetric stretching potential curve of water (Fig. 2) is calculated at the experimental equilibrium angle \(^4\) of 104.6° (the computed equilibrium configuration is \( R_e = 1.846 \) a. u. and \( \theta_e = 105.0°). \) This curve was then fitted to

\[
E = E_0 + k_2 (\Delta r)^2 + (2k_3/R_e)(\Delta r)^3 \tag{16}
\]

to obtain the force constants \( k_2 \) and \( k_3 \) which compare favorably to other ab initio results (Table II). Reference to Table I demonstrates that the LCAO–Xα method has a distinct advantage over SW–Xα technique when computing equilibrium geometry, excepting the case of \( F_2. \) Upon examination of the least-squares fitting of \( V_{xα} \) for \( F_2, \) we noted that the exchange potential is not reproduced well by the auxiliary functions; a feature not observed with \( N_2, \) \( CO, \) or \( H_2O. \) The deviation between \( V_{xα} \) and the least-squares fitting was particularly bad in the internuclear region, suggesting that inclusion of polarization in the auxiliary set might improve the calculated \( F_2 \) geometry.

From the results described here it would appear that utilization of an expansion technique for both potential and orbitals is feasible in SCF–Xα calculations. No essential difficulties are anticipated as the present method is extended to larger systems; however, to reduce computation time in applications to larger molecular systems, we would fix the core and choose \( \alpha \) in manner suggested by Baerends et al. \(^{1,11}\)

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A new computational approach to Slater's SCF-$X\alpha$ equation

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I. INTRODUCTION

A major virtue of the discrete-variational scheme applied to Hartree-Fock-Slater (or SCF-$X\alpha$) theory is removal of the muffin-tin approximation which is inherent to the scattered-wave ($SW-X\alpha$) technique. The DV-$X\alpha$ method is quite flexible with respect to the choice of basis functions; for example, a numerical basis set can be much smaller than an analytic basis set and yet yield molecular properties with comparable accuracy. However, the number of sample points per atom required to obtain reasonable accuracy in the total energy may become large and thus equilibrium geometries require generous amounts of computation time.

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A. The SCF-$X\alpha$ model

References to earlier works on the SCF-$X\alpha$ theory are discussed in recent reviews, and we display here equations germane to the subsequent development of the computational method. In the SCF-$X\alpha$ model, the one-electron Hamiltonian (in atomic units) is given by

$$H = -\frac{1}{2} \nabla^2 \phi + \sum_{i} (-Z_i/r_i) + V_C(1) + V_{X\alpha}(1),$$

where $\phi$ is the exchange parameter, $n_i$ are orbital occupation numbers, and $\rho$ is the total electron density. The orbitals $\phi_i$ satisfy the one-electron equation

$$H \phi_i = E_\phi \phi_i,$$

and

$$\rho = \sum_i n_i \phi^*_i \phi_i,$$

where $\phi$ is the exchange parameter, $n_i$ are orbital occupation numbers, and $\rho$ is the total electron density. The orbitals $\phi_i$ satisfy the one-electron equation

$$H \phi_i = E_\phi \phi_i,$$

and Eqs. (1)-(3) are solved self-consistently. The (statistical) total energy $E$ is given by

$$E = \sum_i n_i \langle \phi_i | H - \frac{1}{2} V_C - \frac{1}{2} V_{X\alpha} | \phi_i \rangle,$$

The one-electron equation (3) can be derived by applying the variational principle to the total energy (4). The transition-state procedure of Slater simplifies the determination of excitation and ionization energies and appears to be more accurate than Koopmans' theorem applied to Hartree-Fock results. From a computational point of view, replacement of the nonlocal exchange operator of Hartree-Fock theory by the local $X\alpha$ potential is the key feature which permits rapid calculations for moderately large molecular systems.

B. The LCAO-$X\alpha$ method

The $X\alpha$ potential $V_{X\alpha}$ and the electron density appearing in the Coulomb potential $V_C$ are least-squares fitted to auxiliary functions centered at the nuclei, viz.,

$$\rho(r) = \sum_i a_i f_i(r),$$

and

$$\phi(r) = \sum_i a_i g_i(r),$$

where $\alpha$ is the exchange parameter, $n_i$ are orbital occupation numbers, and $\rho$ is the total electron density. The orbitals $\phi_i$ satisfy the one-electron equation

$$H \phi_i = E_\phi \phi_i,$$

and Eqs. (1)-(3) are solved self-consistently. The (statistical) total energy $E$ is given by

$$E = \sum_i n_i \langle \phi_i | H - \frac{1}{2} V_C - \frac{1}{2} V_{X\alpha} | \phi_i \rangle,$$
FIG. 1. Experimental and theoretical ionization energies of $N_2$, $F_2$, $CO$, and $H_2O$ molecules. HF (Ref. 10) and $X\alpha$ (Refs. 11, 12) results obtained by Koopmans’s theorem and transition state procedure, respectively. Experimental data are taken from Ref. 13. Dotted lines are estimated vertical ionization energies.

where $x_i$ are analytic functions centered at nuclei. This leads to the familiar secular equation,

$$\sum_j (\langle x_i, \hat{H} x_j \rangle - \epsilon_k \langle x_i, x_j \rangle) c_{jk} = 0. \quad (10)$$

In terms of the solutions of Eq. (10), the electron density is given by

$$\rho = \sum_{i} \sum_{l} n_s C_{ls}^* C_{js} x_i^* x_j. \quad (11)$$

In solving the SCF equations (5)–(11), we start from the expansion coefficients $a_i$ and $b_i$ which are found from a least-squares fit to a superposition of atomic Hartree–Fock potentials. The coefficients $a_i$ and $b_i$ uniquely determine the starting Hamiltonian $\hat{H}$. Upon solving the eigenvalue equation (10), a new electron density (11) and, correspondingly, a new $X\alpha$ potential are obtained. Expansion coefficients $a_i$ and $b_i$ are recalculated by least-squares fitting. The iteration is
TABLE I. Bond lengths (a. u.) and bond angles (degrees).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Coordinate</th>
<th>Near HF(^a)</th>
<th>LCAO-X(a)</th>
<th>DV-X(a)(^b)</th>
<th>SW-X(a)(^c)</th>
<th>Expt.(^d)</th>
</tr>
</thead>
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<tr>
<td>N(_2)</td>
<td>(R_{\theta})</td>
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<td>2.07</td>
<td>2.48</td>
<td>4.1</td>
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</tr>
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<td>F(_2)</td>
<td>(R_{\theta})</td>
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<td>6.0</td>
<td>...</td>
<td>4.3</td>
<td>2.68</td>
</tr>
<tr>
<td>CO</td>
<td>(R_{\theta})</td>
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<td>2.32</td>
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<td>2.13</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>(R_{OH})</td>
<td>1.779</td>
<td>1.846</td>
<td>...</td>
<td>1,880</td>
<td>1,809</td>
</tr>
</tbody>
</table>

\(^b\)Reference 1.
\(^c\)Reference 12.

C. Auxiliary and basis functions

The auxiliary fitting functions \(f_i\) and \(g_i\) for \(\rho\) and \(V_{Xa}\), respectively, are chosen to be linear combinations of 1s Gaussians centered at nuclei. Since \(\rho \) and \(V_{Xa}\) differ considerably in their spatial shape, we employ different sets for the functions \(f_i\) and \(g_i\). First, the Hartree-Fock atomic electron density \(\rho\) and the corresponding \(\rho^{1/3}\) are fitted as linear combinations of primitive 1s Gaussians. Then the functions \(f_i\) and \(g_i\) are obtained by contracting the 1s Gaussians and are fixed for each atom. (This procedure is similar to that to obtain contracted Gaussian basis for orbitals, such as 4-31G basis.\(^d\)) The contracted atomic functions are combined further to give symmetry-adapted auxiliary functions which, unlike orbital basis functions, are always totally symmetric. We have used two or three symmetry-adapted functions for the core region of \(\rho\) and \(V_{Xa}\) and two for the bonding region.

Basis functions \(\chi_j\) appearing in the expansion of the molecular orbitals are the contracted atomic Gaussian basis functions (4-31G) obtained by Pople.\(^e\) There is no advantage in using a larger basis set without, at the same time, enlarging the number of auxiliary functions. Employment of the same, well-defined, atomic basis sets has been shown to be advantageous in predicting physical properties of molecular systems.\(^f\) For all calculations presented in this paper, the same atomic auxiliary and basis functions have been employed and no attempt has been made to optimize them in molecular calculations.

With these choices of auxiliary and basis functions, the matrix elements of Eq. (10) are calculated analytically. It is gratifying to note that the most time-consuming integral in the scheme is the nuclear attraction integral and computation times are not particularly

TABLE II. Symmetric stretching force constants (10\(^5\) dyn/cm) for water.

<table>
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<tr>
<th>Energy parameter</th>
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<th>LCAO-X(a)</th>
<th>SW-X(a)(^c)</th>
<th>Expt.(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>9.89</td>
<td>8.46</td>
<td>7.88</td>
<td>8.35</td>
</tr>
<tr>
<td>(k_2)</td>
<td>-10.51</td>
<td>-10.99</td>
<td>...</td>
<td>-9.87</td>
</tr>
</tbody>
</table>

\(^b\)Reference 12.
\(^c\)Reference 14.
sensitive to the number of functions $f_i$ and $g_i$ used to expand the potentials. Two moments (18 iterations in double precision for a calculation of the water molecule on an UNIVAC 1108) reflects the computational speed of the method.

There is only one parameter in the model, namely, the exchange scaling parameter $\alpha$, which is chosen to be weighted average (e.g., $\alpha = \langle 2\alpha_h + \alpha_0 \rangle$) of the atomic $\alpha$'s obtained by Schwarz.

D. Electron density and Xα potential fit

Expansion coefficients $a_i$ and $b_i$ in Eqs. (5) and (6) are determined by minimizing, respectively,

$$\frac{1}{\mu} \sum_i \int \left[ \rho(r) - \sum_i a_i f_i(r) \right]^2 \, dr,$$

and

$$\frac{1}{\mu} \sum_i \int \left[ \rho_i(r) - \sum_i b_i g_i(r) \right]^2 \, dr,$$

$$\left( \sum_i \int W(r_i) \left[ \rho_i(r) \right]^{1/3} - \sum_i b_i g_i(r_i) \right)^2,$$

where $c = -3a(3/8\pi)^{1/3}$, $V_i$ is the spherical core volume around nucleus $I$, and $\rho_i^{1/3}$ is the spherically averaged $\rho_i^{1/3}$ within $V_i$, $W(r)$ is a weight function, and the summation is over a discrete set of sample points $r_i$. Minimization leads to simultaneous equations for $a_i$ and $b_i$, respectively.

For $\rho$, all matrix and vector elements of the simultaneous equation are calculated analytically; however, for $cp^{1/3}$ the sample point distribution remains to be specified. Care must be exercised in choosing the sample points for potential curve calculations, since the total energy is sensitive to this choice and will yield, on occasions, small discontinuities in the potential curve. To avoid this undesirable feature, the distribution of sample points is set to change continuously during changes of the nuclear configuration keeping the total number of points constant. Sample points are chosen about each nucleus in the space exterior to core volumes $V_i$, and along the three Cartesian axes and diagonals of each octant. The radial distribution $r_0, r_1, \ldots, r_n$ is

$$r_n = D_i(R/R_0) \left[ 1 + A(1 + B + \ldots + B^n) \right],$$

where $D_i$ is the radius of $V_i$ and $1/2$ of Slater's atomic radius. $A$ and $B$ are 0.2 and 1.2, respectively. The radial distribution changes as the intermolecular distance $R$ is altered from its equilibrium value $R_0$. With this modification the present program produces smooth potential curves. The number of sample points used is a maximum of 120 for $H_2O$ and thus is one to two orders of magnitude less than that of the DV-Xα method.

III. RESULTS AND DISCUSSION

Theoretical and experimental ionization energies are compared in Fig. 1. Hartree-Fock (HF) ionization energies result from Koopmans's theorem applied to near HF calculations, and Xα ionization energies are calculated at the experimental equilibrium geometry by the transition-state procedure. As seen in Fig. 1, the Xα methods yield the correct ordering of ionized states for $N_2$ and $F_2$, in contrast to HF calculations. Avoidance of the muffin-tin approximation in the LCAO-Xα scheme yields accurate energy level differences, but the levels are displaced uniformly from the experimental data, and the LCAO-Xα results are not caused by a computational deficiency in the latter method, but is due to a different treatment of valence electrons. In the DV-Xα calculations, the core electrons are "frozen" and $\alpha$ is chosen to describe valence electrons; the present calculation includes both core and valence electrons and employs an exchange scaling parameter appropriate to both core and valence electrons. Finally, we have observed that the ionization energies are quite insensitive to the distribution of sample points used to fit $V_{X\alpha}$, finding a similar to that of the DV-Xα scheme.

It is generally recognized that the SCF-Xα model provides a rapid computational route to ionization energies, but its reliability in predicting equilibrium molecular conformations is an open question. The present computational method with its analytic bases permits easy access to potential curves, and it is found that good equilibrium geometries can be calculated for $N_2$, $CO$, and $H_2O$. These results are presented in Table I, where the symmetric stretching potential curve of water (Fig. 2) is calculated at the experimental equilibrium angle of $104.5^\circ$ (the computed equilibrium conformation is $R_e = 1.846$ a.u., and $\theta_e = 105.0^\circ$). This curve was then fitted to

$$R = R_0 + k_2(\Delta r)^2 + (2k_3/R_e)(\Delta r)^5$$

(16)
to obtain the force constants $k_2$ and $k_3$ which compare favorably to other ab initio results (Table II). Reference to Table I demonstrates that the LCAO-Xα method has a distinct advantage over SW-Xα technique when computing equilibrium geometry, excepting the case of $F_2$. Upon examination of the least-squares fitting of $V_{X\alpha}$ for $F_2$, we noted that the exchange potential is not reproduced well by the auxiliary functions; a feature noted not observed with $N_2$, $CO$, or $H_2O$. The deviation between $V_{X\alpha}$ and the least-squares fitting was particularly bad in the internuclear region, suggesting that inclusion of polarization in the auxiliary set might improve the calculated $F_2$ geometry.

From the results described here it would appear that utilization of an expansion technique for both potential and orbitals is feasible in SCF-Xα calculations. No essential difficulties are anticipated as the present method is extended to larger systems; however, to reduce computation time in applications to larger molecular systems, we would fix the core and choose $\alpha$ in manner suggested by Baerends et al."

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*Supported in part by grants from the National Science Foundation (GP-17061) and National Institutes of Health (AM-14344).


H. Sambe and R. H. Felton: Slater's SCF-Xα


8 J. C. Slater, Quantum Theory of Molecules and Solids (Mc-


A new computational approach to Slater's SCF–Xα equation

Hideo Sambe and Ronald H. Felton

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

(Received 16 September 1974)

A new computational scheme is presented for the performance of LCAO–MO calculations in the SCF–Xα model. The scheme is intended to be applicable for large systems and to be more accurate than the scattered-wave SCF–Xα method. The Xα potential is fitted by least-squares to a linear combination of Gaussians, and the approximated SCF–Xα equation is solved by the conventional Rayleigh–Ritz variational method. The muffin-tin approximation is avoided, and matrix elements are calculated analytically in contrast to the discrete variational scheme. Some illustrative results are given for the ionization energies and equilibrium geometries of small molecules. It is found that over-all performance of the method is satisfactory for both ionization energies and equilibrium geometries.

I. INTRODUCTION

A major virtue of the discrete-variational scheme (DV–Xα) applied to Hartree-Fock-Slater (or SCF–Xα) theory is removal of the muffin-tin approximation which is inherent to the scattered-wave (SW–Xα) technique. The DV–Xα method is quite flexible with respect to the choice of basis functions; for example, a numerical basis set can be much smaller than an analytic basis set and yet yield molecular properties with comparable accuracy. However, the number of sample points per atom required to obtain reasonable accuracy in the total energy may become large and thus equilibrium geometries require generous amounts of computation time.

An obstacle in solving the SCF–Xα equation occurs with the ρ1/3 dependence of the Xα potential, where ρ is the electron density. In a straightforward application of the Rayleigh–Ritz variational method with analytic basis functions, cumbersome integrals arise from the Xα potential. The discrete variational method overcomes this difficulty by numerical evaluation of the relevant integrals. The computational method we now present circumvents this problem by expanding the Xα potential by a least-squares fit to auxiliary functions, chosen so as to yield simple integrals. To reduce the number of two-electron integrals arising from Coulomb interaction, we also expand the electron density appearing in the Coulomb potential with auxiliary functions. The matrix elements of the one-electron Hamiltonian are then calculated analytically. In Sec. II the computational method is described and in Sec. III results on illustrative examples are presented and discussed.

II. THE LCAO-SCF–Xα METHOD

A. The SCF–Xα model

References to earlier works on the SCF–Xα theory are discussed in recent reviews, and we display here equations germane to the subsequent development of the computational method. In the SCF–Xα model, the one-electron Hamiltonian (in atomic units) is given by

\[ H = -\frac{1}{2} \nabla^2 + \sum_{\alpha} \left( -\frac{Z_n}{r_{1\alpha}} + V_C(1) + V_{X\alpha}(1) \right), \]

\[ V_C(1) = \int \rho(2)/r_{12} dV, \]

\[ V_{X\alpha}(1) = -3\alpha \left[ (3/8\pi) \rho(1) \right]^{1/3}, \]

and

\[ \rho = \sum_{\alpha} n_{\alpha} \phi_{\alpha}^* \phi_{\alpha}, \]

where \( \alpha \) is the exchange parameter, \( n_{\alpha} \) are orbital occupation numbers, and \( \rho \) is the total electron density. The orbitals \( \phi_{\alpha} \) satisfy the one-electron equation

\[ H\phi_{\alpha} = \epsilon_{\alpha} \phi_{\alpha}, \]

and Eqs. (1)-(3) are solved self-consistently. The (statistical) total energy \( E \) is given by

\[ E = \sum_{\alpha} n_{\alpha} \langle \phi_{\alpha} | \left( -\frac{1}{2} \nabla^2 + V_C - \frac{1}{2} V_{X\alpha} \right) \phi_{\alpha} \rangle. \]

The one-electron equation (3) can be derived by applying the variational principle to the total energy (4). The transition-state procedure of Slater simplifies the determination of excitation and ionization energies and appears to be more accurate than Koopmans' theorem applied to Hartree–Fock results. From a computational point of view, replacement of the nonlocal exchange operator of Hartree–Fock theory by the local Xα potential is the key feature which permits rapid calculations for moderately large molecular systems.

B. The LCAO–Xα method

The Xα potential \( V_{X\alpha} \) and the electron density appearing in the Coulomb potential \( V_C \) are least-squares fitted to auxiliary functions centered at the nuclei, viz.,

\[ \rho(r) = \sum_{i} a_i f_i(r), \]

\[ -3\alpha \left[ (3/8\pi) \rho(1) \right]^{1/3} = \sum_{i} b_i g_i(r). \]

The one-electron Hamiltonian becomes

\[ \tilde{H} = -\frac{1}{2} \nabla^2(1) + \sum_{\alpha} \left( -\frac{Z_n}{r_{1\alpha}} + \tilde{V}_C(1) + \tilde{V}_{X\alpha}(1) \right), \]

\[ \tilde{V}_C(1) = \sum_{i} a_i \int f_i(2)/r_{12} dV, \]

\[ \tilde{V}_{X\alpha}(1) = \sum_{i} b_i g_i(1). \]

To solve the corresponding one-electron equation,

\[ \tilde{H}\phi_{\alpha} = \epsilon_{\alpha} \phi_{\alpha}, \]

we employ the Rayleigh–Ritz variational method with linear variational functions for \( \phi_{\alpha} \),

\[ \phi_{\alpha} = \sum_{i} \chi_i C_{i\alpha}. \]
where \( \chi_i \) are analytic functions centered at nuclei. This leads to the familiar secular equation,

\[
\sum_j \left( \langle x_i | \tilde{H} | x_j \rangle - \epsilon_x \langle x_i | x_j \rangle \right) C_{ji} = 0. \tag{10}
\]

In terms of the solutions of Eq. (10), the electron density is given by

\[
\rho = \sum_{ij} \sum_k n_{ik} C_{ik}^* C_{jk} \chi_i^* \chi_j. \tag{11}
\]

In solving the SCF equations (5)–(11), we start from the expansion coefficients \( a_i \) and \( b_i \) which are found from a least-squares fit to a superposition of atomic Hartree–Fock potentials. The coefficients \( a_i \) and \( b_i \) uniquely determine the starting Hamiltonian \( \tilde{H} \). Upon solving the eigenvalue equation (10), a new electron density (11) and, correspondingly, a new \( X\alpha \) potential are obtained. Expansion coefficients \( a_i \) and \( b_i \) are re-calculated by least-squares fitting. The iteration is
TABLE I. Bond lengths (a. u.) and bond angles (degrees).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Coordinate</th>
<th>Near HF</th>
<th>LCAO-Xa</th>
<th>DV-Xa</th>
<th>SW-Xa</th>
<th>Expt.</th>
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</thead>
<tbody>
<tr>
<td>N₂</td>
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<td>2.48</td>
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<td>F₂</td>
<td>Rₑ</td>
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<tr>
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<td>Rₑ</td>
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<tr>
<td>H₂O</td>
<td>R(Ｏ—Ｈ)</td>
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<td></td>
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<td></td>
<td>180.0</td>
<td>104.5</td>
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</table>

bReference 1.
cReference 12.

determined when the differences between successive values of a₁ and b₁ are each less than 10⁻⁴, which corresponds to six and eight digit accuracy in the orbitals and the total energy, respectively. (It is found that a₁ and b₁ are more sensitive during iteration than are the orbital expansion coefficients Cᵢₑ or the total energy; therefore, a₁ and b₁ provide the convergence criterion.) The total energy is then calculated from

\[ E = \sum_{i,j} \sum_{k} n_k C_{i;k}^* C_{j;k} \langle \chi_i, \tilde{H} - \frac{1}{2} \tilde{V}_C - \frac{1}{2} \tilde{V}_{Xa} \rangle \chi_j \],

(12)

where \( \tilde{H} \), \( \tilde{V}_C \), and \( \tilde{V}_{Xa} \) are given by Eq. (7).

Note that the one-electron Hamiltonian \( \tilde{H} \) does not employ the muffin-tin approximation and can be as close as desired to the true SCF-Xa Hamiltonian by employing increased numbers of auxiliary and basis functions. Determination of the Coulomb potential from a least-squares analytic fit to the electron density has been employed by several authors and our approach is similar to that of Baerends et al.

C. Auxiliary and basis functions

The auxiliary fitting functions \( f_i \) and \( g_i \) for \( \rho \) and \( V_{Xa} \), respectively, are chosen to be linear combinations of \( 1s \) Gaussians centered at nuclei. Since \( \rho \) and \( V_{Xa} \) differ considerably in their spatial shape, we employ different sets for the functions \( f_i \) and \( g_i \). First, the Hartree-Fock atomic electron density \( \rho \) and the corresponding \( \rho_{Xa} \) are fitted as linear combinations of \( 1s \) Gaussians. Then the functions \( f_i \) and \( g_i \) are obtained by contracting the \( 1s \) Gaussians and are fixed for each atom. This procedure is similar to that to obtain contracted Gaussian basis for orbitals, such as 4-31G basis. The contracted atomic functions are combined further to give symmetry-adapted auxiliary functions which, unlike orbital basis functions, are always totally symmetric. We have used two or three symmetry-adapted functions for the core region of \( \rho \) and \( V_{Xa} \) and two for the bonding region.

Basis functions \( \chi_i \) appearing in the expansion of the molecular orbitals are the contracted atomic Gaussian basis functions (4-31G) obtained by Pople. There is no advantage in using a larger basis set without, at the same time, enlarging the number of auxiliary functions. Employment of the same, well-defined, atomic basis sets has been shown to be advantageous in predicting physical properties of molecular systems. For all calculations presented in this paper, the same atomic auxiliary and basis functions have been employed and no attempt has been made to optimize them in molecular calculations.

With these choices of auxiliary and basis functions, the matrix elements of Eq. (10) are calculated analytically. It is gratifying to note that the most time-consuming integral in the scheme is the nuclear attraction integral and computation times are not particularly

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<tbody>
<tr>
<td>( k_e )</td>
<td>9.89</td>
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<tr>
<td>( k_2 )</td>
<td>10.51</td>
<td>10.69</td>
<td></td>
<td></td>
<td>9.87</td>
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bReference 12.
cReference 14.
sensitive to the number of functions \( f_i \) and \( g_i \) used to expand the potentials. Two minutes (18 iterations in double precision for a calculation of the water molecule on an UNIVAC 1108) reflects the computational speed of the method.

There is only one parameter in the model, namely, the exchange scaling parameter \( \alpha \), which is chosen to be weighted average \( \left[ \frac{1}{2}(2\alpha_{\text{g}} + \alpha_{\text{c}}) \right] \) of the atomic \( \alpha \)'s obtained by Schwarz.  

D. Electron density and Xα potential fit

Expansion coefficients \( a_i \) and \( b_i \) in Eqs. (5) and (6) are determined by minimizing, respectively,

\[
\int \left[ \rho(r) - \sum_i a_i f_i(r) \right]^2 \, dr,
\]

and

\[
\int \left[ c \sum_{j=1}^n \left( \frac{r}{R_j} \right)^{1/3} - \sum_{j} b_j g_j(r) \right]^2 \, dr
\]

\[
+ \sum_{u} W(r_u) |c \rho(r_u)^{1/3} - \sum_{j} b_j g_j(r_u)|^2 ,
\]

where \( c = 3 \alpha (3/8 \pi)^{1/3}, V_i \) is the spherical core volume around nucleus \( I \), \( \rho_{1/3}^i \) is the spherically averaged \( \rho^{1/3} \) within \( V_i \), \( W(r) \) is a weight function, and the summation is over a discrete set of sample points \( r_u \). Minimization leads to simultaneous equations for \( a_i \) and \( b_i \), respectively.

For \( \rho \), all matrix and vector elements of the simultaneous equation are calculated analytically; however, for \( c \rho^{1/3} \) the sample point distribution remains to be specified. Care must be exercised in choosing the sample points for potential curve calculations, since the total energy is sensitive to this choice and will yield, on occasions, small discontinuities in the potential curve. To avoid this undesirable feature, the distribution of sample points is set to change continuously during changes of the nuclear configuration keeping the total number of points constant. Sample points are chosen about each nucleus in the space exterior to core volumes \( V_i \), and along the three Cartesian axes and diagonals of each octant. The radial distribution \( r_0, r_1, \ldots, r_n \) is

\[
r_n = D_i \left( R/R_i \right)^{1/3} \left[ 1 + A \left( 1 + B + \cdots + B^n \right) \right],
\]

where \( D_i \) is the radius of \( V_i \) and is one-half of Slater's \( r_0 \) atomic radius. \( A \) and \( B \) are 0.2 and 1.2, respectively. The radial distribution changes as the intermolecular distance \( R \) is altered from its equilibrium value \( R_e \). With this modification the present program produces smooth potential curves. The number of sample points used is a maximum of 120 for \( H_2O \) and thus is one to two orders of magnitude less than that of the DV–Xα method.

III. RESULTS AND DISCUSSION

Theoretical and experimental ionization energies are compared in Fig. 1. Hartree–Fock (HF) ionization energies result from Koopmans's theorem applied to near HF calculations, and Xα ionization energies are calculated at the experimental equilibrium geometry by the transition-state procedure. As seen in Fig. 1, the Xα methods yield the correct ordering of ionized states for \( N_2 \) and \( F_2 \), in contrast to HF calculations. Avoidance of the muffin-tin approximation in the LCAO–Xα scheme yields accurate energy level differences, but the levels are displaced uniformly from the experimental data. The discrepancy between the DV–Xα results, which are in excellent agreement with the experimental data, and the LCAO–Xα results are not caused by a computational deficiency in the latter method, but is due to a different treatment of valence electrons. In the DV–Xα calculations core electrons are "frozen" and \( \alpha \) is chosen to describe valence electrons; the present calculation includes both core and valence electrons and employs an exchange scaling parameter appropriate to both core and valence electrons. Finally, we have observed that the ionization energies are quite insensitive to the distribution of sample points used to fit \( V_{Xα} \), a finding similar to that of the DV–Xα scheme.

It is generally recognized that the SCF–Xα model provides a rapid computational route to ionization energies, but its reliability in predicting equilibrium molecular conformations is an open question. The present computational method with its analytic bases permits easy access to potential curves, and it is found that good equilibrium geometries can be calculated for \( N_2, CO, \) and \( H_2O \). These results are presented in Table I. The symmetric stretching potential curve of water (Fig. 2) is calculated at the experimental equilibrium angle \( 104.46° \) (the computed equilibrium conformation is \( R_e = 1,846 \) a.u. and \( \theta_e = 105.0° \)). This curve was then fitted to

\[
E = E_0 + k_2 (\Delta r)^2 + (2k_3/R_e) (\Delta r)^3
\]

(16)

to obtain the force constants \( k_2 \) and \( k_3 \) which compare favorably to other \textit{ab initio} results (Table II). Reference to Table I demonstrates that the LCAO–Xα method has a distinct advantage over SW–Xα technique when computing equilibrium geometry, excepting the case of \( F_2 \). Upon examination of the least-squares fitting of \( V_{Xα} \) for \( F_2 \), we noted that the exchange potential is not reproduced well by the auxiliary functions; a feature not observed with \( N_2, CO, \) or \( H_2O \). The deviation between \( V_{Xα} \) and the least-squares fitting was particularly bad in the internuclear region, suggesting that inclusion of polarization in the auxiliary set might improve the calculated \( F_2 \) geometry.

From the results described here it would appear that utilization of an expansion technique for both potential and orbitals is feasible in SCF–Xα calculations. No essential difficulties are anticipated as the present method is extended to larger systems; however, to reduce computation time in applications to larger molecular systems, we would fix the core and choose \( \alpha \) in manner suggested by Baerends \textit{et al.} \cite{11}

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\cite{12}


\cite{13}


