To the Graduate Council:

I am submitting herewith a dissertation written by Noppawan Tanpipat entitled " *Ab initio* relativistic effective potential and relativistic configuration interaction calculations on diatomic molecules containing heavy elements." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

John E. Bloor, Major Professor

We have read this dissertation and recommend its acceptance:

Accepted for the Council:

Vice Provost
and Dean of The Graduate School

AB INITIO RELATIVISTIC EFFECTIVE POTENTIAL AND RELATIVISTIC CONFIGURATION INTERACTION CALCULATIONS ON DIATOMIC MOLECULES CONTAINING HEAVY ELEMENTS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Noppawan Tanpipat

December 1987

Dedicated to the memory of my late father

ACKNOWLEDGEMENT

The author wishes to express her gratitude and great appreciation to Dr. John E. Bloor for his advice, encouragement and instruction during the course of this work. His valuable expertise and guidance has assisted the completion of this work.

The author also would like to thank Dr. O. L. Keller, Jr., for the financial support through a DOE assistantship throughout the period of graduate study. Thanks are attributed to the ARCO and Science Alliance fellowships during the past three years in the graduate school as well.

The author extends sincere appreciation to Dr. K. Balasubramanian of the Department of Chemistry, Arizona State University, and to Dr. P. A. Christiansen of the Department of Chemistry, Clarkson College of Technology, for all the help given at the initial stage of this work. Special thanks also go to Alice Beauchene of the University Computing Center for much advice and guidance in the installation of the computer programs.

Great appreciation is expressed to the University of Tennessee Computer Center and the Department of Computer Science for the computer time and facilities.

Finally the author would like to thank her family for all the encouragement, inspiration and support given through out the time.

ABSTRACT

Ab initio relativistic effective potential and relativistic CI techniques have been used to perform calculations on the hydrides, oxides, fluorides and chlorides of scandium, lutetium and lawrencium.

In order to establish the validity of the method, the results on the hydrides, oxides, fluorides and chlorides are compared with previous calculations both at the SCF and CI levels. The calculated spectroscopic properties (R_e, D_e and ω_e) are also compared with the available experimental results. In general, they are in good agreement.

The wavefunctions produced are used to interpret the bonding in the twelve molecules investigated with particular emphasis on the effects of the relativistic terms included in the Hamiltonian. The results show that the bonding and spectroscopic constants for the lawrencium compounds are surprisingly similar to those values found for lutetium.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
	The Actinide Hypothesis	3
	Effective Potentials	7
	The Proposed Study	18
	Treating Scandium, Lutetium and Lawrencium as 3-electron atoms	20
II.	THEORY OF *AB INITIO* EFFECTIVE POTENTIAL CALCULATIONS	22
	Development of Effective Potentials	22
	Background	22
	Model Potentials	24
	Effective Core Potentials	27
	Shape-Consistent Pseudo-Orbitals	33
	Other Methods For Effective Potential Construction	35
	Relativistic Effective Potentials From Atomic Dirac-Hartree-Fock Calculations	36
	Dirac-Hartree-Fock Atomic Calculations	36
	Relativistic Effects On Valence Electrons	42
	Relativistic Effective Potentials	43
	Other Methods For Relativistic Effective Potential Construction	49
	Relativistic Effective Potentials In Molecular Hartree-Fock Calculations	50
	Configuration Interaction	53

TABLE OF CONTENTS (Continued)

CHAPTER		PAGE
III.	COMPUTATIONAL DETAILS	61
	Regional Separation	62
	Relativistic Effective Potential Construction	62
	DHF program	62
	SCREP program	67
	Exponent Optimization	70
	AHF program	70
	Molecular REP-SCF Calculations	77
	DER2 program	78
	LPS program	79
	EPSON program	81
	RTRN program	82
	GVB program	82
	PASO2 program	87
	Configuration Interaction Calculations	89
	Spectroscopic Constant Calculations	93
IV.	INPUT FOR THE REP-SCF/RCI CALCULATIONS ON MH, MO, MF AND MCl (M = Sc, Lu and Lr)	98
	Input Data	98
V.	RESULTS AND DISCUSSION OF RESULTS FOR MH, MO, MF AND MCl (M = Sc, Lu and Lr)	112
	Accuracy of Results	112
	Spectroscopic Results	119
	MH Molecules	119

TABLE OF CONTENTS (Continued)

CHAPTER		PAGE
	MO Molecules	125
	MF Molecules	129
	MCl Molecules	132
	Bonding	133
	MH Molecules	133
	MO Molecules	135
	MF Molecules	137
	MCl Molecules	139
VI.	SUMMARY AND CONCLUSION	141
LIST OF REFERENCES		144
APPENDICES		158
	Appendix A	159
	Appendix B	166
	Appendix C	176
	Appendix D	186
	Appendix E	194
	Appendix F	206
VITA		208

LIST OF TABLES

TABLE		PAGE
I.	HALF LIVES AND NUMBERS OF ATOMS AVAILABLE FOR THE ISOTOPES COMMONLY PRODUCED FOR CHEMICAL STUDIES OF Fm, Md, No and Lr	2
II.	OXIDATION STATES OF LANTHANIDES AND ACTINIDES IN SOLUTION	5
III.	ELECTRONIC STRUCTURE OF LANTHANIDES AND ACTINIDES	6
IV.	STATISTICAL DATA FOR D_e AND ω_e VALUES (REP-SCF CALCULATIONS)	96
V.	STATISTICAL DATA FOR D_e AND ω_e VALUES (RCI CALCULATIONS)	97
VI.	DOUBLE ZETA BASIS SETS OF Sc, Lu AND Lr	99
VII.	DOUBLE ZETA BASIS SETS OF H, O, F AND Cl	100
VIII.	AREP FOR Sc	101
IX.	AREPs FOR O, F AND Cl	102
X.	Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScH, LuH AND LrH	104
XI.	Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScO, LuO AND LrO	105
XII.	Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScF AND ScCl	107
XIII.	Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF LuF, LrF, LuCl and LrCl	109

LIST OF TABLES (Continued)

TABLE		PAGE
XIV.	NUMBER OF REFERENCE CONFIGURATIONS AND TOTAL CONFIGURATIONS	111
XV.	ORBITAL ENERGIES FROM REP-AHF AND ALL-ELECTRON DF/HF CALCULATION (a.u.)	113
XVI.	BOND LENGTHS OF MH, MO, MF AND MCl	114
XVII.	VIBAATIONAL FREQUENCIES AT THE GROUND STATE OF MH, MO, MF AND MCl	115
XVIII.	DISSOCIATION ENERGIES OF MH, MO, MF AND MCl	116
XIX.	SOME PREVIOUS SPECTROSCOPIC RESULTS OF THE REP-SCF/RCI CALCULATIONS	117
XX.	CALCULATED SPECTROSCOPIC CONSTANTS OF THE GROUND STATE ($^1\Sigma^+$) OF ScH	121
XXI.	SPECTROSCOPIC CONSTANTS AT THE GROUND STATE OF LuH AND LrH	124
XXII.	SPECTROSCOPIC CONSTANTS AND CHARGE DENSITIES FOR ScO	127
XXIII.	SPECTROSCOPIC CONSTANTS AT THE GROUND STATE OF ScF	131
XXIV.	MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScH, LuH AND LrH	134
XXV.	MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScO, LuO AND LrO	136
XXVI.	MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScF, LuF AND LrF	138

LIST OF TABLES (Continued)

TABLE		PAGE
XXVII.	MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScCl, LuCl AND LrCl.....	140
XXVIII.	PREVIOUS CALCULATIONS ON HEAVY ELEMENTS.....	159
XXIX.	POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MH	186
XXX.	POTENTIAL ENERGIES FROM THE RCI CALCULATIONS FOR MH....	187
XXXI.	POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MO	188
XXXII.	POTENTIAL ENERGIES FROM THE RCI CALCULATIONS FOR MO....	189
XXXIII.	POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MF	190
XXXIV.	POTENTIAL ENERGIES FROM THE RCI CALCULATIONS FOR MF....	191
XXXV.	POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MCl	192
XXXVI.	POTENTIAL ENERGIES FROM THE RCI CALCULATIONS FOR MCl...	193
XXXVII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScH	194
XXXVIII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScO	195
XXXIX.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScF	196
XL.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScCl	197
XLI.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuH	198
XLII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuO	199
XLIII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuF	200
XLIV.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuCl	201
XLV.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrH	202
XLVI.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrO	203
XLVII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrF	204
XLVIII.	CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrCl	205
XLIX.	ACRONYMS AND CORRESPONDING NAMES.....	206

CHAPTER I

INTRODUCTION

The history of transuranium elements began with the discovery in 1934 by E. Fermi, E. Amaldi, O. D'Agostino, F. Rasetti and E. Segrè that neutron irradiation of uranium led to a considerable number of radioactive substances.[1] The chemical investigation of these radioactive substances, however, resulted in the discovery of the fission process rather than the discovery of the transuranium elements. In their original work Fermi and his co-workers were led to assign the observed radioactivity to transuranium elements. In 1940, the discoveries of the first synthetic transuranium elements, neptunium (Z=93), by McMillan and Abelson[2] and and plutonium (Z=94) by Seaborg, McMillan, Kennedy and Wahl[3] were made. This was extremely important, not only from the standpoint of opening up the transuranium field, but these discoveries were also responsible for the break-through which eventually led to an understanding of the electronic structure of the heavy elements (beginning with thorium (Z=90)) and their place in the periodic system.[1,3-9]

Although some of the rare earth elements were discovered in nature almost 200 years ago, their chemistry has only been investigated in depth in the past 50 years. The interest in the first rare earth *f*-transition series has experienced a parallel growth with interest in the transuranium elements because of the possibility of analogous behavior between the two series of elements. Studies on the lanthanides and actinides can be divided into three categories. First,

the discovery of nuclear fission indicates a need for better understanding of the chemistry of the lanthanides and transuranium series. Second, the lanthanide elements have become increasingly important in industry and, of course, knowledge of chemistry of the elements thorium (Z=90), uranium (Z=92) and plutonium (Z=94) is important for the efficient use of their compounds as nuclear fuels.[4] Third, chemical investigations, particularly theoretical studies, are very important and desirable for the other actinide elements because of their relatively low availability and their relatively high radioactivity (the half lives and numbers of atoms available of the commonly produced isotopes for chemical studies of fermium (Z=100), mendelevium (Z=101), nobelium (Z=102) and lawrencium (Z=103) are shown in Table I).

TABLE I

HALF LIVES AND NUMBERS OF ATOMS AVAILABLE FOR THE ISOTOPES COMMONLY PRODUCED FOR CHEMICAL STUDIES OF Fm, Md, No and Lr[5]

Element	Half life	Average Atoms/Experiment
^{255}Fm	20.1 hours	10^{12}
^{256}Md	77 minutes	10^{6}
^{255}No	3.1 minutes	10^{3}
^{256}Lr	31 seconds	10

The work described in this dissertation concerns itself with a theoretical investigation of the relationship between the lanthanides and the heavier elements as well as the possibility of theoretically predicting the properties of the transactinide elements.

The Actinide Hypothesis

Before the discovery of the transuranium elements, the heaviest natural elements thorium (Z=90), protactinium (Z=91) and uranium (Z=92) were considered possible homologues of the transition elements. They were placed in the corresponding positions just below the sixth period "transition" elements-hafnium (Z=72), tantalum (Z=73) and tungsten (Z=74)-whose 5*d* shells are being filled.[6]

After the discovery of the transuranium elements, McMillan and Abelson[2] were able to show that neptunium (Z=93) resembles uranium (Z=92) in its chemical properties and bears no resemblance to rhenium (Z=75). Their interpretation of the experimental evidence was that there exists a new "rare earth" group of similar elements starting with uranium (Z=92). In 1942 Seaborg and Wahl performed their first tracer experiments on plutonium (Z=94) and neptunium (Z=93). They made a suggestion that this new rare earth series might begin earlier than uranium (Z=92) and that thorium (Z=90) or actinium (Z=89) might be the zeroth element in the series.[6]

Following the first tracer work on the transuranium elements, neptunium and plutonium were investigated extensively with substantial weighable quantities. Extensive investigation for the following evidence: chemical properties, absorption spectra in aqueous solution

and crystals, crystallographic structure data, magnetic susceptibly data and spectroscopic data on these heavy elements was performed.[6-9] All this information, especially the chemical evidence concerning americium and curium, seemed to lead to a self-consistent and unambiguous picture concerning the nature of this new rare earth series.

All this evidence led to a definite view that it is the 5*f* shell that is being filled in these heavy elements. The evidence seemed sufficient enough for Seaborg[6-9] to suggest that this rare-earth-like series begins with actinium (Z=89) in the same sense that the rare earth or "lanthanide" series begin with lanthanum (Z=57). Such an "actinide" series is suggested on this basis. In another words it is the "actinide hypothesis."

However, the actinide series differs from the lanthanide series in having more oxidation states above the III state as shown in Table II. The relative binding energy of the n*f* electrons compared to (n+1)*d* electrons increases with increasing atomic number and ionic charge but the increase in binding of the 5*f* electrons is not as large as that of the 4*f* electrons. This explains the greater tendency for higher oxidation states in the actinide elements.

Nevertheless, the salient point is that the characteristic oxidation state is the III state and the series is placed in the periodic table on this basis. The ground state electronic structure of the neutral gaseous atom of each element in the actinides compared to the lanthanides is shown in Table III. The similarity occurs in the filling in the *f*-shell of both series.

TABLE II

OXIDATION STATES OF LANTHANIDES[10] AND ACTINIDES[11] IN SOLUTION

(Very unstable oxidation states are denoted as (X);

very stable oxidation states are as **X**)

	2+	3+	4+		2+	3+	4+	5+	6+	7+
La		X		Ac		**X**				
Ce		X	X	Th			**X**			
Pr		X		Pa		X	X	**X**		
Nd		X		U		X	X	X	**X**	
Pm		X		Np		X	X	**X**	X	X
Sm	(X)	X		Pu		X	**X**	X	X	
Eu	X	X		Am	X		**X**	**X**	X	X
Gd		X		Cm		**X**	X			
Tb		X		Bk		**X**	X			
Dy		X		Cf	X	**X**				
Ho		X		Es	X	**X**				
Er		X		Fm	X	**X**				
Tm		X		Md	X	**X**				
Yb	(X)	X		No	**X**	X				
Lu		X		Lr		**X**				

TABLE III

ELECTRONIC STRUCTURE OF LANTHANIDES AND ACTINIDES[11]

(Lanthanides with a xenon core and actinides with a radon core)

Lanthanides		Actinides	
La	$5d^1\ 6s^2$	Ac	$6d^1\ 7s^2$
Ce	$4f^2\ 6s^2$	Th	$6d^2\ 7s^2$
Pr	$4f^3\ 6s^2$	Pa	$5f^2\ 6d\ 7s^2$
Nd	$4f^4\ 6s^2$	U	$5f^3\ 6d\ 7s^2$
Pm	$4f^5\ 6s^2$	Np	$5f^5\ 7s^2$
Sm	$4f^6\ 6s^2$	Pu	$5f^6\ 7s^2$
Eu	$4f^7\ 6s^2$	Am	$5f^7\ 7s^2$
Gd	$4f^7\ 5d\ 6s^2$	Cm	$5f^7\ 6d\ 7s^2$
Tb	$4f^9\ 6s^2$	Bk	$5f^8\ 6d\ 7s^2$
Dy	$4f^{10}\ 6s^2$	Cf	$5f^{10}\ 7s^2$
Ho	$4f^{11}\ 6s^2$	Es	$5f^{11}\ 7s^2$
Er	$4f^{12}\ 6s^2$	Fm	$5f^{12}\ 7s^2$
Tm	$4f^{13}\ 6s^2$	Md	$5f^{13}\ 7s^2$
Yb	$4f^{14}\ 6s^2$	No	$5f^{14}\ 7s^2$
Lu	$4f^{14}\ 5d\ 6s^2$	Lr**	$5f^{14}\ 6d\ 7s^2$
			or $5f^{14}\ 7p\ 7s^2$

**Lr is predicted to have either a $5f^{14}\ 6d\ 7s^2$ or a $5f^{14}\ 7p\ 7s^2$ electronic configuration.[12-15] The energy difference between the two possible ground states is no more than a few thousand wave numbers, which is slightly greater than the errors in the method of calculations. However, there appears to be no experimental method for resolving this question by direct experiment.

The recognition of the similarity in chemical behavior in the actinide and lanthanide elements has been an important contributing factor in the synthesis and isolation of the transcurium elements. Most of the chemical identification has been carried out by eluting the elements from columns of cation exchange resin. The pattern of the elution behavior from the resin bed of the lanthanide elements made it possible to predict with good accuracy the expected elution position for a new actinide element. This technique has constituted the most definitive chemical evidence in the discovery of the elements berkelium (Z=97) through mendelevium (Z=101)[10,16], while nobelium (Z=102) was identified by the use of a double-recoil technique.[17] Lawrencium (Z=103) has been the first actinide element to be identified through purely instrumental methods[17] because of the low yield and high radioactivity shown in Table I.

Effective Potentials

The chemical similarities within the individual groups of the periodic table arise because the valence electrons determine the chemical properties. The core electrons, being much more strongly bound to the atomic nuclei, are only slightly affected by the molecular environment and act predominantly to shield the nuclei and to provide an effective field in which the valence electrons move. The observed regularities simplify the interpretation of the chemical behavior and provide a framework for organizing and categorizing observations.

The theoretical study of the electronic structure and properties of molecules and solids is made simpler if the atomic core electrons

are considered invariant in different molecular environments. Since the complexity of *ab initio* calculations used to produce electronic wavefunctions (WFs) increases rapidly with the number of electrons, dramatic savings (especially for the heavier elements) can be realized if the core electrons are regarded as invariant so that only the valence electrons need to be considered explicitly.

Many theories and approximations have been advanced for reformulating the Schrödinger equation in terms of valence electrons only.[18] This is not an easy practical task, although formally one may write the essential equations rather trivially. The total WF is first written in terms of two parts, the core WF and the valence WF. Although the exact WF cannot be factored this way in general, certain approximate WF, e.g. the Hartree-Fock WF, may be. If the core WF is known, a valence-only equation may be written:

$$H_{val}\,\Phi_{val} = E_{val}\,\Phi_{val} \tag{1.1}$$

in which Φ_{val} is the valence WF, $E_{val} = E - E_{core}$ and H_{val} is given as

$$H_{val} = \sum_{i=1}^{n_v} \left(h_i + \sum_{j>i}^{n_v} \frac{1}{r_{ij}} \right) + U_{core} \tag{1.2}$$

where n_v is a number of valence electrons, U_{core} is the operator arising from the core-valence interaction part of the Hamiltonian. It is a nonlocal integral operator because of the exchange terms. The exact form of U_{core} depends on the form of the core WF.

A variational solution of Eqs. (1.1-1.2) requires that the valence WF be maintained orthogonal to the core WF and that the core-

valence interaction terms be evaluated. For a HF core, the orthogonality constraint is satisfied by requiring the valence WFs to be orthogonal to the core WFs. The coulomb and exchange terms can then be evaluated directly for a given set of WFs. This is the basis of the "frozen core" approximation. The computational savings realized from this method are, however, limited, since all of the core-valence two-electron integrals must still be evaluated and the orthogonality constraints must be explicitly included in the valence variational equations.

Much greater simplification and savings can be achieved if the core-valence orthogonality constraint and the nonlocal core-valence interaction term, U_{core}, are replaced by a single operator appearing in the valence Hamiltonian. This operator is formulated to prevent the collapse of the valence WF into the core region without explicitly imposing orthogonality, it also provides the correct core potential "seen" by the valence electrons. Such an operator is known as an effective potential (EP).

There are many methods available for generating EPs, and the most successful methods to date are based on HF and Dirac-Fock (DF) or Dirac-Hartree-Fock (DHF) calculations on atoms. A detailed discussion of many of the successful *ab initio* methods for generating EPs will be given in the following chapter. Although the theoretical framework may be less than rigorous, the practical conclusion based on ten years of experience is that valence-electron-only calculations employing properly formulated EPs can produce quantitative results that compare favorably well with all-electron calculations.[19,20]

The true utility of EPs is that they provide a method for producing useful and quantitative theoretical results for systems that are otherwise untreatable at this time. Since conventionally, molecular WFs are represented by a linear combination of atomic orbitals (LCAO) expansion, a substantial reduction in calculational time for solving the Schrödinger equation is realized because the basis sets used do not include functions that describe the atomic core orbitals. These reductions make calculations tractable on larger molecules particularly those containing heavier atoms.

The all-electron DF calculations on atoms of Desclaux and Kim[21] and Grant[22] show that relativistic effects are predominantly core effects. This is true because the core electrons spend most of their time near the nucleus, where effective velocities are so large as to require relativistic correction. The valence electrons are affected primarily indirectly through their interaction with the relativistic core. These findings indicated that the extension of the EP concept to include relativistic effects is very desirable. In recent years a number of methods have been developed for obtaining relativistic effective potentials (REPs) that are analogous to those for non-relativistic EPs. A discussion for some of these methods will be presented in the following chapter. While non-relativistic EPs are dependent on the orbital angular momentum (i.e. *l*-dependent), the REPs are dependent on the total (spin plus orbital) angular momentum (i.e. *j*-dependent). The *j*-dependence of REPs implies that they contain information on spin-orbit (SO) coupling. Methods for extracting an effective SO potential using a SO operator will also be discussed.

Nevertheless, it is possible to eliminate the j-dependence of the REPs by averaging the $j=l+1/2$ and $j=l-1/2$ components to produce an l-dependent averaged relativistic effective potential (AREP), which can be used just like the non-relativistic EPs in molecular calculations. This approach provides a relatively simple and practical method for introducing relativistic effects into molecular quantum chemistry.

REPs and AREPs are now being applied extensively in quantum calculations of molecules containing the heavy atoms, particularly transition metals, and compare well with the few available all-electron methods. Although agreement with all-electron calculations and experimental data is the ultimate test of these potentials, the known limitations and possible sources of error have not been serious enough to discourage their use, particularly for the calculations of potential energy curves and spectroscopic constants of ground and excited states. In the relativistic case, few comparisons have been made with all-electron DHF molecular calculations. However, these few results were encouraging enough for us to proceed with the work described here.

The idea of treating core electrons as a simple effective potential in which the valence electrons move is not new, Hellman[23,24] and Gombas[25] were the first to suggest replacing the interaction of the valence and core electrons in an atom with a pseudopotential in 1935. However, much of the earlier work was of a rather approximate nature. Since that time, solid-state physics, particularly the study of metallic binding, has been a driving force behind the EP method. Moreover, during the last ten years new more accurate methods for obtaining the potentials have been developed and there has been an

increasing interest in the use of EPs and REPs in molecular structure calculations.[19]

A big breakthrough occurred in 1959, when Phillips and Kleinman[26] suggested replacing the explicit core-valence orthogonality constraints by a modification of the valence Hamiltonian as they introduced a nonempirical approach to finding pseudopotentials. This potential was nonlocal, in the sense that each angular-momentum component of the valence pseudo-orbital about an atomic center felt a different potential (arising from different core states).

The first systematic development of EPs based on *ab initio* atomic all-electron calculations is probably that of Goddard *et al.* in 1972.[27] They follow the Phillips-Kleinman approach in expressing the pseudo-orbital as a linear combination of the valence function and core functions. The coefficients of the core functions are adjusted by fitting the smoothness and expandability condition of the pseudo-WF. The *ab initio* calculations upon which these EPs are based on are HF calculations, so that the radial equations for the WFs contain nonlocal exchange operators. This complicates the problem of finding a local effective potential to replace the core. One way of dealing with this problem is to use a practical representation for an EP basis set (power of r times Gaussians) which is satisfied by the pseudo-orbital.[27,28] This method of choosing pseudo-orbitals was first introduced into the the local-density-functional approach by Topiol *et al.*,[29] who dealt directly with the local numerical potential produced by inverting the Schrödinger equation. The above fitting criterion allowed them to ignore the r^{-2} divergence at small r occurring in the exact effective

potential (this arises from the r^{l+1} behavior of the WF) with minimum error.

In treating heavy atoms, relativistic effects should be included by solving the Dirac equation which is written as

$$H_D\psi = E\psi \tag{1.3}$$

where H_D is a single electron Dirac Hamiltonian,

$$H_D = c\alpha.\mathbf{p} + \beta mc^2 - \frac{z}{r} \tag{1.4}$$

One of the first attempts to extend the Phillips-Kleinman method to include relativistic effects into the *ab initio* core potentials was done by Lee, Ermler and Pitzer[30] in 1977 who reported calculations on the Xe and Au atoms. Since this pioneer work other researchers have developed other ways of generating REPs.[20,31]

It was soon found that any calculation using either EPs or REPs obtained employing the Phillips-Kleinman pseudo-orbital construction tends to underestimate the repulsive region of the potential energy curves. Examples are the work of Kahn *et al.*[32] on F_2, the work of Hay, Wadt and Kahn[33] on F_2 and Cl_2, and work on the heavier diatomic molecules by Ermler, Lee, Pitzer and Winter[34] and by Wadt, Hay and Kahn.[35] The bond lengths obtained were too short and dissociation energies obtained were too large.

The problem was shown to be due to the "orthogonality hole"[36] caused by too much charge in the core region. This problem is serious in the case of a self-consistent-field (SCF) calculation, since the

incorrect distribution of the valence charge between the valence and core regions will cause errors in the Coulomb potential. The problem of the "orthogonality hole" is not, however, a necessary consequence of replacing an all-electron potential by a valence pseudopotential, it is a consequence of the Phillips-Kleinman construction.

To correct this problem, the pseudo-WF (or orbital) used to construct an EP or REP for an atom needs to have two important properties: it should be nodeless and it should, when normalized, become identical to the true value WF beyond some core radius.

One corrective approach was introduced by Redondo *et al.*[37] who modified the Goddard method by partitioning the basis functions into two groups, one long range and one short range. The coefficients of the long-range basis functions are fixed at their values in the normalized valence WFs. Members of the short-range groups are added with coefficients varied to satisfy the required conditions of nodelessness, normalization, r^{l+1} behavior and smoothness of the resulting pseudo-orbital. The fitted potential is then generated from these WFs. This construction makes no explicit use of the core WFs (which are a particular linear combination of the short-range basis set). The pseudo-orbital converges smoothly to the valence orbital around a radius determined by the division of the basis set. This in principle provides additional flexibility in optimizing the pseudo-orbital.

An alternative approach for obtaining pseudo-orbitals, which gave even better REPs, was introduced by Christiansen, Lee and Pitzer.[38] They were able to show that a source of errors in the EPs was due to

improper partition of the valence and core space in the Phillips-Kleinman pseudo-orbital transformation. The critical feature of their work was that they chose the pseudo-orbital derived from the DHF atomic calculations to be identical to the valence HF valence orbital beyond some matching radius, and inside this radius the REP was expanded as a polynomial. A five-term polynomial with r^{l+1} as the leading power was chosen to give the correct normalization. Further, the first three derivatives of the pseudo-orbital were required to match the valence functions at the matching radius. The matched derivatives ensure continuous behavior of the effective potential. This construction does not guarantee a nodeless pseudo-orbital, but the choice of matching radius can be varied to achieve this goal.[38] This technique is the one used to produce the REPs in this work. The detailed procedure and equations will be given in the following chapter.

All the above constructions give EPs which diverge with repulsive r^{-2} behavior at small r. This is a consequence of the r^{l+1} behavior of the pseudo-orbital, which appears to be an arbitrary requirement. For pseudo-orbitals which are based on linear combinations of the valence (and possible core) orbitals, the alternative to relaxing this condition is a $-Z/r$ attractive singularity at small r, where Z is the nuclear charge.[28] In addition, the r^{l+1} requirement serves to minimize the core content of a Phillips-Kleinman-type pseudo-orbital,[29,39] and hence to minimize the orthogonality hole problem.

For the relativistic atom, each electron's orbital angular-momentum and spin must be coupled, so that different energies and WFs are found for the two possible values of the total angular-momentum

quantum number, $j=l+1/2$ and $j=l-1/2$. Two different effective potentials are thus needed for each value of l. It is however more convenient to take the weighted sum and difference of the potentials.[40] These j-averaged potentials have been shown to yield results which are similar to those obtained using a "scalar" version of the Dirac equation in which the SO term is removed.[41] The "differenced" effective potential is in fact a SO effective potential. It reduces to zero outside the core since the effective potentials for all j converge to the full potential. Unlike the true SO potential, which diverges as r^{-3} at small r,[42] the SO effective potential can be smooth and nonsingular in the core region. The effect of SO coupling is then included in the configuration interaction (CI) part of the calculation as discussed below.

A number of molecular calculations using REPs have been performed. Many of them[35,43-50] were obtained by procedures which add in the SO effect as a perturbative correction in the final step using a WF set up in a l-s coupling formalism as it would be for a non-relativistic calculation. The appropriate REPs for such calculation are the averaged REPs (AREPs), i.e. the weighted averaged REPs for $j=l+1/2$ and $j=l-1/2$. For the atomic calculations using the Pauli approximation, with the SO terms deleted, one obtains the approximate AREPs directly.[43] Standard CI techniques are used to obtain molecular potential curves for the 1-s states without SO coupling. SO coupling is finally introduced by a semiempirical method using experimental atomic spectral data.[48] Some results obtained by the semiempirical methods are probably quite accurate, but it is a very questionable

procedure when the orbitals contributing large SO terms are involved in bonding.

Another *ab initio* REP calculation procedure which includes the SO effect in the SCF process was developed on a single configuration basis by Lee, Ermler and Pitzer.[51] This approach was also extended to a multiconfiguration SCF (MCSCF) method by Christiansen and Pitzer[52,53] who used it in calculations on the TlH, Tl_2, and Tl_2^+ molecules. In this procedure the SCF computations are done directly in ω-ω coupling to allow the inclusion of the major effects of electron correlation and to obtain proper dissociation. The MCSCF calculation can include 10 spinor configurations. The results for TlH, Tl_2, and Tl_2^+ molecules appear to be reliable and accurate as far as can be expected from so few configurations. The bond distances are well determined, but the calculated dissociation energies are only at best semiquantitative. This approach was also found to be far from adequate for systems with large SO effects. Thus an approach which can accommodate a large number of configurations is more desirable. In addition, a desirable method should also be capable of extension to the treatment of several excited states.

An *ab initio* approach based on a recognition that an *ab initio* SO operator can be derived from differences in the REP for $j=l+1/2$ and $j=l-1/2$ was developed in 1981.[40] This method made it possible for Christiansen, Balasubramanian and Pitzer[54] to assemble a complete calculational program which begins with molecular orbitals (MOs) in *l-s* coupling and which includes electron correlation and SO coupling via a high-order CI step, i.e. the SO terms are introduced at the CI step on

an equal basis with the electron repulsion. In this method the REPs are averaged with respect to the spin at the SCF stage where relativistic effects such as mass-velocity correction, Darwin correction, etc., are included, but the SO interaction is not yet introduced. However, since the SO operator is obtained as the difference between the *l+1/2* and the *l-1/2* potential, the SO integrals over MOs are best introduced as one-electron integrals at the CI stage. This procedure has the advantage of introducing SO interaction variationally rather than through the conventional perturbative scheme. Further, this method allows for mixing of configurations which would not mix in the absence of SO interaction. It is the CI technique used in this work and will be described in some details in the later chapters. The method has been tested on a number of diatomic molecules[54-73] in the past few years.

The Proposed Study

As shown in appendix A, neptunium (Z=93), plutonium (Z=94), lawrencium (Z=103), elements 104 and element 106 are the only synthetic elements investigated theoretically. However, if only transuranium elements (Z=93-103) are considered, neptunium (Z=93), plutonium (Z=94) and lawrencium (Z=103) are the three elements for which the calculations have been performed.

Besides the local density functional approach, two other methods of calculations have been used to calculate two of these three transuranium elements. DF-one center expansion (DF-OCE) calculation on LrH[74] (as well as (104)H_4 and (106)H_6 compounds) and REP calculation on

PuF_6[75] where REPs for Pu are prepared via the *ab initio* technique are those two reported in the literature. However, the DF-OCE calculation is rather a crude approximation compared to the REP calculation.

The earlier discussion on the actinide hypothesis (p.3-7) shows that studies on the rare earth elements (lanthanides and actinides), especially the transuranium elements, are very important. The REP calculation method is employed in this work to perform a comprehensive investigation of ground state properties of the *f*-block elements. Complete calculations on selected metal elements in diatomic hydrides, oxides, fluorides and chlorides have been carried out.

Scandium (Z=21), lutetium (Z=71) and lawrencium (Z=103) elements, all with n*d* (n+1)s^2 ground state valence configuration ($6d^1$ $7s^2$ for lawrencium, $5d^1$ $6s^2$ for lutetium and $3d^1$ $4s^2$ for scandium), are the candidates in this work because of the present limitation in the programs employed. The programs are restricted to molecules with maximum *l*-quantum number in the valence of *I*=2. This implies that only full *f*-shell elements of the lanthanide and actinide series can be handled in the calculations by treating the *f*-electrons as core electrons.

The reliability of the results obtained are discussed in chapter V. Wherever possible comparisons with the previous results (experimental and theoretical) are also made.

Treating scandium, lutetium and lawrencium as 3-electron atoms

In this work, core electrons for all the elements, except hydrogen atom, are replaced by Gaussian AREPs or numerical REPs wherever appropriate. Analytical AREPs for scandium, oxygen, fluorine and chlorine atoms of Christiansen and co-workers[76,77] are adopted in this work. Numerical REPs for lutetium and lawrencium are generated via the *ab initio* technique as will be discussed in detail in chapter II.

According to the available AREPs for scandium of Pacios and Christiansen,[76] two types of AREPs are reported, one for $3s^2\ 3p^6\ 3d^1\ 4s^2$ in the valence (*spd*-AREP) and the other one for $3d^1\ 4s^2$ in the valence (*sd*-AREP). The *spd*-AREP potential is a result of treating scandium as an 11-electron atom and the *sd*-AREP is a result of treating scandium as a 3-electron atom.

If lutetium and lawrencium are treated like scandium in the first case they will become 25-electron atoms and *spdf*-AREP (or REP) will be needed as they possess 14-*f*-electrons in the valence basis. However, this case cannot be handled by the present computer programs due to the limitation that the highest *l*-quantum number of valence electrons must not exceed *l*=2 (*d*-orbital).

To be able to perform the proposed study under these circumstances, the *sd*-REPs for lutetium and lawrencium are the choices of REPs to be generated in this work. Then $5s^2\ 5p^6\ 4f^{14}$ in lutetium and $6s^2\ 6p^6\ 5f^{14}$ in lawrencium are considered as core electrons with the $5d^1\ 6s^2$ and $6d^1\ 7s^2$ parts considered as the valence shells for

lutetium and lawrencium, respectively. For the analogy and comparison purposes, $3d^1\ 4s^2$ are also considered valence for scandium. As a result, scandium, lutetium and lawrencium atoms are treated as 3-electron atoms where (A)REPs are used in the place of core electrons.

Moreover, only $2s^2\ 2p^4$, $2s^2\ 2p^5$ and $3s^2\ 3p^5$ are treated explicitly for oxygen, fluorine and chlorine atoms, respectively. AREPs[77] are used in the place of core electrons in these three cases.

CHAPTER II

THEORY OF *AB INITIO* EFFECTIVE POTENTIAL CALCULATIONS

This chapter will deal with development in theories of EPs and REPs and the quantum mechanics and techniques used in the calculations of REPs in this work. Some other methods of EP and REP construction will also be mentioned briefly. The molecular HF-SCF calculation employing EPs and relativistic (SO included) CI calculation will also be discussed.

Development of Effective Potentials

Background

After Hellman[23,24] and Gombas,[25] first, suggested replacing the interaction of the valence and core electrons in an atom with an EP, new methods for obtaining the potentials have been developed. The most successful work along these lines was that of Phillips and Kleinman[26] and known as the method of pseudopotential. They provided a sound theoretical basis for replacing the explicit core-valence orthogonality constraints by modifying of the valence Hamiltonian. The valence eigenfunctions of an effective one-electron Hamiltonian are given by

$$H_V\phi_V \equiv (H_V + U^{core})\,\phi_V = E_V\,\phi_V \qquad (2.1)$$

where ϕ_V satisfies the orthogonality constraint

$$\langle\phi_V\,|\phi_C\rangle = 0 \qquad (2.2)$$

and for all core-like solutions of the same Hamiltonian

$$H_V \phi_C = E_C \phi_C \tag{2.3}$$

in which ϕ_V is defined as

$$\phi_V = \lambda_V - \sum_C \langle \lambda_V | \phi_C \rangle \phi_C \tag{2.4}$$

Eq. (2.4) shows that for any λ_V, ϕ_C will be orthogonal to the core orbitals and Eq. (2.1) can be rewritten as

$$\left(h + U^{core} + U^{PK} \right) \lambda_V = E_V \lambda_V \tag{2.5}$$

where U^{PK} is a repulsive nonlocal potential defined by

$$U^{PK} \lambda = \sum_C \langle \phi_C | \lambda \rangle \left[E_V - E_C \right] \phi_C \tag{2.6}$$

Eq. (2.5) is satisfied by any function of the form

$$\lambda_V = a_V \phi_V + \sum_C a_C \phi_C \tag{2.7}$$

for arbitrary choices of the coefficients a_V and a_C. Cohen and Heine[78] and Austin *et al.*[79] have suggested several ways to determine these coefficients. These include making λ_V as smooth as possible so that it may be represented by a minimal number of plane waves in solid state calculations. U^{PK} is called the pseudopotential and λ_V is the pseudo-orbital. Note that U^{PK} is energy dependent as it depends on λ_V. Also U^{core} is nonlocal due to exchange operators introduced by the antisymmetrizer.

The one-electron Phillips-Kleinman method was later generalized by Weeks and Rice[80] to the cases where the ϕ_C are not eigenfunctions of H_V and those with many-valence electrons. The relevant equations are

$$(H_V + U^{GPK})X_V = E_V X_V \tag{2.8}$$

where

$$U^{GPK} = - H_V \boldsymbol{P} - \boldsymbol{P}H_V + \boldsymbol{P}H_V\boldsymbol{P} + E_V\boldsymbol{P} \tag{2.9}$$

and

$$\boldsymbol{P} = \sum_c |\phi_C\rangle\langle\phi_C| \tag{2.10}$$

where X_V is a many-electron valence pseudo-WF (that need not be orthogonal to the core), and U^{GPK} is the generalized Phillips-Kleinman pseudopotential and $\boldsymbol{P}$ is the projection operator defined by the requirement that it project from any function particylarly lies in the core space. The valence Hamiltonian H_V, contains the interactions among the valence electrons as well as the core-valence interactions. However, because of the complexity of this method, solving Eqs. (2.8-2.10) still obviates the advantages of using pseudopotentials in the calculations.

Model Potentials

From a mathematical point of view, a model method is just one of the two techniques (the other one is the *ab initio* method) in solving quantum mechanics. Model potential (MP) methods have been used as substitutes for the rigorous Phillips-Kleinman analysis.[80-92] MPs are effective potentials that replace both the pseudopotential and the

core-valence interaction terms in the valence Hamiltonian to give a one-electron valence equation of the form

$$(h + U_m)\phi_v = E_v\phi_v \tag{2.11}$$

The term MP is used because U_m is given a specific form with adjustable parameters that are determined by some criterion such as matching the known eigenvalue spectrum of an atom. Such empirical schemes are possible only for one- or two-valence electron atoms and are not extendable to the entire periodic table.

Several MP theories based on *ab initio* all-electron atomic calculations have been introduced.[93-100] The method that has received the most widespread use in molecular calculations is due to Bonifacic and Huzinaga.[93-96] In this theory, the valence Hamiltonian for a single valence electron is given by

$$h_i = -\frac{1}{2}\Delta_i^2 - \frac{(Z - n_C)}{r_i} - \sum_j A_j \frac{e^{-\alpha_j r_i 2}}{r_i} + \sum_c B_C |\phi_C\rangle\langle\phi_C| \tag{2.12}$$

The exponential term is a local potential, which replaces the core-valence coulomb and exchange potentials. The last term has its origin in the orthogonality-constrained variation of the valence orbital[86] and ensures that the optimum valence orbital will be orthogonal to all core orbitals. The screening of nuclear charge by the core electrons has been taken into account by absorbing n_C/r_i into the MP. This is the usual practice in effective potential methods. The parameters A_j, α_j and B_C are determined by any one of many methods. The B_C parameters can be related to the core orbital eigenvalues,[93,94,97] but are often

varied to produce the best fits to the valence orbitals and eigenvalues taken from atomic all-electron calculations.[101] System with many valence electrons are handled by taking the total valence Hamiltonian to be a sum of one-electron Hamiltonians (Eq. (2.12)) plus the r_{ij}^{-1} Coulombic repulsion terms for all valence electrons.

Since each valence orbital has overlap only with core orbitals of the same angular symmetry, the MP is inherently *l*-dependent by virtue of the core projection term. The exchange contribution to the core-valence interaction is also *l*-dependent, but the exponential term in Eq. (2.12) is usually assumed to be independent of *l*. It is interesting to note that in the limit of a complete variational solution, a MP of this type will produce valence orbitals that have all of the nodal structure needed to maintain orthogonality to the core orbitals. This could be a serious drawback in large molecular calculations where one wishes to restrict the size of the basis set as small as possible. On the other hand, the calculation of electronic properties that have significant contributions from the inner parts of the orbitals will be more reliable. Bonifacic and Huzinaga[94,95] have suggested a simplification that restricts the sum of core projectors in Eq. (2.12) to include only the outer core orbitals in heavy atoms so that the basis set for the inner shells may be removed. Wahlgren and co-worker[102-106] have discussed the dangers associated with restricted basis sets in these MP methods. Pettersson and Wahlgren[106] have proposed using a valence basis set that has been pre-orthogonalized to the core functions in order to reduce the dimension of the valence

variational equations. However, this method requires an extra four-index transformation of the two-electron integrals.

Recently, MP parameters and valence orbitals have been generated for the transition metal atoms from scandium (Z=21) to mercury (Z=80) in two separated sets: *sd*-MPs and *spd*-MPs.[107,108] The *sd*-MPs are the resulted potentials from treating only (n+1)*s* and n*d* explicitly in the valence while the *spd*-MPs are yielded from treating (n+1)*s* (n+1)*p* and n*d* explicitly.

Effective Core Potentials

In 1968 Goddard[109] introduced a new approach for generating EPs from the nonorthogonal, smooth and nodeless atomic orbitals produced by a Goddard's G1 (generalized SCF) method.[110-112] These potentials are local and simply pseudopotentials. They are known as G1 atomic effective potentials (GAEP).

In an independent particle theory, the orbital equation may be written as

$$(h + U)\phi_i \equiv \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{l(l+1)}{2r^2} + U\right)\phi_i = \varepsilon_i\phi_i \qquad (2.13)$$

where U is the nonlocal potential due to interactions with the other electrons in the system. If ϕ_i is nodeless, it is possible to define an equivalent equation

$$(h + U_i) = \varepsilon_i\phi_i \qquad (2.14)$$

where $U_i(r)$ is given by

$$U_i(r) = \varepsilon_i + \frac{Z}{r} - \frac{l(l+1)}{2r^2} + \frac{\nabla^2\phi_i(r)}{\phi_i(r)} \qquad (2.15)$$

GREP have been derived for a limited number of first row atoms and applied to some molecular calculations,[27,113-115] but their use has not been widespread.

Although the G1 method and GREP have not been widely used by workers outside Goddard's group, the form of Eq. (2.15) is very suggestive and has led to many advances in the determination of effective potentials for use in molecular calculations. Some advantages of effective potentials are:[31]

1). They are local by definition and therefore easy to use.

2). They depend on the angular momentum of the valence orbital (l-dependent).

3). They can be defined for any nodeless orbital ϕ_i with energies ε_i.

4). Since ϕ_i is nodeless, it represents the lowest energy solution of Eq. (2.14).

In 1974 Melius and Goddard[28] suggested that HF orbitals could be used in place of G1 orbitals to define the local effective potentials for atoms. Recalling the Phillips-Kleinman pseudo-orbitals, they proposed that a linear combination of core and valence orbitals (as in Eq. (2.7)) could be used to produce a nodeless pseudo-orbital that could be substituted, along with the valence HF eigenvalue, into Eq. (2.15). The linear coefficients in Eq. (2.7) were obtained by requiring the kinetic energy of the pseudo-orbital to be minimized as was proposed by Austin *et al.*[79], since the minimum kinetic energy

orbitals were found to be nodeless and similar to G1 orbitals for a single valence electron.

For a single valence electron, the potential obtained by inverting the HF equation for a nodeless pseudo-orbital corresponds to replacing the nonlocal core potential, U_C, and the pseudopotential of the Phillips-Kleinman equation, U^{PK}, with a local EP, U^{eff}, as shown below

$$(h + U_C + U^{PK})\lambda \equiv (h + U^{eff})\lambda = \varepsilon\lambda \qquad (2.16)$$

This is similar to the MP approach mentioned previously but the local potential is determined uniquely by Eq. (2.15). The problem is no longer to find an appropriate potential, but rather to find an appropriate way to specify the pseudo-orbital, λ_C. Since the interest goes into molecular structure calculations, the desirable characteristics of λ that have an impact on such calculations is listed in the following.[31]

1). Because the difficulty and costs of molecular calculations rise rapidly with the number of primitive basis functions used to expand the orbitals, λ should be as smooth as possible in the core region so that it may be represented by as few basis functions as possible.

2). Because molecular interactions are often proportional to the overlaps of the outer parts of the valence orbitals of the constituent atoms, λ should resemble the actual Hartree-Fock orbital as much as possible in that region.

3). Because localization of the potential "freezes" the exchange contributions that involve the valence orbital, the local potential is exact only for the pseudo-orbital that is used to generate it. To enhance the prospects for transferability of the atomic potential to the molecular environment, the atomic state used to obtain λ must not differ dramatically from the normal range of valences and ionization level encountered in molecular structure.

If the third property on the list above is enforced, one must derive the EPs from many-valence electron atomic WFs. A widely used method for accomplishing these properties was developed in 1976 by Kahn, Baybutt and Truhlar.[32] The equation for a valence orbital with angular momentum l is given as

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{l(l+1)}{2r^2} + U_{val} + U_{core}\right)\phi_i = \varepsilon_i\phi_i \qquad (2.17)$$

where U_{core} and U_{val} represent the Coulomb and exchange potentials due to the core electrons and other valence electrons, respectively. This equation is replaced by

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z_{eff}}{r} + \frac{l(l+1)}{2r^2} + U'_{val} + U_l^{eff}\right)\lambda_l = \varepsilon_l\lambda_l \qquad (2.18)$$

where λ_l is a pseudo-orbital constructed from the HF orbitals, and U_l^{eff} is the effective potential called an effective core potential (ECP). Z_{eff} is the effective nuclear charge equal to the nuclear

charge minus the number of core electrons, so that the shielding is included in U_l^{eff}. The prime on U'_{val} indicates that the valence potential is evaluated over pseudo-orbitals rather than the original valence orbitals. The ECP is obtained by inverting Eq. (2.18) as:

$$U_l^{eff} = \varepsilon_l + \frac{Z_{eff}}{r} - \frac{l(l+1)}{2r^2} + \frac{\left(\frac{1}{2}\nabla^2 - U'_{val}\right)\lambda_l}{\lambda_l} \qquad (2.19)$$

Each valence orbital with a given angular momentum generates a unique potential. If core orbitals of the same angular momentum exist, then the potential is generally repulsive since it must prevent collapse of the pseudo-orbital into the core region. If there are no core orbitals with the same angular momentum, the potential is attractive and primarily represents the unscreening of the nuclear charges as the valence electron penetrates the core region. The ECP also contains core-valence exchange interactions, but these are not large when compared to the Coulombic interactions for high l-values. Thus, the potentials for all angular momenta larger than the highest value in the core are found to be very similar. The total ECP for an atom can be written as

$$U^{eff} = \sum_{l=0}^{\infty} U_l^{eff} \sum_m |l,m\rangle\langle l,m| \qquad (2.20)$$

where the projectors $\sum_m |l,m\rangle\langle l,m|$ ensure that the l-dependent potentials operate only on the proper components of the valence WF. Since the potentials with l-values larger than the maximum found in the core are nearly identical, one may approximate the ECP by

$$U^{eff} = U_L^{eff} + \sum_{l=0}^{L} \left(U_l^{eff} - U_L^{eff} \right) \sum_m |l,m><l,m| \qquad (2.21)$$

where L is one more than the highest l found in the core. HF solutions from more than one atomic state may be needed to define the potentials for all l-values in Eq. (2.20).

The atomic orbitals and eigenvalues needed in the construction of the ECP are easily obtained from exact numerical Hartree-Fock WFs produced by codes such as the one developed by Froese-Fischer.[116] Several prescriptions exist for producing nodeless pseudo-orbitals from the all-electron orbitals. Kahn *et al.*[32] proposed taking a linear combination of core and valence orbitals Eq. (2.7) and then determining the linear coefficients by minimizing the kinetic energy subject to a constraint to eliminate any residual cusp behavior at the origin. This procedure produces smooth and nodeless valence pseudo-orbitals, but the normalization constraint forces the coefficient a_V in Eq. (2.7) to be less than unity. Thus, pseudo-orbitals defined in this way will not match the all-electron orbitals even outside the core region,[37] and the difference between U_{val} and U'_{val} can cause U_l^{eff} to extend improperly beyond the radius where core-valence interactions are expected to be small. Such behavior is shown in the comparison of l=1 potentials for oxygen atom with the 2*s*-2*p* valence interactions evaluated with a 2*s* pseudo-orbital generated by the method of Kahn *et al.*,[32] and with the exact Hartree-Fock 2*s* orbital. The long tail on the first potential is due to the $U_{val} - U'_{val}$ difference when the nodeless 2*s* orbital is used. The inaccuracies introduced into molecular calculations by the long-range tails have been observed by

Hay *et al.*,[33] who proposed smoothly truncating the tails in order to minimize the effects. Redondo *et al.*[37] suggested avoiding the problem either by not normalizing the pseudo-orbital (i.e. $a_v = 1.0$ in Eq. (2.7)), or by using a basis set expansion of the orbitals in which the coefficients of the outermost basis functions in the pseudo-orbital are restricted to be identical to those in the all-electron orbital.

Shape-Consistent Pseudo-Orbitals

A method for constructing the desirable pseudo-orbitals have been introduced by Christiansen, Lee and Pitzer.[38] This treatment forces the pseudo-orbitals to match precisely the Hartree-Fock orbitals in the valence region in which the pseudo-orbital is represented as

$$\lambda_{lj}(r) = \begin{pmatrix} F_{lj}(r) & \text{for} \quad r \leq r_m \\ \\ \phi_{lj}(r) & \text{for} \quad r \geq r_m \end{pmatrix}, \tag{2.22}$$

$$\langle \lambda_{lj} | \lambda_{lj} \rangle = 1 \tag{2.23}$$

where $F_{lj}(r)$ is defined as

$$F_{lj}(r) = \sum_{i=0}^{4} c_i \, r^{i+N} \tag{2.24}$$

r_m is a match radius, and $\phi_{lj}(r)$ is the numerical tabulated radial functions from the large component of the DHF valence-spinor.[30] $F_{lj}(r)$ is chosen to cancel the radial oscillations in the core region and thereby eliminate nodes but goes smoothly to zero in the valence region. In practice $F_{lj}(r)$ has been determined by matching a five term polynomial to $\phi_{lj}(r)$ at some radial point r_m. $F_{lj}(r)$ is then the

difference between the polynomial and $\phi_{lj}(r)$ for r values less than r_m, and it is equal to zero elsewhere. The polynomial coefficients c_i were determined by matching the amplitude and first three derivatives of λ_{lj} and ϕ_{lj} at r_m with the constraint that λ_{lj} is normalized. The match radius is made as small as possible, while satisfying the requirement that λ_{lj} have only one maximum and two inflection points. r_m is usually chosen to be the innermost point for which a "smooth" function could be obtained. In addition, Krauss and Stevens[31] have found the optimum match radius to be consistently near the outermost maximum of the all-electron orbital, and suggested that very little is lost by fixing it at the maximum. The lead power in the polynomial was typically chosen to be l+2.

The important feature is that for large values of r, $\lambda_{lj}(r)$ and $\phi_{lj}(r)$ are identical or in another word the resulting pseudo-orbital is identical to the Hartree-Fock orbital in the valence region. Such pseudo-orbitals (or spinors), originally proposed by Durand and Barthelat[117] for use in a MP procedure, are sometimes referred to as "shape-conserving," "norm-conserving," or "shape-consistent" pseudo-orbitals.

The comparison between the pseudo-orbitals for the chlorine atom produced by the shape-consistent method of Christiansen, Lee and Pitzer[38] and the one from the Phillips-Kleinman method has been made by Balasubramanian.[20] The result is the maximum of the Phillips-Kleinman orbital is at smaller radius than that of the all-electron orbital or the orbital obtained by Christiansen, Lee and Pitzer's method. The EP,

U_v^{EP}, is obtained by requiring that it reproduce the pseudo-orbitals, λ_V, and the true eigenvalue, ε_V, of the Hartree-Fock orbital.

Rappé *et al.*[118] have also proposed a procedure whereby the pseudo-orbital is constructed with a basis set expansion that is optimized to reproduce the long-range part of the HF orbital while directly minimizing the valence interaction difference. Although this could produce orbitals that are not necessarily smooth, they are guaranteed to be fit exactly by the chosen basis set. Potentials generated by this technique have been called "shape and Hamiltonian consistent." Still another shape-consistent method has been developed by Durand, Barthelat and co-workers,[118,119] which also involves a basis set expansion of the pseudo-orbital, but minimizes the deviation from the HF orbital outside some match radius.

Other Methods for Effective Potential Construction

There are alternatives to the use of Eq. (2.19) for generating the effective potentials. Melius *et al.*[120] suggested determining a potential by minimizing

$$S = \sum_{\mu} \left(\langle \phi_\mu | h + U_l^{eff} + U_{val}' - \varepsilon_l | \lambda_l \rangle \right)^2 \qquad (2.25)$$

where $[\phi_\mu]$ is a suitably chosen set of basis functions. Reasonably compact expansions of U_l^{eff} have been achieved in this way.[37,121] Barthelat *et al.*[119] have proposed determining the effective potential by minimizing

$$\| O \| = \left(\langle \lambda_l | O^2 | \lambda_l \rangle \right)^{1/2} \qquad (2.26)$$

The operator O is defined by

$$O = \varepsilon_l' |\lambda_l'\rangle\langle\lambda_l'| - \varepsilon_l |\lambda_l\rangle\langle\lambda_l| \qquad (2.27)$$

where ε_l and λ_l are the "exact" eigenvalue and pseudo-orbital respectively. The ε_l' and λ_l' are the eigenvalue and pseudo-orbital obtaining by solving

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z_{eff}}{r} + \frac{l(l+1)}{2r^2} + U_{val}' + U^{eff} \right) \lambda_l' = \varepsilon_l' \lambda_l' \qquad (2.28)$$

The methods discussed above for generating ECPs are based on all-electron Hartree-Fock calculations. As will be seen in the following section that they are easily extended to incorporate relativistic effects.

Relativistic Effective Potentials from Atomic Dirac-Hartree-Fock Calculations

The REP is obtained from the atomic DHF calculations using a method that is essentially a relativistic modification of the ECP method developed by Goddard[109] and Kahn *et al.*[32] and their co-workers for the non-relativistic case as discussed in the previous section.

Dirac-Hartree-Fock Atomic Calculation

In order to take relativistic effects into account properly one should start by solving the atomic Dirac equation. In practice a DHF computer code developed by Desclaux[122] is employed as a starting

calculation whose details are described in chapter III. The relativistic corrections are made by assuming that the velocity of the electron is always small with respect to the velocity of light. The time-independent Dirac equation for one electron is written as

$$h_D\Psi = E\Psi \tag{2.29}$$

where h_D is given by

$$h_D = c\alpha.\mathbf{p} + \beta mc^2 - \frac{z}{r} \tag{2.30}$$

in which $\mathbf{p}$ is the momentum operator, $ih\nabla$, and

$$\alpha.\mathbf{p} = \alpha_x.p_x + \alpha_y.p_y + \alpha_z.p_z \tag{2.31}$$

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \qquad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix},$$

$$\alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix},$$

m is the particle rest mass, $c = 1/\alpha$ is the velocity of light, α is the fine-structure constant.

The α and β in the Dirac equation may also be expressed in a two-component form of the Pauli spin matrices as

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

where $\sigma = (\sigma_x, \sigma_y, \sigma_z)$, and

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

in which I is a 2*2 identity matrix

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The Hamiltonian in Eq. (2.30), however, is not adequate for the relativistic system involving more-than-one-electron. For a many-electron atom the relativistic DHF Hamiltonian is given by

$$H^{rel} = \sum_i h_D(i) + \sum_{i<j} \left(\frac{1}{r_{ij}} + H_{Br}(i,j) \right) \tag{2.32}$$

in which $1/r_{ij}$ is the Coulomb repulsion and h_D(i), the one-electron Dirac Hamiltonian, is given by

$$h_D(i) = c.\alpha_i.\mathbf{p}_i + m\beta_i c^2 - \frac{z}{r_i} \tag{2.33}$$

$H_{Br}(i,j)$, the Breit correction, arises from the magnetic interaction between two electrons. The Breit operator, which partially takes into account the relativistic interaction between the electrons, is of the form

$$H_{Br} = - \sum_{i<j} \frac{1}{r_{ij}} \left(\alpha_i \cdot \alpha_j + \frac{(\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right) \tag{2.34}$$

where α_i and α_j are Dirac matrices and r_{12} is the distance between the electrons 1 and 2. The eigenfunction of H_{Br} is thus a 16-component spinor, since each electron has a four-component spinor function. This correction is of the order α^2 (where $\alpha = 1/137.036$ is the fine structure constant). This contribution is normally introduced as a first-order perturbation to the Dirac Hamiltonian after having determined the radial WFs by omitting the $H_{Br}(i,j)$ terms in Eq. (2.32). Inclusion of the Breit interaction in the Dirac Hamiltonian, however, leads to results that are not consistent with the laws of quantum electrodynamics since the Breit Hamiltonian is not Lorentz-invariant.[123] In addition, the effects of the Breit interaction on chemical properties have not yet been studied in full detail. However, a semiempirical scaling method which corrects for two-electron screening of the valence spin-orbit by the core was developed by Steven and Krauss.[124,125] They showed that the total Breit corrections to the spin-orbit splitting is approximately 15% in the first row and 5% in the second row. Although this correction is of significant importance in calculating the properties of core electrons, it appears to be very small in the valence region. Thus $H_{Br}(i,j)$ is ignored from the relativistic Hamiltonian in Eq. (2.32) and will be introduced as a first-order perturbation to energy after self-consistency in the DHF calculation is achieved.

The relativistic Hamiltonian used in the Desclaux DHF computer program for a many-electron atom then becomes

$$H^{rel} = \sum_i h_D(i) + \sum_{i<j} \frac{1}{r_{ij}} \qquad (2.35)$$

The eigenfunctions of the Dirac Hamiltonian are four-component spinors and are expressed as

$$\psi_{nkm}(r,\theta,\phi) = \frac{1}{r}\begin{pmatrix} P_{nk}(r) & \chi_{km}(\theta,\phi) \\ iQ_{nk}(r) & \chi_{-km}(\theta,\phi) \end{pmatrix} \qquad (2.36)$$

where

$$\chi_{km}(\theta,\phi) = \sum_{\sigma=\pm 1/2} C(\lambda\tfrac{1}{2}j;m-\sigma,\sigma)\ Y_{\lambda}^{m-\sigma}(\theta,\phi)\ \phi_{1/2}^{\sigma} \qquad (2.37)$$

$Y_{\lambda}^{m-\sigma}$ is a spherical harmonic. The Pauli spinors are

$$\phi_{1/2}^{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \phi_{1/2}^{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$C(\lambda\frac{1}{2}j;m-\sigma,\sigma)$ are the Clebsch-Gordan coefficients. Finally, k and λ are the relativistic quantum numbers which are defined as

$$k = j + \frac{1}{2}$$
$$\lambda = k \qquad \text{if} \qquad j = l - \frac{1}{2}$$

or

$$k = -(j - \frac{1}{2})$$
$$\lambda = -(k + 1) \qquad \text{if} \qquad j = l + \frac{1}{2}$$

The Q_{nk}'s are known as the small components and P_{nk}'s are the large components. They satisfy the following differential equations for a central force field, $V(r)$,[30]:

$$\frac{dP_{nk}}{dr} + k\frac{P_{nk}}{r} - \left(\frac{2}{\alpha} + \alpha\left(V(r) - \varepsilon_{nk}\right)\right) Q_{nk} = 0 \qquad (2.38)$$

$$\frac{dQ_{nk}}{dr} - k\frac{Q_{nk}}{r} + \alpha\left(V(r) - \varepsilon_{nk}\right) P_{nk} = 0 \qquad (2.39)$$

In addition, if the small components Q_{nk} are eliminated, the non-relativistic limit is reached and Eqs. (2.38-2.39) reduce to the familiar Schrödinger equation as shown by Grant.[22]

To construct the DF equations it is assumed that WFs for an atom having N electrons may be expressed as an antisymmetrized product of four-component Dirac spinors shown in Eq. (2.36). For cases where a single antisymmetrized product is an eigenfunction of the total angular momentum operator, the N-electron atomic WF may be written as

$$\Psi^R = A\left((\psi_1^C\ \psi_2^C \ldots \psi_m^C)(\psi_1^V\ \psi_2^V \ldots \psi_n^V)\right) \qquad (2.40)$$

where A is an antisymmetrizer, m is the number of core electrons, and n is the number of valence electrons. The total energy is then given as

$$E_T^R = \langle \psi^R | H^{rel} | \psi^R \rangle = E_T^R + E_V^R + E_{CV}^R \qquad (2.41)$$

which is divided into core, valence and core-valence interaction energies. The last two terms can be combined using a modified Hamiltonian and the WF corresponding to the valence electrons

$$E_V + E_{CV} = \langle \psi_V^R | H_V^{rel} | \psi_V^R \rangle \qquad (2.42)$$

where

$$H_v^{rel} = \sum_v \left(h_D(v) + \sum_v \left(J_C(v) - K_C(v) \right) \right) + \sum_{v>v'} r_{vv'}^{-1}, \qquad (2.43)$$

in which $J_C(v)$ and $K_C(v)$ are coulomb and exchange operators. H_v^{rel} includes the original Dirac one-electron Hamiltonian for the valence electrons plus additional terms that represent the electrostatic effect of the core on the valence orbital.

Relativistic Effects On Valence Electrons

In a four-component WF, the magnitude of the small components is a measure of the relativistic effects in these systems, however its contribution is relatively significant near the nucleus and decreases rapidly as the radial distance increases. The electron densities represented by small components are negligible compared to those represented by large components for valence electrons. It has been shown by Lee[126] that the electron densities from the small components in the valence electrons is only 0.03% in a uranium atom.

The negligible effect of these small components in the valence region were also demonstrated by Lee, Ermler and Pitzer[30] in the comparison of relativistic and non-relativistic radial solutions for the 6*s* orbital of Pb and by Schwarz[127] on the properties of molecules containing heavy elements. The valence electrons appear to be essentially non-relativistic in the valence region. This evidence suggests that it is reasonable to assume that small components can be neglected in calculations that emphasize the description of valence electrons. Therefore, the relativistic core WFs remain a four-component property while the valence WFs contain only the large

components. As a result, treating the valence electrons non-relativistically, but in a field of an REP derived from a DHF calculation for the atom, may be a reasonable approximation.

Relativistic Effective Potentials

The shape-consistent algorithm of Christiansen *et al.*[38] is employed to define nodeless pseudo-spinors. The wave equation for one valence electron may be written as

$$(h_D + U^{core})\ \lambda_v^R = \varepsilon_v \lambda_v^R \tag{2.44}$$

U^{core} is the REP in the form of a 4*4 matrix that operates on the four-components pseudo-spinors λ_v^R .

The REP U^{core} may be expanded in the angular factors of Eq. (2.36) and used to construct the DF equations in terms of the radial pseudo-WF

$$\frac{d}{dr}\begin{pmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{pmatrix} = \begin{pmatrix} \frac{k_v}{r} & \left(\frac{2}{\alpha}\right) + \alpha\left(\varepsilon_v - U_v^Q(r)\right) \\ -\alpha\left(\varepsilon_v - U_v^P(r)\right) & \frac{k_v}{r} \end{pmatrix} \begin{pmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{pmatrix} , \tag{2.45}$$

where $U_v^P(r)$ and $U_v^Q(r)$ are large and small radial components of the REPs. In principle $U_v^P(r)$ and $U_v^Q(r)$ may be extracted using any pseudo-spinor having components P_v^{ps} and Q_v^{ps} where such REPs would be continuous at points corresponding to nodes in P_v^{ps}. This particular

problem is removed if nodeless pseudo-spinors are used. However, nodes cannot be rigorously removed simultaneously from the large and small components.

The procedure of the construction of REPs developed by Lee, Ermler and Pitzer[30] based on the non-relativistic EP construction by Kahn and Goddard[113] assumes that the small components can be negligible in the valence region as discussed earlier. In this method the relativistic WFs contain only large components. The appropriate one-electron radial equation becomes

$$\left(h_V(r) + U_V^{REP}(r)\right) P_V^{PS} = \varepsilon_V P_V^{PS} \qquad (2.46)$$

where h_V is the non-relativistic Schrödinger Hamiltonian for the valence

electrons. The $U_V^{REP}(r)$ term in Eq. (2.46) contains all one-electron relativistic effects of the atom being considered. This approximation appears to be reasonable since the most pronounced relativistic effects are present near the nucleus.

The wave equation for the single-electron case is written as

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U_V^{REP}(r)\right) P_V^{PS} = \varepsilon_V P_V^{PS} \qquad (2.47)$$

where Z is the atomic number. The effective potential $U_V^{REP}(r)$ is obtained by requiring that it reproduced the pseudo-spinor P_V^{PS} and the true eigenvalue of the DHF orbital. The local effective potential is then given by

$$U_v^{REP}(r) = \frac{\left(\varepsilon_v + \frac{1}{2}\nabla^2 + \frac{Z}{r}\right)P_v^{ps}}{P_v^{ps}}, \qquad (2.48)$$

In the case of more than one electron in the valence region, the wave equation becomes

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z_v}{r} + U_{lj}^{REP}(r) + W_{lj}\right)\lambda_{lj} = \varepsilon_{lj}\,\lambda_{lj} \qquad (2.49)$$

and

$$U_{lj}^{REP} = \frac{\left(-\frac{1}{2}\nabla^2 + \frac{Z_v}{r} - W_{lj} + \varepsilon_{lj}\right)\lambda_{lj}}{\lambda_{lj}} \qquad (2.50)$$

where W_{lj} is the two-electron integrals involving pseudo-spinor λ_{lj} and all the remaining pseudo-spinors. It is clear from Eq. (2.50) that a different REP arises for each pseudo-spinor. The complete REP is conveniently expanded in terms of products of radial functions and angular momentum projection operators as:

$$U^{REP} = \sum_{l=0}^{\infty} \sum_{j=|l-1/2|}^{l+1/2} \sum_{lm=-j}^{j} U_{lj}^{REP}(r)\ |l,j,m><l,j,m|\ , \qquad (2.51)$$

where the projection operator $|l,j,m><l,j,m|$ is comprised of the two-component angular functions of Eq. (2.36) that are the eigenfunctions of the Dirac Hamiltonian.

The expression for the relativistic effective potentials involves an infinite sum over l. This requires calculations of the radial potentials for all the excited states of the atom, which is impractical. However, the radial functions stop to change

significantly after l and j numbers exceed those of electrons in the core where l is called l_{max}. Consequently, it is a good approximation to stop at maximum l and j values denoted by L and J, respectively. The modified relativistic effective potential can be written as

$$U^{REP} = U^{REP}_{LJ}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^{j} \left(U^{REP}_{lj}(r) - U^{REP}_{LJ}(r) \right) |l,j,m><l,j,m|, \tag{2.52}$$

where L is suggested to be at least one higher than the maximum l value in the core (l_{max}), as $L = l_{max} + 1$. Thus the desirable minimal values of L for Sc, Lu and Lr are 2, 4 and 4, respectively.

While U^{REP} in Eq. (2.52) are spin-differenced REPs in the numerical form, weighted-averaged REPs (AREP) with respect to spin is defined as

$$U^{AREP} = U^{AREP}_{L}(r) + \sum_{l=0}^{L-1} \sum_{m=-l}^{l} \left(U^{AREP}_{l}(r) - U^{AREP}_{L}(r) \right) |l,m><l,m|, \tag{2.53}$$

where

$$U^{AREP}_{l}(r) = \frac{1}{(2l+1)} \left(l U_{(l,l-1/2)}^{REP}(r) + (l+1) U_{(l,l+1/2)}^{REP}(r) \right) \tag{2.54}$$

These potentials resemble non-relativistic effective potentials. The AREP has the advantage that it may be used in standard molecular calculations that are based on Λ-S coupling. The relativistic effects are included in the AREP from the Dirac Hamiltonian, except for the SO coupling. This form of AREP is the same as that presented by Kahn *et al.*[32] which is based on the relativistic treatment of Cowan and

Griffin.[128] The Hamiltonian employed by Cowan and Griffin[128] is essentially the Pauli approximation to the Dirac Hamiltonian with the omission of the SO term.

Hafner and Schwarz[129] and Ermler *et al.*[40] have suggested that the spin-orbit operator can be obtained as the difference of different j values but identical l values. The resulting spin-orbit operator is simply the difference of the l+1/2 and l-1/2 relativistic effective potentials as shown below.

$$U^{SO} = \sum_{l=1}^{L} \Delta U_l^{REP}(r) * \left[\frac{1}{(2l+1)} \sum_{M=-l-1/2}^{l+1/2} |l, l+\tfrac{1}{2}, m\rangle \langle l, l+\tfrac{1}{2}, m| - \frac{l+1}{2l+1} \sum_{m=-l+1/2}^{l-1/2} |l, l-\tfrac{1}{2}, m\rangle \langle l, l-\tfrac{1}{2}, m| \right] \quad (2.555)$$

where

$$\Delta U_l^{REP}(r) = U_{(l,l+1/2)}^{REP}(r) - U_{(l,l-1/2)}^{REP}(r) \quad (2.56)$$

Therefore, the total relativistic potential is

$$U^{REP} = U^{AREP} + U^{SO} \quad (2.57)$$

Since this spin-orbit operator is derived from relativistic *ab initio* potentials, it is also an *ab initio* operator.

The $U_{lj}^{REP}(r)$, $U_l^{AREP}(r)$ and $\Delta U_l^{REP}(r)$ in the equation of H^{SO} are derived in the form of numerical functions consistent with the large components of Dirac spinors as calculated using the DF program of

Desclaux. These operators have been used in their numerical form in calculations of diatomic systems where basis sets of Slater-type functions (STFs) are employed.[44,45,51,54] Moreover, the EPs can be presented as the expansions of exponential or Gaussian functions.[30,32,34] The general form of the M term-expansions is

$$U_l^{AREP}(r) = r^{-2} \sum_{i=1}^{M} C_{li}\, r^{nli} exp\ (-\zeta_{li} r^x) \qquad (2.58)$$

where x=1 for exponential and x=2 for Gaussian functions and C_{li}, n_{li} and ζ_{li} are chosen to obtain the best non-linear least squares fit for the numerical potentials. The optimum values of C_{li} and ζ_{li} are the results. The U_L^{AREP} are fitted directly while the U_l^{AREP} $(l<L)$ potentials are first modified by subtracting off the "L" function

$$U_{l-L}^{AREP}(r) = U_l^{AREP}(r) - U_L^{AREP}(r) \qquad (2.59)$$

and then fitted. The exponents determined in Eq. (2.58) are then used to fit the SO operators in the form

$$U_l^{SO} = \frac{l}{2l+1} \Delta U_l^{REP}(r) \qquad (2.60)$$

These Gaussian analytical functions for the *ab initio* AREPs and spin-orbit operators for Li through Ar[77] and K through Kr[76] have been generated via the shape-consistent method.[38] However, the numerical REPs derived from the numerical DHF-WFs have also been employed in a number of quantum calculations with considerable success. Other methods of generating relativistic effective potentials will be mentioned briefly.

Other Methods for Relativistic Effective Potential Construction

The Pauli Hamiltonian without the spin-orbit operator have been employed by Hay, Wadt and co-workers[43,48,129-133] to derive for REPs. Since the SO interaction is not included in their effective potentials, these potentials are analogous to spin-averaged relativistic potentials. However, the results of the Hay-Wadt REP compare reasonably well with the AREP derived from the DHF calculations. Although these potentials do not provide an *ab initio* SO operator, one can introduce this operator variationally either in a MCSCF or in a CI scheme. In another words, the SO interaction can be included in the final step as a perturbation using the semiempirical method.

Schwarz and co-workers[134-136] have developed a relativistic MP method. In this method the REP is expressed as

$$V_{rel}^{eff} = V_{rel} + \sum_{l(,j,m_j)}^{core} |l,j,m_j\rangle\, V_{lj}(r)\, \langle l,j,m_j| \quad , \tag{2.61}$$

where

$$V_{rel}(r) = -\frac{Z_{eff} + A\, exp\,(\alpha r)}{r}, \tag{2.62}$$

$$V_{lj}(r) = B_{lj}\, exp\,(-\beta_{lj} r) \quad , \tag{2.63}$$

where Z_{eff} is the effective charge of the atomic core. The parameters α, β_{lj}, A and B_{lj} were adjusted until the effective Hamiltonian reproduces the valence-electron spectrum of the alkalai-like systems. The resulting effective potentials are spin-dependent so that they

include SO interaction. Schwarz and co-workers[136] have developed a complex two and four-index transformation over two-component spinors which enable them to introduce these potentials in MCSCF or CI calculations. They have also applied the relativistic MP method to a number of molecules containing heavy atoms.[134,137-140] More recently, Mark, Marian and Schwarz[141] have considered the use of relativistic Dirac-Breit approach to estimate the fine structure splitting in F_2 and F_2^+. Also, Schwarz and Chu[142] have calculated relativistic contributions to ionization energies and bond lengths using both semiempirical and *ab initio* DF calculations. Esser[143] has recently developed a relativistic multireference configuration interaction method for many electron WFs and has applied to some heavy atoms such as Pb and Hg.

Relativistic Effective Potentials in Molecular Hartree-Fock Calculations

In both atomic and molecular REP-SCF calculations, the assumption is made that the valence electrons can be described non-relativistically in terms of only the large components of the atomic orbitals expressed in terms of STF expansion. This approximation thus allows the use of molecular programs in Λ-S coupling which, as a result, requires the deletion of SO coupling from the REPs. To follow this approach, two REPs for a given nonzero *l*-quantum number, i.e., for $p_{1/2}$ and $p_{3/2}$ or $d_{3/2}$ and $d_{5/2}$, etc. are thus weighted with respect to spin to obtained an AREP.

The atomic HF-SCF calculation for valence electrons with REP is required to test the REPs generated in this work. As a result, STF exponents are obtained for valence electrons. In this work the double zeta STF exponents are employed. The Hamiltonian for the n_V valence electrons in the atomic HF calculation is written as

$$H = \sum_{i=1}^{n_V} h_i + \sum_{i>j}^{n_V} \frac{1}{r_{ij}} \tag{2.64}$$

where r_{ij} is the distance between electron i and j,

$$h_i = -\frac{1}{2}\nabla_i^2 - \frac{Z_V}{r_i}\left(U^{REP}(r) - \frac{Z_V}{r_i}\right) \tag{2.65}$$

in which Z_V is number of valence electrons and $U^{REP}(r)$ is defined as in Eq. (2.52). The eigenfunctions of the Hamiltonian in Eq. (2.64) are the antisymmetrized products of the large components $(1/r)P_{nk}(r),\chi_{km}(\theta,\phi)$ of the atomic orbitals ψ_{nkm} shown in Eq. (2.36). The radial functions are represented in the expansions as follows:

$$\frac{1}{r}P_{nk}(r) = \sum_{p=1}^{B} C_{nkp}R_{kp}(r) \tag{2.66}$$

where $R_{kp}(r)$ are the STFs.

In the molecular calculation, the REP-SCF calculation is first performed on a ground state configuration of diatomic molecules. The STF basis sets whose radial functions are expanded in two-component relativistic spinors are employed. AREPs/REPs are used in the place of core electrons. The HF Hamiltonian is the same as that in Eq. (2.64)

where n_V and r_{ij} have the same meanings as described previously but h_i is defined as

$$h_i = -\frac{1}{2}\nabla_i^2 + \sum_{\alpha=1}^{N}\left(-\frac{Z_\alpha}{r_{\alpha i}} + U_\alpha^{REP}\right) \qquad (2.67)$$

where Z_α is the nuclear charge of nucleus α and N is the number of nuclei. U_α^{REP} can be approximated by

$$U_\alpha^{REP} = U_{LJ}^{REP}(r_{\alpha i}) + \sum_{l=0}^{L-1}\sum_{j=|l-1/2|}^{l+1/2}\sum_{m=-j}^{j}\left(U_{lj}^{EP}(r_{\alpha i}) - U_{LJ}^{REP}(r_{\alpha i})\right) |l,j,m\rangle_\alpha\langle l,j,m|_\alpha \qquad (2.68)$$

where the projection operators are written as

$$|l,j,m\rangle\langle l,j,m| = \left(\sum_{\sigma=\pm 1/2} C(l\tfrac{1}{2}j;\ m-\sigma,\sigma)\ Y_\lambda^{m-\sigma}(\theta,\phi)\ \phi_{1/2}^{\sigma}\right) * \left(\sum_{\sigma=\pm 1/2} C(l\tfrac{1}{2}j;\ m-\sigma,\sigma)\ Y_\lambda^{m-\sigma}(\theta,\phi)\ \phi_{1/2}^{\sigma}\right) \qquad (2.69)$$

with the notation the same as discussed previously. If N=1 in Eq. (2.67) this form reduces to the atomic case. However, only N=2 is used in the molecular calculation in this work. In the actual calculation, all the one- and two-electron integrals and integrals over angular projection operators of the above Hamiltonian with two components basis

function are calculated as linear combinations of appropriate non-relativistic integrals.

This calculation is perform in this fashion simply because the SO coupling and the correlation will be taken care of in the CI step which employs the HF MOs in the basis set. In another words, the molecular HF-SCF calculation is an intermediate step to prepare the HF-MOs for the CI calculation.

Configuration Interaction

The correlation energy (E_{corr}) is defined as the difference between the exact energy and the HF energy,

$$E_{corr} = \varepsilon_0 - E_0 \tag{2.70}$$

Out of many methods available, the method of CI is chosen to obtain the correlation energy. The CI method employed in the present work also includes the SO coupling. However, it can be changed to a non-relativistic CI by turning off the SO operator. Relativistic CI method allows more configurations to mix than what is possible without SO coupling. The configurations employed are the ω-ω coupling MO configurations in the relativistic CI calculations or the Λ-S coupling MO configurations in the non-relativistic limit.

Because the HF energy is an upper bound to the exact energy, the correlation energy in a non-approximate calculation must be negative. The CI approach is conceptually (but not computationally) quite simple. The basic idea is to diagonalize the N-electron Hamiltonian in a basis of N-electron functions (Slater determinants). In other words, the

exact WF is represented by a linear combination of N-electron trial functions where the linear variational method is used to obtain the mixing coefficients.

In principle, the mechanism of CI provides an exact solution of the many-electron problem. In practice, however, one can only handle a finite set of N-electron trial functions. Consequently, CI provides only upper bounds to the exact energies. Unfortunately, even for small molecules and moderately sized basis sets, the number of N-electron determinants rapidly becomes enormous and one must truncate the trial function some way. A form of truncated trial function contains determinants which differ from ψ_0 by at-most two spin orbitals is employed in this work. Such a calculation is referred to as singly and doubly excited CI (SDCI).

Suppose the determinant is formed from $|\psi_0>$, then one can form a large number of other N -electron determinants from all possible spin orbitals. It is convenient to describe the other determinants by stating how they differ from $|\psi_0>$. Thus the set of possible determinants include $|\psi_0>$, the singly excited determinants $|\psi_a^r>$ (which differ from $|\psi_0>$ in having the spin orbital λ_a replaced by λ_r), the doubly excited determinants $|\psi_{ab}^{rs}>$, etc., up to N-tuply excited determinants. One can use these many-electron WFs as a basis in which to expand the exact many-electron WFs $|\Phi_0>$. If $|\psi_0>$ is a reasonable approximation to $|\Phi_0>$, then the variation principle states that a better approximation (which becomes exact as the basis becomes complete) is

$$|\Phi_0\rangle = c_0|\psi_0\rangle + \sum_{ar} c_a^r |\psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\psi_{abc}^{rst}\rangle + \ldots \quad (2.71)$$

This is the form of the full CI WF. To examine the structure of the full CI matrix it is convenient to rewrite the expansion of Eq. (2.71) in a symbolic form as

$$|\Phi_0\rangle = c_0|\psi_0\rangle + c_S|S\rangle + c_D|D\rangle + c_T|T\rangle + c_Q|Q\rangle + \ldots . \quad (2.72)$$

where $|S\rangle$ represents the terms involving single excitations, $|D\rangle$ represents the terms involving double excitation and so on. This equation has the properties:[144]

1). There is no coupling between the HF ground state and single excitation (i.e., $\langle\psi_0|H|S\rangle = 0$.) This is a consequence of Brillouin's theorem which states that all matrix elements of the form $\langle\psi_0|H|\psi_a^r\rangle$ are zero.

2). There is no coupling between $\langle\psi_0|$ and triples or quadruples. Similarly, singles do not mix with quadruples. This is a consequence of the fact that all matrix elements of the Hamiltonian between the Slater determinants which differ by more than 2 spin orbitals are zero.

3). Because single excitations do not mix directly with $\langle\psi_0|$, they can be expected to have a very small effect on the ground state energy. Their effect is not zero as they do mix indirectly; that is, they interact with the double excitations which in turn interact with $\langle\psi_0|$. Although they have negligible effects on the energy of the ground state,

they do influence the charge distribution. However, single excitations are needed for the proper description of one-electron properties such as the dipole moments. Moreover, the situation is entirely different for excited states. In the calculation of the electronic spectra of molecules the single excitations play the primary role.

For the SDCI, the WF is expressed as

$$|\Phi_{SDCI}\rangle = |\psi_0\rangle + \sum_{ar} c_a^r |\psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle \qquad (2.73)$$

The resulting ground state energy obtained from a SDCI calculation is variational. For small molecules, however, it gives the major fraction of the correlation energy.

The CI calculations performed in the present work include an extensive array of single and double excitations from a set of important reference configurations (RCs) formed from bonding and low-lying virtual MOs to ensure that all the important excitations are included in the CI calculation. A number of RCs included in the CI calculation can be one or many more. Since the CI calculation can also be made to include the relativistic effect exclusively the SO coupling, the criteria on which the relativistic CI is obtained will be discussed in detail.

In practice, the difference between the relativistic and non-relativistic CI calculations is only in the preparation of the RCs included in the calculations. In the relativistic case ω-ω coupling

determines the MO configurations included in the set of RCs while the Λ-S coupling is used in the non-relativistic CI calculation.

The selection of RCs for inclusion in the CI calculations is rather complicated. RCs arise from the valence bonding MOs and some low-lying MOs. The methodology for the selection of RCs for the relativistic CI calculations is best determined by referring to particular examples for the series of MH molecules.

In MH molecules, the valence MO configuration is $1\sigma^2 2\sigma^2$ where the 1σ MO arises from a metal $s\sigma$ AO and the 2σ orbital is from a metal $d\sigma$ AO. With two electrons in both the *d* shell and the *s* shell, a complete array of MO configurations for RCs based on promotion within *d* orbitals and antibonding *s* orbital are constructed. For a given configuration, the Λ-S terms can be constructed using standard methods.[145] The ω-ω coupling terms can then be constructed from these Λ-S terms by standard methods.[145] The MO configurations included as RCs, the Λ-S and ω-ω states for the MH molecules are summarized in Table X in chapter IV as well as for the more difficult cases of MX (X = O, F and Cl). The results are given in Table XI and XIII also in chapter IV.

In practice, the MO configurations considered as RCs are ground state configurations and those configurations involving electron promotion from the bonding orbital(s) to the lowest 4 virtual orbital(s). For example, the configurations occupying the antibonding σ^* are unlikely to be important at bond distances near the equilibrium distance, but they must be introduced at the CI stage to ensure proper dissociation. The set of RCs in the CI calculations for MH includes all MO configurations which were found to have significant coefficients

in test calculations at the equilibrium bond distance. The RCs are presented in the Cartesian basis in the actual CI calculations.

In principle, RCs are formed from the coupling of valence atomic spinors as will be described in the following. First the atomic *s*- and *d*-spinors are presented as

$$(1/2)^{1/2} = \begin{pmatrix}\sigma\\0\end{pmatrix} = \sigma\alpha \tag{2.74}$$

$$(1/2)^{-1/2} = \begin{pmatrix}0\\\sigma\end{pmatrix} = \sigma\beta \tag{2.75}$$

$$(3/2)^{1/2} = \begin{pmatrix}\sigma\\\pi^{+}\end{pmatrix} = \sigma\alpha + \pi^{+}\beta = \sigma\alpha + x\beta + iy\beta \tag{2.76}$$

$$(3/2)^{-1/2} = \begin{pmatrix}\pi^{-}\\-\sigma\end{pmatrix} = -\sigma\beta + \pi^{-}\alpha = -\sigma\beta + x\alpha - iy\alpha \tag{2.77}$$

$$(3/2)^{3/2} = \begin{pmatrix}\pi^{+}\\0\end{pmatrix} = \pi^{+}\alpha = x\alpha + iy\alpha \tag{2.78}$$

$$(3/2)^{-3/2} = \begin{pmatrix}0\\\pi^{-}\end{pmatrix} = \pi^{-}\beta = x\beta - iy\beta \tag{2.79}$$

$$(5/2)^{1/2} = \begin{pmatrix}\sigma\\-\pi^{+}\end{pmatrix} = \sigma\alpha - \pi^{+}\beta = \sigma\alpha - x\beta - iy\beta \tag{2.80}$$

$$(5/2)^{-1/2} = \begin{pmatrix}\pi^{-}\\\sigma\end{pmatrix} = \sigma\beta + \pi^{-}\alpha = \sigma\beta + x\alpha - iy\alpha \tag{2.81}$$

$$(5/2)^{3/2} = \begin{pmatrix}\pi^{+}\\\delta^{+}\end{pmatrix} = \pi^{+}\alpha + \delta^{+}\beta = x\alpha + iy\alpha + xx\beta + iyy\beta \tag{2.82}$$

$$(5/2)^{-3/2} = \begin{pmatrix}\delta^{-}\\\pi^{-}\end{pmatrix} = \pi^{-}\beta + \delta^{-}\alpha = x\beta - iy\beta + xx\alpha - iyy\alpha \tag{2.83}$$

$$(5/2)^{5/2} = \begin{pmatrix}\delta^{+}\\0\end{pmatrix} = \delta^{+}\alpha = xx\alpha + iyy\alpha \tag{2.84}$$

$$(5/2)^{-5/2} = \begin{pmatrix} 0 \\ \delta^- \end{pmatrix} = \delta^-\beta = xx\beta - iyy\beta \qquad (2.85)$$

in which the superscript on π and δ indicates the + or - sign of m_l, quantitative coefficients are omitted, and α and β have their usual significance for spin. After the last equal sign in Eqs. (2.74-2.85) the expansion into real Cartesian functions is indicated where x and y are the abbreviations for π_x and π_y and xx and yy are those for δ_{xx} and δ_{yy} respectively.

Although, there are differences in sign conventions for the terms in these spinors in various books and papers, one can always determine the signs from the symmetry. Note that the $(3/2)^{1/2}$ and $(5/2)^{1/2}$ spinors differ only in the signs and quantitative coefficients as do the $(3/2)^{-1/2}$ and $(5/2)^{-1/2}$ coefficients. The most important RCs included in the CI calculations for the ground state $\overset{+}{0}$ state will be based on the coupling scheme presented above.

For example, the important set of configurations for the lowest $\overset{+}{0}$ state in MH molecules simply occupies the 4 spinors shown below:

$$(1/2)^{1/2}_g \quad (1/2)^{-1/2}_g \quad (1/2)^{1/2}_u \quad (1/2)^{-1/2}_u$$

$$= (\sigma_g\alpha)\,(\sigma_g\beta)\,(\sigma_u\alpha)\,(\sigma_u\beta) \qquad (2.86)$$

$$(1/2)^{1/2}_g \quad (1/2)^{-1/2}_g \quad (3/2)^{1/2}_g \quad (3/2)^{-1/2}_g$$

$$= (\sigma_g\alpha)\,(\sigma_g\beta)\,(\sigma_g\alpha + \pi_g^+\beta)\,(-\sigma_g\beta + \pi_g^-\alpha)$$

$$= (\sigma_g\alpha)\,(\sigma_g\beta)\,(\sigma_g\alpha + x\beta + iy\beta)\,(-\sigma_g\beta + x\alpha - iy\alpha) \qquad (2.87)$$

$$(1/2)_g^{1/2} \quad (1/2)_g^{-1/2} \quad (5/2)_g^{5/2} \quad (5/2)_g^{-5/2}$$

$$= (\sigma_g\alpha)(\sigma_g\beta)(\delta_g\alpha)(\delta_g\beta) \tag{2.88}$$

The products of these molecular spinors are expanded into the products of spin-orbitals and finally into the Cartesian basis and presented in these final forms in the CI calculations. The expansion into Cartesian formalism will be discussed in detail in the following chapter.

CHAPTER III

COMPUTATIONAL DETAILS

The REP calculations described in this work can be divided into five steps as follows:

1). The REP construction:- Consists of two (or three) substeps depending on what form of the REP is required. If the numerical form of the REP is considered, only the first two substeps are calculated but if the analytical form of the REP is needed, the third step has to be included.

1.1). Relativistic full-core atomic DHF calculations from which REPs are derived.

1.2). The construction of numerical REPs from DHF energies, WFs and potentials of a reference full-core atom using the "shape-consistent" technique.

1.3) A procedure for fitting analytical functions to the set of numerical REPs[32] (not included in this work).

2). Exponent optimization:- To obtain optimized double STF exponents for a basis set.

3). Molecular REP-SCF calculations:- To obtain the SCF HF-valence MOs for the CI calculation.

4). CI calculations:- These include the SO coupling to obtain the relativistic CI results on WFs and the potential surfaces at different internuclear distances.

5). Spectroscopic constant calculations:- To obtain the spectroscopic constants of equilibrium internuclear distances (R_e's), dissociation energies (D_e's) and vibrational frequencies (ω_e's).

Regional Separation

The first step is to separate the valence and core regions of an atom whose REP needs to be generated, e.g. lutetium and lawrencium. In this work the valence region is considered to contain only the three outermost electrons in the ns^2 and $(n-1)d^1$ shells of lutetium and lawrencium atoms (where n = 6, and 7 respectively). Thus the REPs of lutetium and lawrencium atoms will be used in the place of core electrons with 3 electrons in the valence in the atomic and molecular calculations.

Relativistic Effective Potential Construction

DHF Program

A computer program DHF is used to solve for the atomic DHF WFs. This program is actually a slightly modified Desclaux[122] program to solve a many-electron Dirac-Fock equation for atoms via a numerical self-consistent technique. The only difference between the code used in the present work and the original code is that the atomic WFs of the valence electrons contain only the large components as discussed in the previous chapter. In the Desclaux program the relativistic Hamiltonian is approximated within the Dirac-Fock method by first ignoring the two-electron Breit interaction and including it as a first order

perturbation correction to the energy after self-consistency is achieved.

Only REPs of lutetium and lawrencium atoms have to be generated in this work. They are generated in a numerical form to eliminate any possible error introduced in the process of fitting the potentials with analytical functions and to retain the spin-orbit effects. This is important in molecules containing very heavy atoms since the spin-orbit splitting is often larger than other one-electron effects. It is theoretically more consistent to avoid the averaging. Moreover, the REP integral programs can handle the REPs in both the analytical and numerical forms.

The *ab initio* numerical REPs in this work are generated in the form of Eq. (2.50) and are used in the calculations in the form of Eq. (2.52) where L is generally taken to be one greater than the largest l-quantum number (l_{max}) among the core electrons where l_{max} is 3 and 3 for Lu and Lr atoms respectively.

In practice, the ground state configuration calculation is performed first to obtain the neutral core WFs. The excited configuration calculations are obtained from promoting an electron from the outermost occupied valence orbital to the virtual orbital and letting these two orbitals vary while the core stays neutral and unchanged (or frozen) until finally self consistency is achieved. This procedure is repeated until the virtual orbital with orbital quantum number L ($L=l_{max}+1$) is occupied. In the actual calculations, the input decks for each configuration are set up and are put together after one another. However, the ground state configuration is always set up

first in order to have neutral-core-WFs generated and to keep the core neutral in the excited configuration calculations. All of the atomic WFs generated are stored on tape in the same order as that of the input to be used in the second step for the derivation of the REPs.

How each excited state configuration arises depends on a configuration of the atom considered. For lutetium atom, a ground state electron configuration is $(1s_{1/2})^2$ $(2s_{1/2})^2$ $(2p_{1/2})^2$ $(2p_{3/2})^4$ $(3s_{1/2})^2$ $(3p_{1/2})^2$ $(3p_{3/2})^4$ $(3d_{3/2})^4$ $(3d_{5/2})^6$ $(4s_{1/2})^2$ $(4p_{1/2})^2$ $(4p_{3/2})^4$ $(4d_{3/2})^4$ $(4d_{5/2})^6$ $(4f_{5/2})^6$ $(4f_{7/2})^8$ $(5s_{1/2})^2$ $(5p_{1/2})^2$ $(5p_{3/2})^4$ $(5d_{3/2})^1$ $(6s_{1/2})^2$. The first 19 orbitals are considered as core orbitals while the $5d_{3/2}$ and $6s_{1/2}$ orbitals are considered as valence orbitals. The first excited configuration for lutetium is produced by exciting one electron from a $5d_{3/2}$ orbital to a $5d_{5/2}$ orbital. The next excited configuration then has a $6p_{1/2}$ orbital replacing the $5d_{3/2}$ orbital and so on, i.e. for $6p_{1/2}$, $5f_{5/2}$, $5f_{7/2}$, $5g_{7/2}$ and $5g_{9/2}$ respectively until 9 sets of input decks have been produced.

The input composition of the rundeck for the atomic DHF calculation in terms of card images is:

line 1 TTOT,TPROT (2F12.7)

TTOT = The maximum running time in seconds. If the time used becomes greater than or equal to TTOT, the WFs and all the necessary information to restart the job are written to tape. This parameter is set to be -1.0.

TPROT = The time in seconds which the above information is written every TPROT seconds. This number is set equal to zero.

line 2 Title starts with four asterisks in the first four columns (20A4)

line 3 This line is usually left as a blank line since only single configuration is considered and it also is a default setting.

line 4 NZ, NOI, NORB, NORBSC, IORTH, IENE, NDEP, NLEC, NEC, NUC, IFCWF, NES, INEXWF, NSTEP, IPL, IDR1, IPRFGR, NBRE (4I3,3I1,19I3)

NZ = The atomic number

NOI = The ionicity (NZ minus number of electrons)

NORB = The number of orbitals

NORBSC = Only the first NORBSC orbitals will be made self consistent.

IORTH, IENE, NDEP = 0

NLEC = The index for reading the WFs on tape.

NEC = The index for writing the WFs on tape.

NUC = 0 (default for a finite nucleus)

IFCWF, NES, INEXWF, NSTEP, IPL, IDR1, IPRFGR, NBRE = 0

line 5 A blank line.

line 6 Repeat this line NORB times; for each orbital a line with HP, NQ, LQ, IDO, NMAX, EL, SCC, DG (F12.7, 3I2, I6, 3F12.7)

HP = The estimate of the one-electron energy (negative and in atomic unit).

NQ = The principal quantum number.

LQ = The kappa quantum number.

IDO = Defines the initial WF

1). the WF is obtained by integrating the Dirac equation for a Thomas-Fermi potential (This is a default case).

2). same as above but using the local potential read on line.

3). hydrogenic

4). read on tape

NMAX = The number of tabulation points (must be ≤ 351); default is 351.

EL = Defines the occupation of the orbital.

If > 0 The occupation is the same in all the configurations and equal to the integer part of EL.

If = 0 The occupation numbers have to be read on the next line.

If < 0 The shell is closed in all the configurations.

SCC, DG = 0

If EL = 0, enter a line with the occupation number of the orbital in each configuration (40I2).

line 7 A blank line

The data lines 2-7 are to be repeated for each input deck to be run.

line 8 One line with eight asterisks in the first eight columns.

Only some variables will be mentioned. In the Lu rundecks, NLEC and NEC are defined as (0,1) in the first deck, (1,2) in the second deck and so on as (1,3), (1,4), (1,5), (1,6), (1,7) and (1,8) in the last deck. This means that the WFs generated in the first deck will be used as the initialized WFs in the following decks and the resulted WFs will be stored in that order from 1 to 8. Since the initial WFs for some orbitals in the following decks are taken from the first one, IDO = 4 is defined for all these orbitals. For the new orbitals, i.e. $6p_{1/2}$, $6p_{3/2}$, $5g_{7/2}$ and $5g_{9/2}$, in each of the following decks, IDO = 0 is used. However, for the $5f_{5/2}$ and $5f_{7/2}$ orbitals for which hydrogenic WFs are employed as the initial WFs, the IDO parameter is given as 3 . In this case the DG parameter, which is zero in the IDO $\neq$ 3 case, has to be given. DG = 3.0 is used for both $5f_{5/2}$ and $5f_{7/2}$ orbitals.. The run is complete when self consistency is achieved for all the input rundecks. The numerical WFs are stored on tape and are ready to be used in the next step which produces the shape consistent relativistic effective potential (SCREP).

SCREP Program

As discussed in the previous chapter the use of EPs in any form enables one to eliminate the core electrons and the associated orthogonality constraints from the electronic structure calculations on atoms and molecules. The essential properties that one looks for in EPs are angular momentum dependency, basis set independence, and stability against the variational collapse of their eigenfunctions to

core functions. EPs that contain these properties can be derived from neutral atomic WFs using a pseudo-orbital (spinor) transformation.

For each angular symmetry the radial factor for the outer orbital of the atom is transformed to a pseudo-orbital by a "shape consistent" technique as discussed in chapter II which removes the inner nodes and oscillations. Then an EP for that angular symmetry is calculated by requiring that it reproduce the pseudo-orbital and the true eigenvalue through the one-electron equation as follows:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z_V}{r} + U_{lj}^{EP}(r) + W_{lj}\right)\lambda_{lj} = \varepsilon_{lj}\,\lambda_{lj} \qquad (3.1)$$

where W_{lj} is the potential (comprising the usual Coulomb and exchange terms) due to the interaction of an electron in λ_{lj} with the other electrons in the occupied pseudo-orbitals. The λ_{lj} fitting procedure is referred to Eqs. (2.22-2.24) in chapter II.

The numerical REPs generated in this work are tested out as they can reproduce the true energy eigenvalue through the one-electron equation within the accuracy of 10^{-3}. This testing procedure is performed simultaneously with the exponent optimization process (which will be discussed in detail in the following section) since the reproduction of true eigenvalue of the valence orbitals by the REPs is a criterion of both the best optimized exponents and how good the REPs are. However, this procedure has some difficulties and is quite time consuming. The difficulties occur mostly when the initial guesses for the exponents are too far from the optimized exponents, or in the double zeta exponent case, that the second zeta is too close or too far

to the first one. To obtain smooth convergence, the principal quantum number used can also be varied, if needed.

The computer program employed to obtain the REPs is a SCREP (Shape Consistent Relativistic Effective Potential) program written by P. A. Christiansen. The input instruction for this program is:

line 1 Title (20A4)

line 2 NORB, IUNIT, KUNIT, NEC (4I5)

NORB = The number of orbitals

IUNIT = The input data unit

KUNIT = The output data unit

NEC = The number of data set from the previous DHF calculation

line 3 (One line for each of the NORB orbitals)

LQ, NTAG, LTAG, K, METH, OP1, OP2, OP3, OP4, OP5, OP6, OP7 (10I5)

LQ = The *l* quantum number, used only to determined lead power in orbital

NTAG = The *n* quantum number

LTAG = The kappa quantum number

K > 0 K/10 is innermost R value at which to start searching for R_{match}

= 0 Program finds its own match

= -1 Match at orbital maximum

= -2 Match at max of R * orbital

= -3 Match half way between above two

METH = 1 Match using up through 5th derivative (default)

= 2 Match using up through 4th derivative

= 3 Match using up through 3rd derivative

OP1 = 1 Match at R=K/10, ignoring inflexions

OP2 = 0 Checks inflexions in derivative

OP3 = 1 Print informations on all orbitals found on IUNIT during search

line 4 NZC, NCT (2I5)

NZC = The number of core electrons.

NZT = The atomic number.

line 5 (One line for each of the NORB effective potentials)

(NOC(I,J), J=1,NORB) (40I2)

NOC(I) = The occupation of the Jth orbital for generating the Ith effective potential.

After the run is complete, the spin-differenced numerical REP are the output. However, these numerical REPs are not ready to be used in any atomic or molecular calculations yet because of the fluctuations at long range. These REPs have to be truncated at some distance. The truncated radius for each spin-differenced potential is obtained from the point where the potential approaches zero.

Exponent Optimization

AHF Program

This step is a non-relativistic atomic Hartree-Fock (AHF) calculation performed to obtain the optimized double zeta exponents for the STF basis set used in the following molecular SCF calculation.

The program AHF is employed. This program needs EPs (AREPs or REPs) for the calculations. Two options of orbital types, STF or GTF (Gaussian-type-function), can be chosen from this program. The AHF calculation using EP to obtain the STF exponents is performed in the present work. There are two purposes for this calculation: first, as discussed in the REP construction section, to utilize this program to perform a test on the REPs generated, and second, if the eigenvalues are reproduced for the valence orbitals, to obtain the optimized STF exponents. Since the AHF program is a non-relativistic program, in the case of lutetium and lawrencium where REPs are used explicitly, the spin-differenced-REPs are spin-averaged in the AHF program before they enter the SCF calculations and the eigenvalue is produced in a non-relativistic fashion. This means that the *l*-quantum number is referred to for each orbital considered in the AHF program. As a result, the true eigenvalue for each *l*-orbital is the average of the eigenvalues from the $j=l+1/2$ and $j=l-1/2$ DHF orbitals. The difference between them should not exceed 10^{-3}. In practice, when the exponent of an orbital in the n^{th} iteration differs from that of the $(n-1)^{th}$ iteration by $\leq 10^{-3}$ and the total (valence-electron-only) energy is the most negative, the eigenvalues are reproduced successfully and the optimized exponents are obtained.

The input instruction for this AHF program is:

line 1 LIM (I5)

LIM = The number of data sets to be run in succession. All data sets must be complete even if only on line changes from set to set. This is always

the first line of the data deck and appears only once - i.e. not in succeeding runs done at one time.

line 2 Title line (18A4)

line 3 NFLAG1, NPRINT, NSYM, NVAR, MXVAR, NEXTRA, ISCALE, INCZET, IRD, NPPFLG (16I5)

NFLAG1 = 0 If the STF exponents are optimized.

= 1 If the GTF exponents are optimized.

NPRINT = 0 Do not print the supermatrices.

= 1 Print them.

NSYM = The number of symmetry types,

e.g. H is NSYM = 1 (only S symmetry),

C $1s^2$ $2s^2$ $2p^2$ NSYM = 2 (S and P symmetries).

NVAR = The number of exponents to be optimized.

MXVAR = The maximum number of exponents to be optimized at a time. Usually 1 or 2.

NEXTRA = The number of iterations in optimizing until the minimum energy is reached.

ISCALE = The incremental scale for ZETA,

= 0 For ZETINC (I) = 0.005*ZETA(I),

= 1 For ZETINC (I) = ZSCALE*ZETA(I)

INCZET = 0 To let program determine a ZETINC(I) parameter,

= 1 To input a ZETINC(I) to be varied.

IRD = 0 The default convergence parameters,

= 1 Set new convergence parameters.

NPPFLG = 1 If there is an effective potential,

= 0 Otherwise

line 4 (NBAS(I),I=1,NSYM) (16I5)

NBAS(I) = The number of basis functions of the I^{th} type symmetry. Enter this in the following order.

NBAS(1) → NBAS(S)

NBAS(2) → NBAS(P)

NBAS(3) → NBAS(D)

line 5 (NCSH(I), I=1,NSYM) (16I5)

NCSH(I) = The number of closed shells of the I^{th} symmetry. Enter in order of S, P, D.

line 6 (NOSH(I), I=1,NSYM) (16I5)

NOSH(I) = The number of open shells of the I^{th} symmetry. Enter in order of S, P, D.

Note: This program can only handle one open shell per symmetry.

line 7 (NCCUP(I), I=1,NSYM) (16I5)

NCCUP(I) = The occupation number of the I^{th} open shell. Enter in order of S, P, D. If there are no open shells, "0" must still be input.

Ex: C $1s^2$ $2s^2$ $2p^2$ NCCUP(1) = 0

NCCUP(2) = 2

line 8 (NBVAR(I), I=1,NVAR) (16I5)

NBVAR(I) = The label of the exponent(s) to be varied.

Ex: NBVAR(I) = 3, means ξ_3 will be varied.

The exponents will be varied according to their

order in this line. If NVAR = 0, do not include this line since no optimization is desired.

line 9 ZN, ZSCALE (5E15.8)

ZN = The nuclear charge

ZSCALE = Set the incremental scale, $\Delta\xi$. Usually left as blank.

From this point input follows two routes - one for STF and one for GTF. Only the one for STF will be constructed.

line 10 (IPQN(I), I=1,NBAST) (16I5)

IPQN(I) = The principal quantum number of the I^{th} basis function.

NBAST = The total number of basis functions. If more than 16 basis functions are desired, continue on the succeeding lines.

line 11 (ZETA(I), I=1,NBAST) (5E15.8)

ZETA(I) = ξ_I or the orbital exponent of the I^{th} basis function. Make sure that the basis function I corresponds to ξ_I. That is, enter both in the same order. Continue on as many lines as needed.

line 12 (AJMS(I), I=1,11) (5E15.8)

AJMN(I) = Clementi's coupling coefficients in the order of

AJMN(1) = K_{000}, AJMN(2) = K_{101},

AJMN(3) = K_{110}, AJMN(4) = K_{112},

AJMN(5) = K_{202}, AJMN(6) = K_{211},

AJMN(7) = K_{213}, AJMN(8) = K_{220},

AJMN(9) = K_{222}, AJMN(10) = K_{224},

AJMN(11) = K_{212}

It should take 3 lines to enter these numbers.

line 13 (C(K,IA), K=1,NBAS1) (5E15.8)

C(K,IA) = The trial coefficients,

NBAS1 = The number of functions of the I^{th} symmetry.

Enter them in the order of

C(1,1*s*1), C(2,1*s*2), C(n,1*s*n), .. C(NBAS1,MSN)

C(1,2*p*1), ... C(NBAS1,MPN),

C(1,3*d*1), ... C(NBAS1,MDN)

In other words, enter all S functions first in order of 1S → nS, then P in order of 2P → nP, and then D. Continue as many lines as needed. The ξ's and C's should correspond as followed.

line 10	ξ_{1s1}	ξ_{1s2}	ξ_{1s4}
	⇓	⇓	⇓
line 12	C_{1s1}	C_{1s2}	C_{1s4}

Read Effective Potentials (if NPPLG = 1):

line 14 NAME = Name of the EP

line 15 LMAX, NZCORE, NEPFRM, NVAR, NAVA (16I5)

LMAX = The number of potentials in the EP.

NZCORE = The number for core electrons.

NEPFRM = 0 for the Gaussian EP,

= 1 for the numerical EP.

NVAR = 0 for the averaged-EP (Gaussian potentials),

= 1 for the non-averaged (numerical) EP

NAVA = 10

For numerical potentials (NEPFRM = 1),

line 16 (RMIN(I), RMAX(I), I=1,LMAX) (16F5.4)

RMIN(I) = The radius that the EP starts.

RMAX(I) = The truncated radius of the EP.

LMAX = The maximum *l* quantum number of the core electron plus one.

line 17 Title of the potential of each j quantum number.

line 18 EN, HX, DR(1), NP

EN = The orbital energy.

HX = The incremental scale of the grid point.

DR(1) = The very first grid point.

NP = The total number of grid points in this potential.

line 19 (U(I,NJ), NJ=1,NP)

U(I,NJ) = The I^{th} numerical potential in the EP.

Repeat line 17-19 from I=1 to I=LMAX.

For the Gaussian EP:

line 16 LMAXP (I5)

LMAXP = The total number of potentials

line 17 NPP (I5)

NPP = The number of points in one Gaussian fit. This is the a number of points in the potential *l*-*L* (where $L = l_{max}$) plus the number of points in *L*.

line 18 (NPOT(I), ZEPOT(I), CPOT(I), I=1,NPP) (I10,2F20.10)

NPOT = The exponent for r^{NPOT-2} in the expression

$$\sum_{i=1}^{NPP} r^{NPOT-2}\, e^{-(ZEPOT+r^2)} * COAP$$

ZEPOT = The exponent of the Gaussian expression.

CPOT = The coefficient of the averaged potentials.

Repeat line 17-18 L+1 times (from l=0 up to l=L).

In addition, to obtain the optimized exponents, a few calculations have to be repeated with some parameters changed in each run. To summarize this procedure, the following steps can be followed:

1). Look at NVAR to determine number of ξ's to be varied.

2). Look at NBVAR(I) to determine order of ξ variation.

3). ξ_{I1} is varied first until it is optimized. Then, the ξ_{I2} is optimized, and so on until all ξ's list on NBVAR(I) are optimized.

4). Step 3 is repeated MXVAR times.

5). Next, all are varied simultaneously until a minimum energy is reached.

6). Steps 3-6 can be repeated NEXTRA times.

Up to this point, the most essential parts of the input for the molecular SCF calculation are available.

Molecular REP-SCF Calculations

This step of the diatomic calculations involves a series of programs in one computer job. The series of programs employed consists of programs named DER2, LPS, EPSON, RTRN, GVB and PASO2 respectively. Each program and its input description will be discussed in order as follows:

DER2 Program

DER2 is a diatomic integrals program. The one- and two-electron integrals for the SCF calculations of diatomic molecules are prepared in these calculations. These integrals are stored on tape and passed to the programs along the series to be used. The input instruction is:

'_' stands for a blank space.

Line 1 Title for the run (20A4)

Line 2 _ & INPUT

Line 3 _ _ R= , CHARGE(1)= , , NSYM= , NBF= , , ,

Line 4 _ _ NLMK= , , , , , , , , , , ,

Line 5 _ _ continuation of NLMK , , , , , ,

Line 6 _ _ ZETA= , , , , , , , , , , ,

Line 7 _ _ continuation of ZETA , , , , , ,

Line 8 _ _ NPOLYA=1, NEP=1,

Line 9 _ _ QUAD(1)=0.0,20,1.00,

Line10 _ & END

The DER2 input is format-free. Lines 2 and 10 begin at the second column; lines 3-9 begin input at the third column.

Explanation of variables:

R: The internuclear distance (in Bohr).

CHARGE: The nuclear charges of the 2 atoms separated by a comma.

NSYM: The number of *l* symmetries in the basis set; e.g. *s*, *p*, *d*.

NBF: The total number of basis functions in each m_l value (excluding -1),

e.g. *s*-functions: $m_l = 0$

$$p\text{-functions: } \begin{pmatrix} m_l = 0 \\ m_l = 1 \end{pmatrix}$$

Note: m_l = 0 components of a p-function are concluded as s-functions. For example, for a double-zeta basis set on one atom [$1s_1$, $1s_2$, $2s_1$, $2s_2$, $2p_1$, $2p_2$], input for NBF = 6,2:

6 functions with m_l = 0 (s-functions)

2 functions with m_l = 1 (p-functions)

NLMK: N = The principal quantum number of the basis function.

L = The orbital "l" quantum number.

M = The m_l value (excluding -1).

K = 1 For the first center,

= 2 For the second center.

Ordering for NLMK input:

- all m_l = 0 values for center 1 first,
- all m_l = 0 values for center 2 second,
- all m_l = 1 values for center 1 third,

etc.

e.g. for a basis set above, one can set up the NLMK as:

NLMK = 1001,1001,2001,2001,2101,2101,2111,2111, etc.

ZETA: The STF basis exponents from atom optimization in the same order as NLMKs.

LPS Program

Similarly, this program generates all the needed integrals from the EPs but no SO integrals are produced in this program. These integrals are also passed along the calculations to be used in the RTRN and GVB steps.

line 1 Title

line 2 LMAX, NU, NGP1, NAME, IPRINT, NUP, JDEX (3I5,A8,2X,105)

LMAX = L + 1

NU = 10

NGP1 = 10

NAME = The name of the EP.

IPRINT, NUTP, JDEX = 0

If there is no potential on this center, leave this line blank.

line 3 NAME (as in line 2)

line 4 NPOT, ZCORE, NEPFRM, IPERM, NZ (16I5)

NPOT = The total number of potentials in the EP.

ZCORE = The number fo core electrons.

NEPFRM = 0 Read in numerical EP,

= 1 Read in exponential EP,

= 2 Read in Gaussian EP.

IPERM = 0 If the EP is already averaged (for Gaussian EP).

= 1 To average the spin-differenced EP (for numerical EP).

NZ = The number of valence electrons.

For numerical potentials (NEPFRM = 1),

line 5 (RMIN(I), RMAX(I), I=1,LMAX) (16F5.4)

line 6 Title of the each potential

line 7 EN, HX, DR(1), NP

line 8 (U(I,NJ), NJ=1,NP)

where the description of each parameter in lines 5-8 are the same as those in the AHF input instruction.

Repeat lines 5-8 from I=1 to I=LMAX.

For the Gaussian EP (NEPFRM = 2),

line 5 LMAXP (I5)

LMAXP = The number of potentials

line 6 NPP(I) (I5)

NPP(I) = The number of points in the Gaussian fit. This number is a number of points in the potential 1-LMAX plus a number of points in potential LMAX

line 7 (NPOT(I), ZEPOT(I), COAP(I), I=1,NPP(I)) (I10,2F20.10)

NPOT(I) and ZEPOT(I) are defined the same way as those in the AHF program.

COAP(I) = The coefficient of the average potential.

Repeat lines 6-7 from I=1 to I=,MAXP.

EPSON Program

The EPSON program is set up similarly to the LPS program. However, this program calculates only the SO integrals from the AREPs/REPs for the CI calculation in the final step. The SO integrals generated are stored on tape and passed along to the NEWCI program to be used.

The input instruction for this program is the same as that of the LPS program. Two options of EPs can be input. The instruction for the use of the numerical EP in this program is exactly the same as that in the LPS program. However, it is slightly different in the Gaussian EP

case (NEPFRM = 2). The program description for the EPSON program will be discussed only for the NEPFRM = 2 case.

For the Gaussian EP (NEPFRM = 2),

line 5 LMAXP (I5)

line 6 NPP(I) (I5)

line 7 (NPOT(I), ZEPOT(I), COAP(I), COSP(I), I=1,NPP(I))

(I10,2F20.10)

where NPOT(I) and ZEPOT(I) and COAP(I) are defined in the same way as those in the LPS program.

COSP(I) = The coefficient of the spin-orbit term.

Note that the LMAXth potential should be added at the end of each *l*-potential unless *l*=LMAX. However, for the COSP coefficients, these coefficients are zeroes for all potentials except the LMAXth potential for which the COSP coefficients must be read in. Also, for the *s*-potential, COSP=0 since the spin-orbit operator is zero.

Repeat line 6-7 from I=1 to I=,LMAXP.

RTRN Program

This program does not need any input data through unit 5, instead it reads the input data from tape units 1, 3, 4, 7 and 9. What this program does is convert the atomic orbitals from complex coordinates into real coordinates.

GVB Program

This is the program that actually does the HF-SCF calculations for the molecular WFs, orbital energies, and total molecular valence-electron-only energy. The input needed is:

line 1 Title for the run (10A8)

line 2 (IPARM(I), I=1,16) (16I5)

IPARM(I) = Option parameters.

(1) ≠ 0 Read in F(I), A(KI), B(KI) (From J. Chem. Phys. 55, 5435 (1971)).

(1) = 0 Use spin name of spin number to get F(I) etc.

(2) > 0 Read in entire T matrix.

(2) = 0 Take WSYM to be the unit matrix.

(2) =-1 Read in WSYM for all integers.

(2) =-3 Read in WSYM in A40 format.

(3) = 0

(3) ≠ 0 Do not copy FT04 ⇒ FT12, use FT04 directly.

(4) = 0

(4) ≠ 0 Read occupied orbitals from unit 3.

(5) = 0 Read in occupied orbitals.

(6) The larger IPARM(6) is, the more output is obtained.

(7) > 2 Punches T matrix.

(7) = 1

(7) = 0 Punches occupied orbitals.

(8) = 0 No extrapolation.

(8) = N (N-point) extrapolation. (Not tested)
Extrapolation will start on iteration NX.

(9) = 0 Choose new orbitals by overlap with old.

(9) ≠ 0 Choose the lowest root of each equation.

(10) = 0 IVO = 1

(11) = 0

(12) = 0

(13) = N Read in only N occupied orbitals.

(13) = 0 Read as directed by other options.

(14) = 2 Write T matrix on tape 8.

(14) = 1 Write occupied orbitals on tape 8.

(14) = 0 Do not write any orbitals on tape 8.

(15) = 0

(16) = 0 and

(16) = 1 if NPAIR ≠ 0 (for more than one configuration),

If NPAIR = 1 is used, the GVB-PP (Generalized Valence Bond- Perfect Pairing) calculation which includes two configurations in the calculation.

In this work, single configuration REP-SCF calculations are of the main concern. Therefore, IPARM(I)s are usually input as:

0 0 1 0 0 1 2 0 1 0 0 0 0 0 0 0

line 3 NBF, NSYTYP, MAXIT, NPAIR, NEXT (16I5)

NBF = The number of basis functions in real space, i.e. sigma, pi(x), pi(y), delta(xx) and delta(yy) functions.

See NLMK input in DER2:

functions with m_l = 0 = sigma functions,

functions with m_l = 1 = pi(x) = pi(y) functions, and

functions with m_l = 2 = delta(xx) = delta(yy) functions

NBF = (# sigma) + (# pi(x)) + (# pi(y)) + (# delta(xx)) + (# delta(yy))

NSYTYP = The number of real symmetry types (sigma, pi(x), pi(y), etc.)

MAXIT = The number of iterations allowed = 30

NPAIR = 0 (for single configuration).

NEXT = 30

For each symmetry type:

line 4 (Repeat this line NSYTYP times)

SYM(I), NS(I), MELSYM(I) (A8,I2,I5)

SYM = The symmetry name, I.e. sigma, pi(x), pi(y), etc.

NS(I) = The number of symmetry-adapted functions, i.e. # sigma, # pi(x), # pi(y), etc.

MELSYM (I) = The number of occupied orbitals , i.e. the number of occupied orbitals of each symmetry type.

line 5 (NCONF(I), I=1,NORB)(16I5)

NORB = MELSYM(1) + MELSYM(2) + MELSYM(3) + ...+ MELSYM(NSYTYP)

For each occupied orbital:

NCONF = 0 or 1 Closed shell (occupation = 2).

= 2 Half shell (occupation = 1).

line 6 CONVG (E15.8)

CONVG = The convergence criterion (usually use 0.0000001).

line 7 ASPIN, MULTS (A8,I2)

where MULTS = 1, ASSPIN = SINGLET (Closed shell)

= 2, = DOUBLET

= 3, = TRIPLET, QUINTET, etc. high spin multiplet)

= 4, = SINGLET (Open-shell).

line 8 Skip if NPAIR = 0,

(COEFF(J,KPAIR),J=1,2;KPAIR=1,NPAIR) (5E15.8)

(COEFF(J,KPAIR)) = The coefficients for each configuration in each pair

line 9 AFMAT (16F5.2)

AFMAT = The format to input the AO coefficients usually use 16F5.2

Now: construct MOs from # occupied orbitals of each symmetry.

line 10 TRLAB (name like SGMA 1, PIX 1 for each MO), (10A8)

line 11 TRANS(I), I=1, NORB

TRANS(I) = The coefficients for occupied orbitals. The number of coefficients should be equal to number of basis functions. For example, sigma orbitals will have zero coefficients in pi(x), pi(y) basis functions. This must be repeated for as many occupied orbitals as was input earlier, e.g. for 4 occupied sigma orbitals;

SGMA 1

- MO coefficients

SGMA 2

- MO coefficients

SGMA 3

- MO coefficients

SGMA 4

- MO coefficients

For GVB coefficients:

The GVB program reads form I = 1 to I = # of basis functions; e.g. if NBF = 20, the program needs 20 coefficients. Coefficients should be input in the same order as NLMK in DER2 program; e.g.

SGMA 1

1*s*1,2*s*1,2*pz*1,1*s*2,2*s*2,2*pz*1,2*pz*2,2*px*1,2*px*2,2*py*1,2*py*2.

line 12 WYHSCF

line 13 MULPOP (If a net Mulliken population analysis is needed, otherwise skip this line)

line 14 FINISH

PAS02 Program

The main features of this program are to rearrange the SCF-MOs, from the GVB calculation, in order from the most negative to the most positive orbital and to calculate the total energy of the frozen core if assigned. Some innermost valence MOs can be considered frozen if the orbital energies of these MOs are quite deep compared to those of the more valence MOs. This frozen-scheme is an option in this program. It is used only to keep the possibly least number of electrons in the valence for the CI calculations. The input composition for this program is:

line 1 TITLE (18A4)

TITLE = The problem label.

line 2 ICON(I),I=1,2 (10I5)

ICON(I) = The program control options

ICON(1) = 1 Transforms away NCORE core orbitals specified in ICORE (see below).

ICON(2) = 1 Spin-orbit integrals included.

line 3 NBFIN,NBFOUT,NPAIR,NTAPE (4I5)

NBFIN = The number of input basis functions.

NBFOUT = The number of output basis functions.

NPAIR = 0

NTAPE = 2 (All the integrals are read from tape unit 2).

line 4 NSYM,(NOB(I),I=1,NSYM),(NOCC(I),I=1,NSYM) (16I5)

NSYM = The number of total symmetry.

NOB(I) = The number of basis functions for each symmetry.

NOC(I) = The number of occupied orbital for each symmetry.

line 5 If IPARM(1) = 0, skip this line.

NCORE (I5)

NCORE = The number of orbitals put in core.

line 6 (ICORE(I),I=1,NCORE) (16I5)

ICORE(I) = The list of numbers of the core orbitals.

Configuration Interaction Calculations

The CI program has been written as a machine dependent computer code named NEWCI. Each configuration consists of two types for spin orbitals (α and β), and is stored in a 32-bit word with dimensions of (32,2) in a 32-bit machine (as is the IBM 3081 used in the present work).

The technique used in the CI computer program in this work is called a multireference configuration CI technique. The RCs are set up through the coupling scheme and transformed to the Cartesian coordinates (as discussed in chapter II) for the CI calculations. Single and double excitations are allowed in these RCs to generate many more configurations included in the CI calculations.

The symmetry used in the CI computer code is C_{2v} which contains a_1, a_2, b_1, and b_2 irreducible representations. Therefore, the symmetry transformation from $C_{\alpha v}$ (in the REP-SCF step) to C_{2v} (in the CI step) is in order. The transformation is assigned as:

$C_{\alpha v}$		C_{2v}
σ	becomes	a_1
π_x	becomes	b_1
δ_{xx}	becomes	a_2
π_y	becomes	b_2
δ_{yy}	becomes	a_1

δ_{yy} is combined with σ to obtain an a_1 irreducible representation in C_{2v} symmetry. The input for the CI calculations of ScH will be demonstrated as an example.

First, the basis set of ScH is considered:

Sc : AREP + valence orbitals ($3d^1$ and $4s^2$)

H : $1s^1$ and $2p$ ($2p$ is a polarization function)

Since double zeta basis sets are employed in this work, the number of basis functions obtained are:

atom	AO	# exponents	m_l (+ve only)	#*s*	#*p*	#*d*
Sc	*s*	2	0	2	-	-
	d	2	0, 1, 2	2	2	2
H	*s*	2	0	2	-	-
	p	1	0, 1	1	1	-
Total	-	-	-	7	3	2

From the REP-SCF calculation, the number of basis functions for ScH is:

$C\alpha_v$ orbitals	#AO	#Occupied Orbitals
σ	7	2
π_x	3	0
δ_{xx}	2	0
π_y	3	0
δ_{yy}	2	0
Total	17	2

All of these 17 basis functions (form the REP-SCF calculation) are employed in the CI calculations of ScH. From the $C_{\alpha v}$ - C_{2v} symmetry transformation, the basis set of ScH for the CI calculation under C_{2v} symmetry becomes 9 a_1, 2 a_2, 3 b_1, and 3 b_2.

However, the input RCs for the CI calculations have to be in a Cartesian basis. This means that the b_1 and b_2 orbitals have to be

presented in a form of π^+ and π^- where the Cartesian coordinates for π^+ and π^- are expressed as:

$$\pi^+ = \pi_x + i\pi_y$$

and

$$\pi^- = \pi_x + i\pi_y$$

For all the MH, MO, MF and MCl molecules, RCs included in the CI calculations will be shown chapter IV.

The input instruction for this NEWCI program is as follows:

line 1 TITLE (10A4)

line 2 NSYM,(NORBS(I), I=1,NSYM),NREF,NSO (20I4)

NSYM = The number of symmetry types (usually 4 for a_1, a_2, b_1 and b_2 types in C_{2v} symmetry).

NORBS(I) = The number of basis functions for the I^{th} symmetry.

NREF = The number of references

NSO = 1 The spin-orbit integral is included.

= 0 The spin-orbit integral is not included.

line 3 NIT,NCONV,NCOF,NSTATE (20I4)

NIT = The maximum number of iterations in each calculation.

NCONV = The convergence parameter (10^{-NCONV})

NCF = The number of CI WFs to be output (default is 20).

NSTATE = The $NROOT^{th}$ ω-ω state

For each reference repeat line 4-10:

line 4 NCSNGL,NCDBL,NSPIN (20I4)

NCSNGL = The number of single excitation.

NCDBL = The number of double excitation.

NSPIN = The number of spin excitation (usually 0)

line 5 Skip this line if NCSNGL = 0.

(NSIN(I,1),NSIN(I,2),I=1,NCSNGL) (20I4)

For the single excitation of class (I) electrons are excited from symmetry NSYMQ(I) to NSYMU(I).

line 6 Skip this line if NCDBL = 0.

(NDBL(I,1),NDBL(I,2),NDBL(I,3),NDBL(I,4),I=1,NCDBL) (20I4)

For the class of double excitations electrons are excited from symmetries NDBL(1) and NDBL(2) to NDBL(3) and NDBL(4).

line 7 Skip this line if NSPIN = 0. (usually skip).

(NSPN(I,1), NSPN(I,2), I=1,NSPIN)

For the spin excitations from symmetry NSPN(1) TO NSPN(2)

line 8 (NRF(I,1),NRF(I,2),I=1,NB) (20(2X,2I1))

NB = The total number of basis functions.

= NOB(1) + NOB(2) + NOB(3) + NOB(4)

NRF(I,1) = The occupation of I^{th} α spin-orbital.

NRF(I,2) = The occupation of I^{th} β spin-orbital.

line 9 (NFRZ(I),I=1,NSYM),NFRVR,(IFRVR(I),I=1,NFRVR) (20I4)

NFRZ(I) = The first NFRZ(I) orbitals of the I^{th} symmetry type will be frozen.

NFRVR = The number of symmetries of the frozen virtual orbitals.

IFRVR(I) = The first IFRVR(I) virtual orbitals will be frozen for the Ith symmetry.

line 10 (COF(I), I=1,NREF) (8F10.6)

COF(I) = The initial guess of CI coefficient for each reference.

Spectroscopic Constant Calculations

This is the last step of the entire calculation. The fitting procedure is described in this section. First, the R_e and $E(R_e)$ parameters were found by fitting the calculated energies $E_{val}(R)$ of Eq. (1.1) as a function of distances using a fifth order polynomial. These data are presented in Appendix D. The second step is fitting the Morse potential, Eq. (3.2), using a non-linear regression technique for each molecule to obtain the spectroscopic values of D_e and β. Simultaneously the ω_e is obtained using Eq. (3.3),

$$E(R-R_e) = D_e \left(1-\exp^{-\beta(R-R_e)}\right)^2 \qquad (3.2)$$

$$\omega_e = \frac{\beta}{\left(\frac{2\pi^2\mu c}{D_e h}\right)1/2} \qquad (3.3)$$

in which μ is reduced mass, c is speed of light, h is Planck's constant.

In practice, two computer programs are used in this fitting procedure. The first computer program (called POLNM) is the fifth order polynomial curve fitting program which uses the Newton-Raphson iteration method to solve for R_e. The $E(R_e)$ quantity is also obtained. The input instructions for this POLNM program are:

line 1 m (I10)

m = The number of data points ($m \geq 8$)

line 2-3 R(I),I=1,m (8F10.6)

R(I) = The internuclear distances

line 4-5 E(I),I=1,m (8F10.6)

E(I) = The energies corresponding to R(I)'s

The spectroscopic parameters D_e and ω_e are calculated in the second step. A non-linear least square regression program obtained from Dr. A. Van Hook of the UTK Department of Chemistry is used in this step to fit the Morse potential. This program was modified to take the following instructions.

line 1 M, ME

M = 2

ME = Number of data points to fit

line 2 RE, ERE

RE = The R_e value

ERE = The $E(R_e)$ value

line 3 R, E(R)

(Repeat line 3 ME times.)

R = The internuclear distances

E(R) = The total valence energies obtained from the REP-SCF/RCI calculations

The results obtained from the regression analysis are summarized in Tables IV-V. It is seen that the Morse equation is fitted extremely well by the results of both the REP-SCF and RCI calculations, especially considering that no data points for $R \geq 10.0$ Bohr (5.29 A°) were used.

An alternative method of obtaining D_e often used in the literature is to take the energy difference between the value at R_e and a value at R = 10.0 Bohr. In general the results obtained from this method were different (usually lower) from the Morse curve values by about 10%, but the trends among the groups were the same. The method used here is preferred because:

(a). The older method presupposes that the calculations give correct dissociations at long distances.

(b). Most of the more reliable experimental values quoted in reference 147 were obtained by fitting the Morse curve. In the case of the oxides, the RCI curves were still moving steeply at 10 Bohr and at 15 Bohr as well as there was a discontinuity at these distances so that a true asymptote was not observed. Finally, since it is well known that the calculations at the SCF level do not dissociate correctly, the Morse fitting method has to be used.

TABLE IV

STATISTICAL DATA FOR D_e and ω_e VALUES (REP-SCF CALCULATIONS)

Molecules	D_e (eV)	ω_e (cm^{-1})
SbH	**6.75±0.07**	**1822±3**
ScH	6.34±0.14	1657±8
LuH	5.55±0.12	1504±7
LrH	4.91±0.10	1333±7
ScO	5.10±0.34	937±13
LuO	5.01±0.38	664±7
LrO[a]	-	-
ScF	7.71±0.16	827±2
LuF	7.44±0.13	650±1
LrF	6.35±0.17	662±2
ScCl	4.98±0.11	487±1
LuCl	4.28±0.27	395±3
LrCl	4.13±0.06	339[b]

[a]The roots (energies) are skipped in the calculations at R = 3.75-4.00 bohr, as a result, the fitting process can not be done.

[b]The deviation is less than 0.5 cm^{-1}.

TABLE V

STATISTICAL DATA FOR D_e and ω_e VALUES (RCI CALCULATIONS)

Molecules	D_e (eV)	ω_e (cm^{-1})
SbH	**2.44±0.06**	**1751±8**
ScH	1.94±0.13	1382±22
LuH	2.71±0.13	1506±17
LrH	3.12±0.13	1332±12
ScO	6.61±0.40	902±10
LuO	5.85±0.11	739±2
LrO[a]	5.45±0.14	681±3
ScF	5.50±0.15	799±2
LuF	7.28±0.10	649±1
LrF	7.10±0.19	614±1
ScCl	4.03±0.10	452±1
LuCl	5.06±0.29	383±2
LrCl	4.30±0.14	349±1

CHAPTER IV

INPUT FOR THE REP-SCF/RCI CALCULATIONS ON MH, MO, MF AND MCl (M = Sc, Lu And Lr)

This chapter presents only the input needed in the REP-SCF/RCI calculations of the ground states of the diatomic hydrides, oxides, fluorides and chlorides of scandium, lutetium and lawrencium.

Input Data

For the single reference REP-SCF calculations, double zeta STFs are used for the basis sets. Valence shell double zeta *s* and *d* basis sets for the metal atoms consist of 3*d* and 4*s* for scandium, 5*d* and 5*s* for lutetium and 6*d* and 7*s* for lawrencium. For oxygen, fluorine and chlorine atoms, the basis sets are 2*s* and 2*p*, 2*s* and 2*p* and 3*s* and 3*p* respectively. Double zeta exponents are optimized in the REP-AHF calculations. The hydrogen atom STF basis set of Cade and Huo[146] is adopted. The double zeta basis sets for all atoms are shown in Tables VI and VII. Analytical AREPs for scandium, oxygen, fluorine and chlorine atoms (Tables VIII and IX) and numerical REPs for lutetium and lawrencium (appendices B and C respectively) are used in the place of core electrons in both atomic and molecular SCF calculations.

In the RCI calculations, single and double excitations from the MOs formed by *s* and *d* on the metal and *s* and *p* on the ligand valence orbitals in multireference configurations are included. The RC inputs are formed based on a formalism described in chapter II under both non-

TABLE VI

DOUBLE ZETA BASIS SETS OF Sc, Lu AND Lr

Atom	Orbital	Exponents
Sc	4s	1.2776
		0.7526
	3d	4.2081
		1.7320
Lu	6s	2.1495
		1.2321
	5d	3.3046
		1.5514
Lr	7s	2.2818
		1.3389
	6d	2.6941
		1.2530

TABLE VII

DOUBLE ZETA BASIS SETS OF H, O, F AND Cl

Atom	Orbital	Exponents
H[a]	1s	1.1264
		1.4108
	2p	1.4409
O	2s	3.9925
		2.2435
	2p	3.6577
		1.5932
F	2s	4.5324
		2.5257
	2p	4.2119
		1.8608
Cl	3s	3.2770
		1.9365
	3p	3.4298
		1.8721

[a]From reference 146

TABLE VIII

AREP FOR Sc[a]

	n	Expn.	AREP coefs.	Spin-orbit coefs.
s-d	2	2.1647	-26.879 376	
	2	2.5199	86.152 006	
	2	3.2800	-158.358 686	
	2	4.3046	153.652 503	
	1	6.1716	-0.100 351	
	0	15.9083	3.418 622	
p-d	2	3.2272	36.969 154	0.584 096
	2	3.8278	-117.414 925	-1.865 295
	2	5.2205	213.542 908	3.591 338
	2	7.1372	-163.694 562	2.819 652
	1	12.8159	5.762 162	0.101 401
	0	4.6662	4.669 928	-0.008 362
d	2	6.9309	-2.569 158	0.007 582
	2	20.4794	-19.512 482	0.052 639
	2	64.6834	-47.747 105	0.198 130
	1	208.6899	-7.688 084	0.377 625

[a]From reference 76

TABLE IX

AREPs FOR O, F and Cl[a]

	n	Expn.	AREP coefs.	Spin-orbit coefs.
		Oxygen		
s-p	2	2.2479	11.216 304	
	2	2.4049	-16.344 477	
	1	4.3740	1.042 944	
	0	2.1892	2.193 891	
p	2	10.0286	-0.798 420	0.007 783
	2	34.1980	-5.766 847	-0.006 249
	1	100.0039	-1.486 456	0.036 949
		Fluorine		
s-p	2	2.8835	12.685 306	
	2	3.1077	-19.302 589	
	1	5.6122	1.002 179	
	0	2.8146	2.245 349	
p	2	44.5166	-6.723 024	-0.006 748
	2	12.9487	-0.929 649	0.013 051
	1	132.4967	-1.526 734	0.054 999
		Chlorine		
s-p	2	3.1474	-63.021 884	
	2	3.6826	187.004 072	
	2	4.4888	-114.419 223	
	1	7.1811	7.646 371	
	0	4.7709	2.999 977	
p	2	2.7051	-52.917 938	-0.665 679
	2	3.2028	159.084 807	2.077 915
	2	3.9857	-118.437 609	-1.709 316
	1	6.5706	5.191 998	0.076 492
	0	4.2848	4.670 786	-0.008 152
l = 2	2	3.3594	-1.336 886	-0.037 438
	2	9.7314	-11.743 701	-0.000 989
	2	29.2508	-30.295 557	0.026 766
	1	90.5456	-6.983 280	0.132 438

[a]From reference 77

relativistic Λ-S coupling and relativistic ω-ω coupling schemes and are presented in Tables X through XIII. The configuration inputs for the CI calculations are divided into four sets. The first set (Table X) is employed for ScH, LuH and LrH molecules and the second set (Table XI) is employed for ScO, LuO and LrO. ScF and ScCl share the third set (Table XII) and the fourth set (Table XIII) is used for LuF, LuCl, LrF and LrCl. The reason for dividing the CI input data this way is that each group was found to have similar characteristics in test calculations. The number of input RCs and the number of total configurations generated in the CI calculations are presented in Table XIV.

TABLE X

Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScH, LuH AND LrH

MO configuration	Λ-s state	ω-ω state
$1\sigma^2\ 2\sigma^2$	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\delta^2$	$^1\Gamma$	4
	$^3\Sigma^-$	$0^+,\ 1$
	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ 1\sigma^*$	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\sigma^{*2}$	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\pi^2$	$^3\Sigma^-$	$0^+,\ 1$
	$^1\Delta$	2
	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ 1\delta$	$^3\Delta$	3, 2, 1
	$^1\Delta$	2
$1\sigma^2\ 2\sigma\ 1\pi$	$^3\pi$	$0^+,\ 0^-,\ 1,\ 2$
	$^1\pi$	1
$1\sigma\ 2\sigma^2\ 1\sigma^*$	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
$2\sigma^2\ 1\sigma^{*2}$	$^1\Sigma^+$	0^+

TABLE XI

Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScO, LuO AND LrO

MO configuration	Λ-S state	ω-ω state
$1\sigma^2\ 2\sigma^2\ 3\sigma\ \pi^4$	$^2\Sigma^+$	1/2
$1\sigma^2\ 2\sigma^2\ 1\sigma^*\pi^4$	$^2\Sigma^+$	1/2
$1\sigma^2\ 2\sigma^2\ 2\sigma^*\pi^4$	$^2\Sigma^+$	1/2
$1\sigma^2\ 2\sigma\ 3\sigma\ 1\sigma^*\pi^4$	$^4\Sigma^+$	3/2
	$^2\Sigma^+$	1/2
$1\sigma^2\ 2\sigma^2\ 3\sigma\ \pi^3\pi^*$	$^4\Sigma^+$	3/2
	$^2\Sigma^+$	1/2
	$^2\Delta$	3/2, 5/2
	$^2\Sigma^-$	1/2
$1\sigma^2\ 2\sigma\ 3\sigma^2\ \pi^4$	$^2\Sigma^+$	1/2
$1\sigma^2\ 2\sigma^2\ \pi^4\ \pi^*$	$^2\Pi$	1/2, 3/2
$1\sigma^2\ 2\sigma^2\ 1\sigma^*\pi^3\pi^*$	$^4\Sigma^+$	3/2
	$^2\Sigma^+$	1/2
	$^2\Delta$	3/2, 5/2
	$^2\Sigma^-$	1/2

TABLE XI (continued)

MO configuration	Λ-S state	ω-ω state
$1\sigma^2\ 2\sigma^2\ 2\sigma^*\pi^3\pi^*$	$^4\Sigma^+$	3/2
	$^2\Sigma^+$	1/2
	$^2\Delta$	3/2, 5/2
	$^2\Sigma^-$	1/2

TABLE XII

Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF ScF AND ScCl

MO configuration	Λ-S state	ω-ω state
$1\sigma^2\ 2\sigma^2\ \pi^4$	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ 1\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\sigma^{*2}\ \pi^4$	$^1\Sigma^+$	0^+
$1\sigma^2\ \delta^2\ \pi^4$	$^1\Gamma$	0^+
	$^3\Sigma^-$	0^+, 1
	$^1\Sigma^+$	0^+
$1\sigma\ 2\sigma^2\ 1\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma\ 2\sigma\ 1\sigma^{*2}\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\sigma^*\ 2\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ 2\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+

TABLE XII (continued)

MO configuration	Λ-S state	ω-ω state
$1\sigma\ 2\sigma\ 1\sigma^*\ 2\sigma^*\ \pi^4$	$^5\Sigma^-$	$0^+,\ 1,\ 2$
	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma^2\ \pi^3\ \pi^*$	$^3\Sigma^+$	$0^-,\ 1$
	$^3\Delta$	$1,\ 2,\ 3$
	$^1\Delta$	2
	$^3\Sigma^-$	$0^+,\ 1$
	$^1\Sigma^+$	0^+
	$^1\Sigma^-$	0^-
$1\sigma\ 2\sigma^2\ 2\sigma^*\ \pi^4$	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+

TABLE XIII

Λ-S AND ω-ω STATES ARISING FROM LOW-LYING MO CONFIGURATIONS OF LuF, LrF, LuCl AND LrCl

MO configuration	Λ-S state	ω-ω state
$1\sigma^2\ 2\sigma^2\ \pi^4$	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ 1\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma^2\ 1\sigma^{*2}\ \pi^4$	$^1\Sigma^+$	0^+
$1\sigma^2\ \delta^2\ \pi^4$	$^1\Gamma$	0^+
	$^3\Sigma^-$	0^+, 1
	$^1\Sigma^+$	0^+
$1\sigma\ 2\sigma\ \delta^2\ \pi^4$	$^1\Gamma$	0^+
	$^3\Sigma^-$	0^+, 1
	$^1\Sigma^+$	0^+
$2\sigma^2\ \delta^2\ \pi^4$	$^1\Gamma$	0^+
	$^3\Sigma^-$	0^+, 1
	$^1\Sigma^+$	0^+
$1\sigma\ 2\sigma^2\ 1\sigma^*\ \pi^4$	$^3\Sigma^+$	0^-, 1
	$^1\Sigma^+$	0^+
$1\sigma^2\ 2\sigma\ \pi^4\ \pi^*$	$^3\pi$	0^-, 0^+, 1, 2
	$^1\pi$	1

TABLE XIII (continued)

MO configuration	Λ-S state	ω-ω state
$1\sigma\ 2\sigma\ 1\sigma^*\ 2\sigma^*\ \pi^4$	$^5\Sigma^-$	$0^+,\ 1,\ 2$
	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
$1\sigma\ 2\sigma^2\ 2\sigma^*\ \pi^4$	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
$2\sigma^2\ 1\sigma^{*2}\ \pi^4$	$^3\Sigma^+$	$0^-,\ 1$
	$^1\Sigma^+$	0^+
	$^1\Sigma^+$	0^+

TABLE XIV

NUMBER OF REFERENCE CONFIGURATIONS AND TOTAL CONFIGURATIONS

Molecule	# RCs	# total Configurations
ScH	48	2624
LuH	48	2624
LrH	48	2624
ScO	37	4643
LuO	37	4643
LrO	37	4643
ScF	26	4695
LuF	33	3588
LrF	33	3588
ScCl	26	4695
LuCl	33	3588
LrCl	33	3588

CHAPTER V

RESULTS AND DISCUSSION OF RESULTS FOR MH, MO, MF AND MCl (M = Sc, Lu And Lr)

The accuracy of the spectroscopic results compared to the experimental results and the nature of the ground state M-X bonding of the diatomic hydrides, oxides, fluorides and chlorides of scandium, lutecium and lawrencium obtained from the REP-SCF/RCI calculations are presented and discussed in this chapter.

Accuracy of Results

First, the accuracy of the numerical results in the present work (PW) is discussed. This is determined by the deviation of the eigenvalues calculated in the AREPS/REPs-AHF calculations for each neutral atom from the AE eigenvalues. A deviation of 10^{-3} a.u. is allowed in the PW. As can be seen in Table XV, the results of the valence *s* and *d* orbital energies using AREPS/REPs and optimized basis sets in the REP-AHF calculations compared to those of the AE calculations are correct up to the third digit. This agreement is a good indication that the effects of the core electrons are being accurately reproduced by the *ab initio* AREPS/REPs.

In order to assess the accuracy of the spectroscopic results from the PW (Table XVI-XVIII), it is necessary to establish the the expected range of deviation of the REP-SCF/RCI method used by looking at the previously reported theoretical results and comparing them to the experimental results. Table XIX presents a comparison of spectroscopic

TABLE XV

ORBITAL ENERGIES FROM REP-AHF AND ALL-ELECTRON DF/HF CALCULATION (a.u.)

Atom	Orbital	DF/HF	REP-AHF	Difference	%Difference
Sc	4*s*	-0.209[a]	-0.211	0.002	1%
Sc	3*d*	-0.331[a]	-0.335	0.004	1%
Lu	6*s*	-0.219	-0.221	0.002	1%
Lu	5*d*	-0.185	-0.193	0.008	4%
Lr	7*s*	-0.244	-0.244	0.000	0.0%
Lr	6d	-0.150	-0.158	0.008	5%
O	2*s*	-1.244[b]	-1.244	0.000	0.0%
O	2*p*	-0.632[b]	-0.628	0.004	1%
F	2*s*	-1.570[b]	-1.572	0.002	0.1%
F	2*p*	-0.723[b]	-0.724	0.001	0.1%
Cl	3*s*	-1.080[b]	-1.076	0.004	0.4%
Cl	3*p*	-0.504[b]	-0.502	0.002	0.4%

[a]From reference 76

[b]From reference 77

TABLE XVI

BOND LENGTHS OF MH, MO, MF AND MCl

Molecule	R_e (Bohr)		
	Exp.	SCF*	RCI*
ScH	-	3.425	3.530
LuH	3.611[a]	3.702 (+3%)	3.706 (+3%)
LrH	-	3.864	3.841
ScO	3.152[a]	3.110 (-1%)	3.169 (+1%)
LuO	3.383[a]	3.465 (+2%)	3.545 (+5%)
LrO	-	-	3.669
ScF	3.378[a]	3.350 (-1%)	3.343 (-1%)
LuF	3.623[a]	3.546 (-2%)	3.546 (-2%)
LrF	-	3.665	3.751
ScCl	4.212[a]	4.382 (+4%)	4.408 (+5%)
LuCl	-	4.602	4.594
LrCl	-	4.762	4.740

[a]From reference 147

*From fitting 8 points in the fifth order polynomial

TABLE XVII

VIBRATIONAL FREQUENCIES AT THE GROUND STATE OF MH, MO, MF AND MCl

Molecule	ω_e (cm^{-1})		
	Exp	SCF*	RCI*
ScH	-	1657	1382
LuH	1520[a]	1504 (-1%)	1506 (-1%)
LrH	-	1333	1332
ScO	965[a]	937 (-3%)	902 (-6%)
LuO	842[a]	664 (-27%)	739 (-12%)
LrO[b]	-	-	681
ScF	736[a]	827 (+12%)	799 (+8%)
LuF	612[a]	650 (+6%)	649 (+6%)
LrF	-	662	614
ScCl	447[a]	487 (+9%)	452 (+1%)
LuCl	-	395	383
LrCl	-	339	349

*From fitting the Morse equation

[a]From reference 147

TABLE XVIII

DISSOCIATION ENERGIES OF MH, MO, MF AND MCl

Molecule	D_e (eV)		
	Exp	SCF*	RCI*
ScH	-	6.34	1.94
LuH	(3.25)[a]	5.55 (+71%)	2.71 (-16%)
LrH	-	4.91	3.12
ScO	6.96[b]	5.10 (-27%)	6.61 (-5%)
LuO	7.19[b]	5.01 (-30%)	5.85 (-19%)
LrO[c]	-	-	5.45
ScF	6.17[b]	7.71 (+25%)	5.50 (-11%)
LuF	-	7.44	7.28
LrF	-	6.35	7.10
ScCl	(3.45)[a]	4.98 (+44%)	3.61 (+5%)
LuCl	-	4.28	5.06
LrCl	-	4.13	4.30

*From fitting the Morse equation

[a]From $D_e = \frac{\omega_e^2}{4\omega_e x_e}$, where ω_e and $\omega_e x_e$ are obtained from reference 147

[b]Thermochemical value collected in reference 147

[c]The correct root (energy) is skipped at 4.00 Bohr in the SCF calculations. As a result the fitting process can not be done.

TABLE XIX

SOME PREVIOUS SPECTROSCOPIC RESULTS OF THE REP-SCF/RCI CALCULATIONS*

Molecule	R_e (Bohr)			D_e (eV)			ω_e (cm^{-1})		
	calc	exp	%dev.	calc	exp	%dev.	calc	exp	%dev.
SbH*	**3.426**	**3.25**	**+5%**	**2.44**	-	-	**1751**	-	-
SbH[a]	3.42	3.25	+5%	2.26	-	-	1763	-	-
SnH[b]	3.56	3.36	+3%	2.30	-	-	1600	1715	-7%
TeH[c]	3.34	3.29	+2%	2.31	-	-	1839	-	-
TlH[d]	3.76	3.53	**+6%**	1.81	1.97	-8%	1300	1391	-7%
PbH[e]	3.68	3.48	+6%	1.64	1.59	+3%	1418	1564	-9%
BiH[f]	3.59	3.42	+5%	2.17	-	-	1619	1636	-1%
PbO[g]	3.82	3.63	+5%	3.00	3.83	**-22%**	715	721	-1%
TlF[h]	3.86	3.93	-2%	3.86	4.57	-16%	592	477	**+24%**
PbF[i]	3.93	3.89	+1%	3.75	3.69	+2%	540	503	+7%
BiF[j]	3.95	3.87	+2%	-	-	-	502	511	-2%

*From a polynomial curve fitting procedure and the assumption of true asymtote except the **SbH*** case in which the ω_e and D_e results are obtained from fitting the Morse potential.

[a]From reference 73

[b]From reference 48

[c]From reference 72

[d]From reference 54

[e]From reference 60

[f]From reference 65

[g]From reference 57

[h]From reference 63

[i]From reference 64

[j]From reference 71

parameters from the literature obtained by using the REP-SCF/RCI method on diatomic molecules containing *p*-open-shell transition metals with the corresponding experimental results. These diatomic molecules are SbH,[73] SnH,[48] TeH,[72] TlH,[54] PbH,[60] BiH,[65] PbO,[57] TlF,[63] PbF[64] and BiF.[71] The results are obtained from fitting four points of data at the bottom of the energy curve in a third order polynomial. The deviations from the experimental results of these R_e, D_e and ω_e values appear to be both positive and negative. The largest absolute differences are 6% for R_e, 22% for D_e and 24% for ω_e.

The spectroscopic results from the PW (Tables XVI-XVIII) are obtained using both the polynomial fit and the Morse potential fit as described in chapter III, p.95. Table XVI presents the R_e data obtained form the fifth order polynomial fit which gives deviations from the experimental results within the expected range of ≤5%. The deviations of the D_e and ω_e parameters from the experimental results (Tables XVII and XVIII) are also within the expected range of 19%.

The results of SbH obtained from fitting the Morse potential are also shown in Table XIX (bold letters) to compare with those obtained using the third order polynomial curve fitting.[73] One can see that the difference in R_e is quite small. However, the difference in D_e and ω_e are slightly larger than the deviation from the statistical analysis shown in Tables IV-V, pp.96-97.

Spectroscopic Results

The results and discussions of the results on the spectroscopic constants R_e, D_e and ω_e obtained in the PW for the hydrides, oxides, fluorides and chlorides of scandium, lutetium and lawrencium are presented and discussed. The discussions are divided into four groups according to the four types of diatomic molecules investigated starting with the hydride group.

MH molecules

For the ground state Sc atom, the ^4F ($3d^2$ $4s^1$) state is known to be 1.44 eV above the ^2D ($3d^1$ $4s^2$) atomic ground state.[148] Due to the large size of this excitation energy, it is expected that the bonding in ScH will mainly arise from the $3d^1$ $4s^2$ configuration. From Hund's rule, the $^3\Delta$ ($1\sigma^2 1\delta 2\sigma$) state is expected to be a ground state of ScH where the 1σ, 1δ, 2σ orbitals represent the MOs which originate from the $4s$, $3d$ AOs of Sc and the 1s AO of the hydrogen atom, respectively. This simple picture is found by earlier calculations: the SCF-HF calculations of Scott and Richards,[149,150] the limited MCSCF calculations of Das,[151] the SCF calculation of Bauschlicher and Walsch[152], and the SCF calculations of Anglada *et al.*[153a] and Peyerimhoff.[153b] For example, at the SCF level of calculations, Anglada *et al.*[153a] found that the $^3\Delta$ state was more stable than the $^1\Sigma^+$ ($1\sigma^2 2\sigma^2$) state by 0.7-0.8 eV. Moreover, the open shell 2σ MO in the $^3\Delta$ state was observed to possess mixed $4s4p$ character in the neighborhood of the equilibrium separation.

The bond length of the $^3\Delta$ state (*s*-bonding) predicted in these calculations is longer than the bond length of the $^1\Sigma^+$ state (*d*-bonding) and is explained by the fact that the 3*d* orbital was a much shorter radial orbital relative to the 4*s* orbital.

More recent calculations which include electron correlation (full-valence MCSCF (FV-MCSCF) and first-order CI (FO-CI)) have been performed on ScH by Bauschlicher and Walch.[152] In this work the 1*s*, 2*s*, 2*p*, 3*s* and 3*p* orbitals are treated as core orbitals and the 3*d*, 4*s* and 4*p* on Sc and 1*s* on hydrogen are included as valence orbitals. Both the FV-MCSCF and FO-CI methods predict that the $^1\Sigma^+$ state is the ground state and has the expected short bond length associated with *d*-bonding. The separation of the $^1\Sigma^+$ and $^3\Delta$ states were identical in both the FV-MCSCF and FO-CI calculations with the $^1\Sigma^+$ state placed 0.29 eV below the $^3\Delta$ state.

A $^1\Sigma^+$ ground state of ScH is also found in the MRD-CI calculations of Anglada *et al.*[153a]. Two calculations were performed: one with only 4 valence electrons included in the CI calculations and one with 12 electrons included. The CI treatment leads to an energy lowering of both the $^1\Sigma^+$ and $^3\Delta$ states, with the $^1\Sigma^+$ 0.21 eV lower than the $^3\Delta$ state. The 12 electron calculations predict that the $^1\Sigma^+$-$^3\Delta$ separation increases to 0.37 eV. With 4 valence electrons included in the MRD-CI step, the R_e and D_e are reported as 3.40 Bohr and 2.20 eV for the $^1\Sigma^+$ ground state (Table XX), while the corresponding D_e for $^3\Delta$ is found to be 1.99 eV.[153a]

Table XX also contains results from the AE *ab initio* MCSCF/CI calculations of Alvarado-Swaisgood and Harrison[154] on ScH which are in

TABLE XX

CALCULATED SPECTROSCOPIC CONSTANTS OF THE GROUND STATE ($^1\Sigma^+$) OF ScH

(All calculations include correlation from 4 electrons in CI)

Method	R_e (Bohr)	D_e (eV)	ω_e (cm^{-1})	3*d*-population
REP-SCF[a]	3.426 (+1%)	6.34 (+179%)	1657 (+4%)	0.88
RCI[a]	3.532 (+4%)	2.29 (+1%)	1382 (-13%)	-
SDCI[b]	3.38 (-0.3%)	2.16 (+5%)	1607 (+1%)	0.82
CPF[b]	3.39 (0%)	2.27 (0%)	1590 (+0.2%)	0.84
MCPF[b]	3.39	2.27	1587	0.84
FO-CI[c]	3.37 (-0.6%)	-	-	-
MCSCF+1+2[d]	3.38 (-0.3%)	2.00 (-12%)	1524 (-4%)	-
MRD-CI[e]	3.42 (+1%)	2.20 (+3%)	-	-
DF-OCE[f]	3.45 (+2%)	5.91 (+160%)	1715 (+8%)	-

**Numbers in parentheses are the deviations from the MCPF results

[a]PW

[b]From reference 155

[c]From reference 152

[d]From reference 154

[e]From reference 153

[f]From reference 74

excellent agreement with the experimental results for R_e, D_e and ω_e.

From a very recent study on ScH by Chong *et al.*[155], results are presented from three methods (i.e. SDCI, CPF and MCPF). The SDCI, CPF and MCPF calculations are performed for both four and twelve valence electrons for the $^1\Sigma^+$ and $^3\Delta$ states. The SDCI method is a single-reference single and double excitation CI method; the CPF method is a coupled pair function method and the MCFP method is a modified coupled pair function method. The MCFP calculation is the best calculation among these three methods. The inclusion of Sc 3*s* and 3*p* correlation into the 12 electron treatment shows more 3*d* and 4*s* character in the ground state in the MCPF and CPF calculations than in the less sophisticated calculations. It was also found that the D_e decreases at the SDCI level when more electrons are correlated, whereas D_e is essentially unchanged on increasing the correlation at the CPF and MCPF levels. This effect is assumed to arise from size consistency errors in the SDCI that are not present in the size extensive MCPF and CPF methods. Overall the inclusion of 3*s* and 3*p* correlation has a modest effect on ScH. The largest effects in the twelve-electron-CI calculations are an increase in the 3*d* population and a shortening of bond distance by 0.03-0.05 Bohr

Based on these calculations as summarized in Table XX, it appears that the explicit treatment of the four valence electrons in ScH and the representation of the core electrons of scandium by the analytical AREPs as carried out in the PW would be a good approximation. In the previous calculations, the 4*p* AOs did not appear to play a direct role in the calculations other than a slight modification for better

correlation. This fact is strongly supported by the basis set used in the PW where the n*p* orbitals are not included in the valence basis set.

The results for the $^1\Sigma^+$ ground state of ScH from the PW both at the REP-SCF and RCI levels are shown in Table XX. As mentioned earlier, the MCPF method is the most reliable method of the literature calculations, therefore the results from this method are used as the bench reference against which to evaluate the merits of the method used in the PW. The percentage of deviations are also presented in parentheses in Table XX. Although the RCI calculation gives slightly poorer R_e and ω_e compared to the corresponding REP-SCF results, an excellent D_e parameter is obtained from the RCI calculation.

Table XX also contains results obtained by Pyykkö[74] using the DF-OCE approximation method. These results look very similar to those of the REP-SCF calculations, again, indicating that the REP-SCF method gives reasonable results compared to the AE calculations. For LuH and LrH, Table XXI presents a comparison of the previous DF-OCE results with the PW results. The experimental results for LuH are also given.

The R_e and ω_e parameters of both the REP-SCF and the RCI calculations are in good agreement with the experimental values for LuH. Moreover, they give a relatively closer R_e to the experimental result than does the DF-OCE calculation. However, the DF-OCE ω_e agrees better with the experimental ω_e. Since no experimental D_e of LuH has been reported, D_e from the Birge-Sponer extrapolation technique[145] using the experimental ω_e and $x_e\omega_e$ values of LuH is reported. This D_e value for LuH is shown in Table XXI and it agrees quite well with the RCI value of D_e. The REP-SCF value of D_e is approximately 2 eV too

TABLE XXI

SPECTROSCOPIC CONSTANTS AT THE GROUND STATE OF LuH AND LrH

Method	R_e (Bohr)	D_e (eV)	ω_e (cm^{-1})
LuH			
REP-SCF[a]	3.702 (+2%)	5.55 (+71%)	1504 (+9%)
RCI[a]	3.706 (+2%)	2.71 (-16%)	1506 (+9%)
DF-OCE[b]	3.81 (+5%)	5.58 (+72%)	1557 (+2%)
Exp[c]	3.63	3.25	1520
LrH			
REP-SCF[a]	3.864	4.91	1333
RCI[a]	3.841	3.12	1332
DF-OCE[b]	3.86	4.35	1524

[a]PW

[b]From reference 74

[c]From reference 147

large. In addition, as expected, the DF-OCE value of D_e of LuH is very similar to the REP-SCF value of D_e and is almost twice as large as that from experiment.

For LrH, the only available previous results have been reported by Pyykkö using the DF-OCE technique. No experimental spectroscopic parameters have been reported for this molecule. The REP-SCF and RCI values of R_e agree very well with the DF-OCE R_e of LrH. However, the values of ω_e from the REP-SCF and RCI calculations are approximately 200 cm^{-1} smaller than the DF-OCE result for ω_e. The D_e results from the REP-SCF and DF-OCE calculations are, again, very similar and are very much larger than that of the RCI calculation because of the importance of the electron correlation in determining D_e.

MO molecules

The ScO molecule has been extensively used to test effective core potential methods. It has posed difficulties in previous pseudopotential calculations in which the potentials were generated by the MP technique. For example, in the early MP calculations on ScO by Gropen *et al.*,[105] collapse of the ScO molecule resulted. Petterson and Wahlgren[106] tried to correct this problem by treating the 3*p* electrons as chemically inert and well described by the frozen core approximation, however, they concluded that the MP method could not describe adequately the 3*p*-3*d* exchange interactions.

Later MP calculations on ScO were attempted by Huzinaga *et al.*[156] but with more careful preparation of the MP parameters and basis sets, a task which they and others have found to be crucial in securing good

quality results. The previously found "collapse" in the calculations that treated only 3*d*- and 4*s*-electrons in the valence (Sc-2) did not occur and a value of R_e = 2.87 Bohr was obtained compared to the experimental value of 3.152 Bohr.[147] However, this value is still much shorter than the value obtained in the AE calculations (R_e = 3.06 Bohr and 3.19 Bohr from the calculations using STF and GTF basis sets respectively[156]). Moreover, the MP calculations of Huzinaga *et al.*[156] in which they treated the 3*p*-, 3*d*- and 4*s*-electrons explicitly in the valence shell (Sc-1) gave excellent agreement for R_e compared with the AE value as shown in Table XXII.

In order to improve the bond length in the MP calculations in which only 3*d*- and 4*s*-electrons are treated explicitly for Sc, Andezelm *et al.*[157] applied the extended Sakai-Huzinaga MP method[158] on ScO. This new approach approximates the core-valence exchange interactions more accurately for ScO. However, the calculations were performed only at the SCF level. Two sets of MP calculational results were reported. One was the result of explicitly including the 3*d* and 4*s* orbitals (DS-valence) in Sc and the other result was obtained by including the 3*p* electrons in the valence shell with the 3*d*- and 4*s*-electrons (PDS-valence) of scandium. These SCF results for R_e, D_e and ω_e as well as the results of the AE calculations are shown in Table XXII. The R_e and ω_e parameters from both DS and PDS approaches are not only in excellent agreement with the AE values but are also in excellent agreement with the experimental results. Although the D_e value agrees well with the AE D_e, it is, as expected from SCF calculations, very small compared to the experimental D_e.

TABLE XXII

SPECTROSCOPIC CONSTANTS AND CHARGE DENSITIES FOR ScO

Property	REP-SCF[a]	RCI[a]	Exp[b]	DS[c]	PDS[c]	Sc-1[d]	Sc-2[d]	SDCI[e]	CPF[e]	SEFIT[f] CI (+Q)
R_e (Bohr)	3.110 (-1%)	3.169 (+1%)	3.152	3.06 (-3%)	3.14 (-1%)	3.08 (-2%)	2.87 (-9%)	3.110 (-1%)	3.165 (+1%)	3.184 (+1%)
ω_e (cm^{-1})	937 (-3%)	902 (-7%)	965	1056 (+9%)	1083 (+12%)	1047 (+8%)	750 (-22%)	1042 (+8%)	930 (+4%)	974 (+1%)
D_e (eV)	5.10 (-27%)	6.61 **(-5%)**	6.96	2.60 (-63%)	2.60 (-63%)	-	-	-	-	5.84 (-16%)
3d pop.	1.32	-	-	-	-	-	1.16	1.43	-	-
4s pop.	0.92	-	-	-	-	-	0.82	0.84	-	-
4pσ pop.	-	-	-	-	-	-	0.20	0.14	-	-
4pπ pop.	-	-	-	-	-	-	-	-	-	-
3dσ pop.	0.62	-	-	-	-	-	0.55	0.63	-	-
3dπ pop.	0.70	-	-	-	-	-	0.62	0.80	-	-
Charge	0.76	-	-	-	-	-	0.74	0.54	-	-

Numbers in parentheses are the deviations from the experimental data

[a] PW

[b] From reference 147

[c] From reference 157

(The AE R_e = 3.16 Bohr (+0.2%), ω_e = 1062 cm^{-1} (+10%) and D_e = 2.62 eV (-62%))

[d] From reference 156

(The AE STF basis set's R_e = 3.06 Bohr (-3%) and the AE GTF basis set's R_e = 3.19 Bohr (+1%))

[e] From reference 159

[f] From reference 160 (MEFIT gives D_e = 5.89 eV ((-15%).

More sophisticated AE calculations (SDCI and CPF) have been performed on ScO by Bauschlicher and Langhoff.[159] Seventeen electrons from the oxygen 2*s* and 2*p* and the scandium 3*s*, 3*p*, 3*d* and 4*s* orbitals were included in the correlation treatment in the SDCI and CPF steps. The SDCI and CPF results of R_e and ω_e are also shown in Table XXII, column 9 and 10. These results are in excellent agreement with the experimental results.

Recently, another EP method called the "adjusted *ab initio* pseudopotential technique" has been applied to ScO by Preuss *et al.*[160] This study was at the SCF/CI level of calculation. A Ne-like core is used for the pseudopotential of scandium and two types of pseudopotential were constructed: a SEFIT (single-electron fit) and a MEFIT (multielectron fit).

The spectroscopic parameters R_e, D_e and ω_e at the CI level of the calculations using the SEFIT pseudopotential (Table XXII column 11) and the D_e from the calculations using the MEFIT pseudopotential are in excellent agreement with the experimental results. The SCF results of ScO are also similar to those of Andezelm *et al.*[157] The REP-SCF and RCI calculations on ScO of the PQ are also reported in Table XXII, columns 2 and 3. The R_e values from both the REP-SCF and RCI calculation are in excellent agreement with the experimental result. The REP-SCF calculation gives ω_e slightly closer to the experimental ω_e than the RCI result. However, both ω_e values are in good agreement with the experimental value. Among all the reported D_e values (Table XXII), the best D_e result is obtained from the RCI calculation of the PW.

The spectroscopic results for LuO and LrO from the REP-SCF and RCI calculations are presented in comparison with the experimental values in Tables XVI-XVIII (pp.114-116). The R_e, D_e and ω_e results of the RCI calculations on LuO are in better agreement with the experimental results than those from the REP-SCF calculations. Table XVII (p.115) and Table XVIII (p.116) show that the D_e and ω_e results for LuO from the REP-SCF calculation are disappointing but the RCI values are still within the acceptable range for calculations of this type. The REP-SCF R_e, D_e and ω_e data for LrO cannot be obtained because of numerical problems in finding the correct energies in the region of R = 3.75-4.50 Bohr. Moreover, the R_e, D_e and ω_e results of LrO from the RCI calculation look very similar to those of LuO and are therefore probably reliable.

MF molecules

For ScF, the AE-GVB (Generalized Valence Bond) and CI calculations by Harrison[161] give a $^1\Sigma^+$ ground state with the first excited state being $^3\Delta$. The order of these states is in agreement with the experimental results[147] and with the pioneering calculations of Carlson and Moser.[162] The $^1\Sigma^+$-$^3\Delta$ separation is reported as 0.3-0.6 eV by Harrison while the experimental value is not known. However, Carlson and Moser[162] suggest a much smaller $^1\Sigma^+$-$^3\Delta$ separation (~0.06 eV).

The GVB/CI results of ScF show that ScF is a very ionic molecule not only at the ground state but also in the first few excited

states.[161] Harrison also predicts that this ionic characteristic of monofluorides will remain for the first transition series.

In the PW two sets of REP calculations of the ground state $^1\Sigma^+$ of ScF are performed at the SCF level. One is a (single-reference) REP-SCF with a configuration of $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ \pi^4$ (the same technique used in the other molecules in the PW). The other is a GVB technique with two configurations of ($1\sigma^2\ 2\sigma^2\ 3\sigma^2\ \pi^4$ - $1\sigma^2\ 2\sigma^2\ 4\sigma^2\ \pi^4$) where 4σ is the first virtual molecular orbital. Both calculations are followed by the same type of RCI calculations. Although the two calculations are started differently, they give the same results after the RCI level. It is very surprising that the two-reference SCF calculation did not improve the final results. However, it provides further justification for the method used for all the other molecules in the PW.

A comparison of the REP-SCF and RCI results for ScF with those of Harrison's GVB/CI calculations as well as experimental values are shown in Table XXIII. From this table, it can be seen that the R_e results from both the REP-SCF and RCI calculations are in excellent agreement with the experimental result for R_e as well as the GVB/CI R_e value. However, the REP-SCF and RCI calculations give an ω_e value which is too large compared to the ω_e obtained from the GVB/CI calculation of reference 161. The 12% error of REP-SCF for ω_e and the 9% error of REP-SCF are still in an acceptable range (especially the RCI calculation) compared to the values obtained for other molecules by other workers using this method (Table XIX, p.117).

Among these three sets of results, the best D_e is obtained from the RCI calculation which is in excellent agreement with the

TABLE XXIII

SPECTROSCOPIC CONSTANTS AT THE GROUND STATE OF ScF

Method	R_e (Bohr)	D_e (eV)	ω_e (cm^{-1})
REP-SCF[a]	3.350 (-1%)	7.71 (+25%)	827 (+12%)
RCI[a]	3.343 (-1%)	5.50 (-11%)	799 (+9%)
GVB/CI[b]	3.42 (+1%)	4.34 (-30%)	728 (-1%)
Exp[c]	3.38	6.17	736

*Numbers in the parentheses are deviation from the experimental results

[a]PW

[b]From reference 161

[c]From reference 147

experimental result. The REP-SCF D_e is slightly too large while the GVB/CI D_e is slightly too small.

The $^1\Sigma^+$ ground state results for both LuF and LrF are presented in Tables XVI-XVIII (pp.114-116). For LuF, both the REP-SCF and RCI calculations give excellent values of R_e and ω_e compared to the experimental result. The only experimental D_e value for LuF is an estimated value of 5.9±0.5 eV given by Zmbov and Margrave.[163] This was obtained by the extrapolation of the known D_e values of the monofluorides of other rare earth elements. Since this value is only an estimated value, it is not included in Table XVIII (p.116).

MCl molecules

The $^1\Sigma^+$ ground state results for ScCl, LuCl and LrCl are shown in Tables XVI-XVIII (pp.114-116). The R_e and ω_e parameters of ScCl from both the REP-SCF and RCI calculations are in excellent agreement with the available experimental values. Again, the D_e value can only be obtained from the Birge-Sponer extrapolation method using the experimental values of ω_e and $\omega_e x_e$ from Ref. 147. This value agrees very well with the D_e from the RCI calculation.

There are no experimental or other theoretical spectroscopic data available in the literature for LuCl and LrCl. The RCI D_e for LuCl shows a large increase over the value for ScCl a feature which is also found for the corresponding fluorides. The slight increase in R_e with atomic number and the drop in ω_e are also similar to the trend seen in the corresponding fluorides.

Bonding

Since correlation and SO coupling are taken care of at the RCI level for all the diatomic molecules, the RCI coefficients at the R_e distance (Appendix E) are first examined to ensure that the ground state configuration from the SCF level is the most important configuration (as they are by ≥90%). This is because the bonding formation of the ground state configuration of each molecule will be deduced from the REP-SCF calculation. From the RCI coefficients of all the diatomic molecules (Appendix E), it appears that the ground state configuration from the SCF level of each molecule contributes approximately ≥90% at the equilibrium bond distance. This is a good evidence to warrant the quantitative use of the Mulliken population analyses of the SCF calculations at the R_e distances to discuss the bonding in these molecules. The discussion is also divided into four groups according to the four types of molecules starting with the MH group.

MH molecules

From the Mulliken population analyses of the MH molecules (Table XXIV), it is clear that the M-H bonding arise from a s^2d^1 configuration of the metal atom. The four valence electrons in MH form two σ-molecular orbitals ($1\sigma^2 2\sigma^2$). The WFs show that there is *sd*-hybridization in both 1σ and 2σ orbitals. However, the main bonding orbital in this group is found as M(*s*+*d*)σ H(1*s*)σ in the 1σ bonding orbital. The amount of *s*-mixing in this orbital decreases as ScH > LuH > LrH while the amount of *d*-mixing increases as ScH < LuH < LrH.

TABLE XXIV

MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScH, LuH AND LrH

Orbital	M				X				Charge
	s	*dσ*	*dπ*	Total *d*	*s*	*pσ*	*pπ*	Total *p*	transfer
ScH									
1σ	0.29	0.36	-	0.36	1.35	-	-	-	-
2σ	1.43	0.52	-	0.52	0.00	-	-	-	-
total	1.72	0.88	-	0.88	1.35	-	-	-	0.35
LuH									
1σ	0.50	0.27	-	0.27	1.22	-	-	-	-
2σ	1.38	0.50	-	0.50	0.13	-	-	-	-
total	1.88	0.77	-	0.77	1.35	-	-	-	0.35
LrH									
1σ	0.76	0.16	-	0.16	1.07	-	-	-	-
2σ	1.13	0.54	-	0.54	0.34	-	-	-	-
total	1.89	0.70	-	0.70	1.41	-	-	-	0.41

This can be explained by referring to Table XV, p.113, where the atomic *s*- and *d*-orbital energies of Sc, Lu and Lr are presented. One can see that the energy of the *s*-orbital is deeper than the energy of *d*-orbital in Sc while the *s*-orbital is slightly shallower than the *d*-orbital in Lu and Lr. This is due to relativistic effects: the orbital contraction of the *s*-orbitals and the expansion of the *d*-orbitals. This is also the reason for the increase of *s*-electrons and the decreasing of the *d*-electrons in bonding in LuH and LrH. The 2σ orbital in ScH is shown to be a pure *sd* non-bonding orbital. However, slight mixing of the 1*s* electron of hydrogen into this orbital is seen in LuH and LrH. In all three molecules, the net charge transfer from the metal atom to the hydrogen atom of about 0.4 electrons indicates a polar covalent bond rather than an ionic bond.

MO molecules

As shown in Table XXV, bonding in the ground $^2\Sigma^+$ state MO molecules is found to arise from the s^1d^2 configuration instead of the s^2d^1 configuration of the metal atoms. There are nine electrons in the three oxides occupying four molecular orbitals which are $1\sigma^2 2\sigma^2 3\sigma\pi_x^2\pi_y^2$, where the 3σ is an open-shell orbital.

In all the three MO molecules, the 1σ orbital is a non-bonding orbital arising from O2sσ. In ScO, the 2σ-bonding orbital is formed from a M3dσAO and a O2pσ AO. No hybridization is found in this orbital of ScO. However, there is a little *sd*-hybridization in the 2σ-bonding orbital in LuO but even more in LrO. In all three molecules, the open-shell 3σ orbital is a non-bonding orbital of $M(d+s)\sigma^1$.

TABLE XXV

MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScO, LuO AND LrO

Orbital	M				X				Charge
	s	*dσ*	*dπ*	Total *d*	*s*	*pσ*	*pπ*	Total *p*	transfer
ScO									
1σ	0.01	0.07	-	0.07	1.91	-	-	-	-
2σ	0.01	0.48	-	0.48	0.04	1.47	-	1.47	-
3σ	0.90	0.07	-	0.07	0.01	0.02	-	0.02	-
$1\pi_x$	-	-	0.35	0.35	-	-	1.66	1.66	-
$1\pi_y$	-	-	0.35	0.35	-	-	1.66	1.66	-
total	0.92	0.62	0.70	1.32	1.96	1.49	3.32	4.81	0.76
LuO									
1σ	0.03	0.03	-	0.03	1.92	0.01	-	0.01	-
2σ	0.07	0.21	-	0.21	0.06	1.67	-	1.67	-
3σ	0.85	0.14	-	0.14	-	0.01	-	0.01	-
$1\pi_x$	-	-	0.40	0.40	-	-	1.60	1.60	-
$1\pi_y$	-	-	0.40	0.40	-	-	1.60	1.60	-
total	0.95	0.38	0.80	1.18	1.98	1.69	3.20	4.89	0.87
LrO									
1σ	0.04	0.05	-	0.05	1.91	-	-	-	-
2σ	0.28	0.18	-	0.18	0.05	1.49	-	1.49	-
3σ	0.77	0.18	-	0.18	-	0.05	-	0.05	-
$1\pi_x$	-	-	0.35	0.35	-	-	1.65	1.65	-
$1\pi_y$	-	-	0.35	0.35	-	-	1.65	1.65	-
total	1.09	0.41	0.70	1.11	1.96	1.54	3.30	4.84	0.80

However, the structure of the π orbitals for the oxides appears to be quite different from that in the MF or MCl cases. In the oxide molecules, the π orbitals are $d\pi$-$p\pi$ bonding whereas in the halide molecules they are non-bonding.

Relativistic effects are also found in the bonding structure of LuO and LrO. These effects are seen in the bonding formation of the 2σ orbital which is the main bonding MO in the oxides. In ScO, the 2σ orbital is found to arise purely from a M3dσAO and a O2pσAO. However, a quite different formation of the 2σ orbital is seen in LuO and LrO where the bonding shows considerable *sd*-hybridization which is even more important in LrO than in LuO. This can be attributed to the relativistic Hamiltonian which causes the *d* atomic orbital energies to decrease and to the relativistic shielding which enables the *d* orbitals in the heavier elements to participate in bonding compared to the lighter elements.

Finally, the total Mulliken population analyses of the oxides show that there is about 0.8 charge transfer from the metal atom to the oxygen atom for all three oxide molecules.

MF molecules

Like the hydrides, the bonding in MF molecules arises from the s^2d^1 configuration of the metal atoms as shown in Table XXVI. There are ten valence electrons in the closed shell $1\sigma^2 2\sigma^2 3\sigma^2 \pi_x^2 \pi_y^2$ molecular configuration.

The bonding in the fluorides apart from the open shell MO is similar to that in the oxides. The 1σ orbital is a non-bonding F2*s*

TABLE XXVI

MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScF, LuF AND LrF

Orbital	M				X				Charge
	s	*dσ*	*dπ*	Total *d*	*s*	*pσ*	*pπ*	Total *p*	transfer
ScF									
1σ	-	0.02	-	0.02	1.97	0.01	-	0.01	-
2σ	-	0.19	-	0.19	0.03	1.78	-	1.78	-
3σ	1.59	0.38	-	0.38	-	0.03	-	0.03	-
$1\pi_x$	-	-	0.10	0.10	-	-	1.90	1.90	-
$1\pi_y$	-	-	0.10	0.10	-	-	1.90	1.90	-
total	1.59	0.59	0.20	0.79	2.00	1.82	3.80	5.62	0.62
LuF									
1σ	-	0.01	-	0.01	1.97	0.01	-	0.01	-
2σ	0.03	0.10	-	0.10	0.03	1.84	-	1.84	-
3σ	1.79	0.21	-	0.21	-	-	-	-	-
$1\pi_x$	-	-	0.10	0.10	-	-	1.90	1.90	-
$1\pi_y$	-	-	0.10	0.10	-	-	1.90	1.90	-
total	1.82	0.32	0.20	0.52	2.00	1.85	3.80	5.65	0.65
LrF									
1σ	0.01	0.02	-	0.02	1.96	0.01	-	0.01	-
2σ	0.06	0.12	-	0.12	0.02	1.84	-	1.84	-
3σ	1.81	0.18	-	0.18	0.01	-	-	-	-
$1\pi_x$	-	-	0.09	0.09	-	-	1.91	1.91	-
$1\pi_y$	-	-	0.09	0.09	-	-	1.91	1.91	-
total	1.88	0.32	0.18	0.50	1.99	1.85	3.82	5.67	0.66

orbital in all three molecules. The bonding in ScF is in the 2σ orbital formed from a metal MdσAO and a F2$p\sigma$ AO. However, a small amount of *sd*-hybridization is found in LuF. The doubly occupied 3σ orbital is a non-bonding orbital arising from a mixture of metal *s* and *d* electrons.

The π_x and π_y orbitals have much less metal $d\pi$ character than in the oxides. As a result, the bonding in MF, is mainly a single σ-bond with a small amount of π contribution.

From the Mulliken population analyses, the charge transfer in each MF molecule from M to F appears to be slightly less than that seen in the corresponding oxides. This can be explained by examining the details of the bonding structure of the oxides compared to fluorides. In the oxides, there is considerable amount of charge transfer in the π bonds. As a result, the charge transfer in the oxides is greater than the charge transfer in the fluorides.

The relativistic effects found in the MH and MO cases are also seen in this case for LuF and LrF.

MCl molecules

As expected, the bonding in the chlorides is similar to the bonding in the fluorides and arises from the s^2d^1 configuration of the metal atoms (Table XXVII). Slight differences in the molecular structure of the chlorides is seen only in the 3σ orbital. In ScCl and LuCl, this orbital is a non-bonding as in ScF and LuF whereas it becomes slightly bonding orbital in LrCl.

TABLE XXVII

MULLIKEN POPULATION ANALYSIS AT THE SCF LEVEL OF ScCl, LuCl AND LrCl

Orbital	M				X				Charge
	s	*dσ*	*dπ*	Total *d*	*s*	*pσ*	*pπ*	Total *p*	transfer
ScCl									
1σ	0.02	0.01	-	0.01	1.97	-	-	-	-
2σ	0.08	0.17	-	0.17	0.03	1.72	-	1.72	-
3σ	1.42	0.58	-	0.58	-	-	-	-	-
$1\pi_x$	-	-	0.05	0.05	-	-	1.95	1.95	-
$1\pi_y$	-	-	0.05	0.05	-	-	1.95	1.95	-
total	1.52	0.76	0.10	0.86	2.00	1.72	3.90	5.62	0.62
LuCl									
1σ	-	-	-	-	2.00	-	-	-	-
2σ	0.11	0.07	-	0.07	0.04	1.78	-	1.78	-
3σ	1.71	0.26	-	0.26	-	0.03	-	0.03	-
$1\pi_x$	-	-	0.11	0.11	-	-	1.89	1.89	-
$1\pi_y$	-	-	0.11	0.11	-	-	1.89	1.89	-
total	1.82	0.33	0.22	0.55	2.04	1.81	3.78	5.59	0.63
LrCl									
1σ	-	-	-	-	2.00	-	-	-	-
2σ	0.19	0.09	-	0.09	0.04	1.69	-	1.69	-
3σ	1.70	0.18	-	0.18	-	0.11	-	0.11	-
$1\pi_x$	-	-	0.11	0.11	-	-	1.89	1.89	-
$1\pi_y$	-	-	0.11	0.11	-	-	1.89	1.89	-
total	1.89	0.27	0.22	0.49	2.04	1.80	3.78	5.58	0.62

CHAPTER VI

SUMMARY AND CONCLUSION

The major goal of this work was to ascertain whether the REP-SCF/RCI method is capable of producing reasonable spectroscopic data and a fairly valuable picture of the bonding for molecules containing transuranium elements for which there are no experimental data. Previous work using the very same technique has been confined to compounds of the main group elements and of a few transition metals.

Because it was not yet possible to treat atoms with open shell *f*-electrons, lawrencium with the valence ground state of $7s^2\ 6d^1$ was chosen as a test transuranium element for this initial study. In order to establish the validity of the method used, calculations were performed on compounds of the isoelectronic atoms of scandium ($4s^2\ 3d^1$) and lutetium ($6s^2\ 5d^1$). The results on the scandium compounds (hydride, oxide, fluoride and chloride) using the REP-SCF/RCI method compared very favorably with the results of other pseudopotential calculations and to sophisticated all-electron calculations. This also included the "state of art" calculations of Bauschlicher[159,173,174] which would be impractical for diatomic molecules containing heavy elements.

For lutetium, there are no previous calculations and only limited experimental data (Tables XVI-XVIII, pp.116-118). The results that are available agree well with the results from the present calculations. Therefore, it seems every reason to expect that the results on the compounds of lawrencium are also reasonable.

In the case of lawrencium, of course, there are no experimental results. However, the calculations show that lawrencium compounds contain properties surprisingly close to the corresponding ones of lutetium. This finding fully substantiates the idea that the bonding in the compounds of the transuranium elements will be very similar to that in the corresponding rare earth compounds.

The calculations show that there is a gradual increase in the relativistic effects in going from scandium to lawrencium. Because the n*s*-electrons are so shallow (although slightly deeper than the (n-1)*d*-electrons), there is a considerable increase in participation of the *s*-orbitals in bonding from scandium to lawrencium. In contrast, a decrease of *d*-orbitals in bonding from scandium to lawrencium is seen. These phenomena can be explained as a manifestation of the relativistic shielding of the valence *d*-orbitals which causes their orbital energies to be shallower and allows them to participate less in bonding while the deeper *s*-orbitals penetrate more in bonding in the lawrencium compounds compared to the bonding in corresponding compounds of scandium.

These calculations which represent the first attempt to systematically treat molecules containing atoms heavier than bismuth (Z=83) are encouraging enough to warrant extension to other molecules. The most obvious step to take in the future is to build into the computer programs the ability to treat the open shells containing *f*-electrons. It would also be advisable to introduce more flexibility to treat the ground state SCF calculation by using the CASSCF (Complete

Active Space Self Consistent Field) method. Calculations of this type have recently been reported for some of the lighter elements.

In order to perform calculations on the lawrencium compounds using this method, it is necessary to have some idea of bond distances. Also, in deciding the exchange parameters for these molecules, it is necessary to have some idea of charge densities on some model compounds such as those obtained in the present work.

The present results can be used to obtain parameters for some of the less sophisticated calculations such as the Dirac-Fock Xα method. The diatomic potential energy curves produced in the present work can also be used in setting up Monte Carlo or molecular dynamics calculation on the properties of solids containing the heavier elements.

LIST OF REFERENCES

LIST OF REFERENCES

1. G. T. Seaborg, "The Transuranium Elements," Yale University Press, Connecticut, pp. 2-3, 1958.

2. E. M. McMillan and P. Abelson, Phys. Rev. 57, 1185 (1940).

3. G. T. Seaborg, E. M. MacMillan, J. W. Kennedy and A. C. Wahl, in "The Transuranium Elements, Nat. Nucl. Energy Series IV," G. T. Seaborg, J. J. Katz and W. W. Manning, ed., McGraw-Hill, New York, pp.1-2, 1949.

4. F. L. Oetting, M. H. Rand and R. J. Ackermann, "The Chemical Thermodynamics of Actinide Elements and Compounds, Part I The Actinide Elements," International Atomic Aenergy Agency, Vienna, 1976.

5. E. K. Hulet, in "Lanthanide and Actinide Chemistry and Spectroscopy (ACS Symposium Series 131)," N. M. Edelstein, ed., American Chemical Society, Washcinton, D. C., pp.239-263, 1980.

6. G. T. Seaborg, J. J. Katz and W. M. Manning, "The Transuranium Elements, Nat. Nucl. Energy Series IV, 14B," McGraw-Hill, New York, 1943.

7. G. T. Seaborg and J. J. Katz, "The Actinide Elements, Nat. Nucl. Energy Series IV, 14A," McGraw-Hill, New York, 1954.

8. J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen & Co. Ltd., London, 1957.

9. G. T. Seaborg, "Man Made Transuranium Elements," Prentic Hall, New Jersy, 1963.

10. E. K. Hulet and D. D. Bode, in "Lanthanides and Actinides," K. W. Bagnall, ed., University Park Press, Baltimore, pp. 1-45, 1972.

11. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, New York, p. 1010, 1980.

12. L. Brewer, J. Opt. Soc. Am. 61, 1101 (1971).

13. K. L. Vander Sluis and L. J. Nugent, Phys. Rev. A 6, 86 (1972).

14. L. J. Nugent, K. L. Vander Sluis, B. Fricke and J. B. Mann, Phys. Rev. A 9, 2270 (1974).

15. J. P. Desclaux and B. Fricke, J. Physique 41, 943 (1980).

16. ibid. 1, pp. 112-159.

17. G. R. Choppin and J. Rydberg, "Nuclear Chemistry: Theory and Applications," Pergamon Press, Oxford, pp. 242-264, 1980.

18. L. Szasz, "Pseudopotential Theory of Atoms and Molecules," John Wiley and Sons, New York, 1985.

19. P. A. Christiansen, W. C. Ermler and K. S. Pitzer, Ann. Rev. Phys. Chem. 36, 407 (1985).

20. K. Balasubramanian and K. S. Pitzer, in "Ab initio Methods in Quantum Chemistry - I," K. P. Lawley, ed., John Wiley and Sons, New York, 1987, pp.287-319.

21. J. P. Desclaux and Y. K. Kim, J. Phys. B 8, 1177 (1975).

22. I. P. Grant, Adv. Phys. 19, 747 (1970).

23. H. Hellmann, J. Chem. Phys. 3, 61 (1935).

24. H. Hellmann, W. Kassatotschkin, J. Chem. Phys. 4, 325 (1936).

25. P. Gombas, Z. Phys. 94, 473 (1935).

26. J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

27. L. R. Kahn and W. A. Goddard III, J. Chem. Phys. 56, 2685 (1972).

28. C. F. Melius and W. A. Goddard III, Phys. Rev. A 10, 1528 (1974).

29. S. Topiol, A. Zunger and M. A. Ratner, Chem. Phys. Lett. 49, 367 (1977).

30. Y. S. Lee, W. C. Ermler and K. S. Pitzer, J. Chem. Phys. 67, 5861 (1977).

31. M. Krauss and W. J. Stevens, Ann. Rev. Phys. Chem. 35, 357 (1984).

32. L. R. Kahn, P. Baybutt and D. G. Truhlar, J. Chem. Phys. 65, 3826 (1976).

33. P. J. Hay, W. R. Wadt and L. R. Kahn, J. Chem. Phys. 68, 3059 (1978).

34. W. C. Ermler, Y. S. Lee, K. S. Pitzer and N. W. Winter, J. Chem. Phys. 69, 976 (1978).

35. W. R. Wadt, P. J. Hay and L. R. Kahn, J. Chem. Phys. 68, 1752 (1978).

36. G. B. Bachelet, D. R. Hamann and M. Schlüter, Phys. Rev. B 26, 4199 (1982).

37. A. Redondo, W. A. Goddard III and T. C. McGill, Phys. Rev. B 15, 5038, (1977).

38. P. A. Christiansen, Y. S. Lee and K. S. Pitzer, J. Chem. Phys. 71, 4445 (1979).

39. A. Zunger, J. Vac. Sci. Technol. 16, 1337 (1979).

40. W. C. Ermler, Y. S. Lee, P. A. Christiansen and K. S. Pitzer, Chem. Phys. Lett. 81, 70 (1981).

41. D. D. Koelling and B. N. Harmon, J. Phys. C 10, 3107 (1977); H. Gollish and L. Fritsche, Phys. Status Solidi B 86, 145 (1978); J. H. Wood and A. M. Boring, Phys. Rev. B 18, 2701 (1978).

42. L. H. Thomas, Nature 117, 514 (1926).

43. L. R. Kahn, P.J. Hay and R. D. Cowan, J. Chem. Phys. 68, 2386 (1978).

44. Y. S. Lee, W. C. Ermler, K. S. Pitzer and A. D. McLean, J. Chem. Phys. 70, 288 (1979).

45. W. C. Ermler, Y. S. Lee and K. S. Pitzer, J. Chem. Phys. 70, 293 (1979).

46. G. Das and A. C. Wahl, J. Chem. Phys. 64, 4672 (1971); 69, 53 (1978).

47. J. S. Cohen, W. R. Wadt and P. J. Hay, J. Chem. Phys. 71, 2955 (1979).

48. P. J. Hay, W. R. Wadt, L. R. Kahn, R. C. Raffenetti and D. H. Phillips, J. Chem. Phys. 71, 1767 (1979).

49. S. N. Datta, C. S. Ewig and J. R. Van Wazer, Chem. Phys. Lett. 57, 83 (1978).

50. H. Basch and S. Topiol, J. Chem. Phys. 71, 802 (1979).

51. Y. S. Lee, W. C. Ermler and K. S. Pitzer, J. Chem. Phys. 73, 360 (1980).

52. P. A. Christiansen and K. S. Pitzer, J. Chem. Phys. 73, 5160 (1980).

53. P. A. Christiansen and K. S. Pitzer, J. Chem. Phys. 74, 1162 (1981).

54. P. A. Christiansen, K. Balasubramanian and K. S. Pitzer, J. Chem. Phys. 76, 5087 (1982).

55. P. A. Christiansen, J. Chem. Phys. 79, 2928 (1983).

56. K. Balasubranmanian and K. S. Pitzer, J. Chem. Phys. 78, 321 (1983).

57. K. Balasubranmanian and K. S. Pitzer, J. Phys. Chem. 87, 4857 (1983).

58. K. Balasubranmanian and K. S. Pitzer, Chem. Phys. Lett. 100, 273 (1983).

59. P. A. Christiansen, Chem. Phys. Lett. 109, 145 (1984).

60. K. Balasubranmanian and K. S. Pitzer, J. Phys. Chem. 88, 1146 (1984).

61. K. Balasubranmanian and K. S. Pitzer, J. Mol. Specrtrosc. 103, 105 (1984).

62. K. Balasubramanian, J. Phys. Chem. 88, 5759 (1984).

63. K. Balasubramanian, J. Chem. Phys. 82, 3741 (1985).

64. K. Balasubramanian, J. Chem. Phys. 83, 2311 (1985).

65. K. Balasubranmanian, Chem. Phys. Lett. 114, 201 (1985).

66. D. A. Chapman, K. Balasubranmanian and S. H. Lin, Chem. Phys. Lett. 118, 192 (1985).

67. K. Balasubranmanian and K. S. Pitzer, J. Mol. Specrtrosc. 110, 339 (1985).

68. K. Balasubramanian, J. Chem. Phys. 85, 1443 (1986).

69. K. Balasubranmanian, J. Mol. Specrtrosc. 115, 258 (1986).

70. K. Balasubranmanian, J. Phys. Chem. 90, 1037 (1986).

71. K. Balasubramanian, Chem. Phys. Lett. 127, 324 (1986).

72. K. Balasubramanian, M. Han and M. Z. Liao, J. Chem. Phys. 86, 4979 (1987).

73. K. Balasubramanian, N. Tanpipat and J. E. Bloor, J. Mol. Spect. 124, 458 (1978).

74. P. Pyykkö, Physica Scripta, 20, 647 (1979).

75. W. R. Wadt, J. Chem. Phys. 86, 339 (1987).

76. M. H. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross and W. C. Ermler, J. Chem. Phys. 84, 6840 (1986).

77. L. F. Pacios and P. A. Christiansen, J. Chem. Phys. 82, 2664 (1985).

78. M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

79. B. J. Austin, V. Heine and L. J. Sham, Phys. Rev. 127, 276 (1962).

80. J. D. Weeks and S. A. Rice, J. Chem. Phys. 49, 2741 (1968).

81. J. D. Weeks, A. Hazi and S. A. Rice, Adv. Chem. Phys. 16, 283 (1969).

82. J. N. Bardley, Case Stud. At. Phys. 4, 299 (1974).

83. L. Szasz and C. Brown, J. Chem. Phys. 63, 4560 (1975).

84. I. V. Abarenkov and V. Heine, Philos. Mag. 12, 529 (1965).

85. A. O. E. Animalu and V. Heine, Philos. Mag. 12, 1249 (1965).

86. L. Szasz and G. McGinn, J. Chem. Phys. 42, 2363 (1965).

87. L. Szasz and G. McGinn, J. Chem. Phys. 45, 2898 (1966).

88. G. Simons and A. Mazzioti, J. Chem. Phys. 52, 2449 (1970).

89. G. Simons, J. Chem. Phys. 55, 756 (1971).

90. T. C. Chang, P. Habitz, B. Pittel and W. H. E. Schwarz, Theor. Chim. Acta, 34, 263 (1974).

91. M. E. Schwartz and J. D. Switalski, J. Chem. Phys. 57, 4125 (1972).

92. M. E. Schwartz and J. D. Switalski, J. Chem. Phys. 57, 4132 (1972).

93. V. Bonifacic and S. Huzinaga, J. Chem. Phys. 60, 2779 (1974).

94. V. Bonifacic and S. Huzinaga, J. Chem. Phys. 62, 1507 (1975).

95. V. Bonifacic and S. Huzinaga, J. Chem. Phys. 62, 1509 (1975).

96. V. Bonifacic and S. Huzinaga, J. Chem. Phys. 64, 956 (1976).

97. G. Höjer and J. Chung, Int. J. Quantum Chem. 14, 623 (1978).

98. R. N. Dixon and J. M. V. Hugo, Mol. Phys. 29, 953 (1975).

99. R. N. Dixon, P. W. Tasker and G. G. Balint-Kurti, Mol. Phys. 34, 1455 (1977).

100. C. S. Ewig, J. R. Van Wazer, J. Chem. Phys. 63, 4035 (1975).

101. Y. Sakai, J. Chem. Phys. 75, 1303 (1981).

102. U. Wahlgren, Chem. Phys. 29, 231 (1978).

103. U. Wahlgren, Chem. Phys. 32, 215 (1978).

104. O. Gropen, U. Wahlgren and L. Pettersson, Chem. Phys. 66, 453 (1982).

105. O. Gropen, U. Wahlgren and L. Pettersson, Chem. Phys. 66, 459 (1982).

106. L. Pettersson and U. Wahlgren, Chem. Phys. 69, 185 (1982).

107. Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, J. Comp. Chem. 8, 226 (1987).

108. Y. Sakai, E. Miyoshi, M. Klobukowski and S. Huzinaga, J. Comp. Chem. 8, 256 (1987).

109. W. A. Goddard III, Phys. Rev. 174, 659 (1968).

110. W. A. Goddard III, Phys. Rev. 157, 73 (1967).

111. W. A. Goddard III, Phys. Rev. 157, 81 (1967).

112. W. A. Goddard III, Phys. Rev. 169, 120 (1968).

113. L. R. Kahn and W. A. Goddard III, Chem. Phys. Lett. 2, 667 (1968).

114. C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3342 (1972).

115. C. F. Melius and W. A. Goddard III, J. Chem. Phys. 56, 3348 (1972).

116. C. F. Fischer, Comp. Phys. Commun. 1, 151 (1969).

117. P. Durand and J. C. Barthelat, Theor. Chim. Acta 38, 283 (1975).

118. A. K. Rappe, T. A. Smedley and W. A. Goddard III, J. Phys. Chem. 85, 1662 (1981).

119. J. C. Barthelat, P. Durand and A. Serafini, Mol. Phys. 33, 159 (1977).

120. C. F. Melius, B. D. Olafson and W. A. Goddard III, Chem. Phys. Lett. 28, 457 (1974).

121. S. Topiol, J. W. Moskowitz and C. F. Melius, J. Chem. Phys. 68, 2364 (1978).

122. J. P. Desclaux, Comput. Phys. Commun. 9, 31 (1975).

123. J. P. Desclaux, in "Relativistic Effects in Atomic Structure Calculatuions: An Introduction," Nato Adv. Study Inst. Ser., Ser. B, Vol. 18, pp. 367-278, (1976).

124. W. J. Stevens and M. Krauss, Chem. Phys. Lett. 86, 320 (1982).

125. W. J. Stevens and M. Krauss, J. Chem. Phys. 76, 3834 (1982).

126. Y. S. Lee, Ph.D. Thesis, University of California, Berkeley, CA (1977).

127. W. H. E. Schwarz, in "Relativistic Effects in Atoms, Molecules and Solids", G. Malli, ed., Plenum, New York, p. 518, 1982.

128. R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am. 66, 1010 (1976).

129. J. S. Cohen, W. R. Wadt and P. J. Hay, J. Chem. Phys. 1, 2955 (1979).

130. P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 270 (1985).

131. W. R. Wadt and P. J. Hay, J. Chem. Phys. 82, 284 (1985).

132. P. J. Hay and W. R. Wadt, J. Chem. Phys. 82, 299 (1985).

133. W. R. Wadt and P. J. Hay and L. R. Kahn, J. Chem. Phys. 68, 3059 (1978).

134. P. Hafner and W. H. E. Schwarz, Chem. Phys. Lett. 65, 537 (1979).

135. P. Hafner and W. H. E. Schwarz, J. Phys. B: At. Mol. Phys. 11, 217 (1978).

136. M. Esser, W. Butscher and W. H. E. Schwarz, Chem. Phys. Lett. 71, 539 (1981).

137. P. Hafner, P. Habitz, Y. Ishikawa, E. Wechsel-Trakowski and W. H. E. Schwarz, Chem. Phys. Lett. 80, 311 (1981).

138. W. H. E. Schwarz and H. Wallmeier, Mol. Phys. 46, 1045 (1982).

139. W. H. E. Schwarz and H. Wallmeier, Chem. Phys. Lett. 85, 94 (1982).

140. F. Mark and W. H. E. Schwarz, Phys. Rev. Lett. 48, 673 (1982).

141. F. Mark, C. Marian and W. H. E. Schwarz, Mol. Phys. 53, 535 (1984).

142. W. H. E. Schwarz and S. Y. Chu, Mol. Phys. 50, 603 (1983).

143. M. Esser, Int. J. Quantum Chem. 26, 313 (1984).

144. A. Szabo and N. S. Ostlund, in "Modern Quantum Chemistry," Macmillan Publishing Company, New York, pp. 231-269, 19882.

145. G. Herzberg, "Molecular Spectra and Molecular Sturcture, I. Spectra of Diatomic Molecules," Van Nostrand Reinhold Company, New York, 1950.

146. P. Cade and W. Huo, J. Chem. Phys. 47, 649 (1967).

147. K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure IV, Constants of Diatomic Molecules," van Nostra and Molecular Structure Company, New York, 1979.

148. C. E. Moore, "Atomic Energy Lefels," Natl. Bur. Stand. (US) 467 (1949).

149. P. R. Scott and W. G. Richards, J. Phys. B 7, 500 (1974).

150. P. R. Scott and W. G. Richards, "Molecular Spectroscopy Vol. 4: A Review of the Literature published during 1974 and early 1975," The Chemical Society, Burlington House, London pp.2-95 (1976).

151. G. Das, J. Chem. Phys. 74, 5766 (1981).

152. C. W. Bauschlicher, Jr. and S. P. Walch, J. Chem. Phys. 76, 4560 (1982).

153. a). J. Anglada, P. J. Bruna, S. D. Peyerimhoff and R. J. Buenker, J. Molecular Structure 93, 199 (1983); b). S. D. Peyerimhoff, Faraday Symp. Chem. Soc. 19, 63 (1984).

154. A. E. Alvarado-Swaisgood and J. F. Harrison, J. Phys. Chem. 89, 5198 (1985).

155. D. P. Chong, S. R. Langhoff, C. W. Bauschlicher, Jr., S. P. Walch and H. Partridge, J. Chem. Phys. 85, 2850 (1986).

156. S. Huzinaga, M. Klobukowski and Y. Sakai, J. Phys. Chem. 88, 4880 (1984).

157. J. Andzelm, E. Radzio, Z. Barandiaran and L. Seijo, J. Chem. Phys. 83, 4565 (1985).

158. Y. Sakai and S. Huzinaga, J. Chem. Phys. 76, 2537, 2552 (1982).

159. C. W. Bauschlicher,Jr. and S. R. Langhoff, J. Chem. Phys. 85, 5936 (1986).

160. M. Dolg, U. Wedig, H. Stoll and H. Preuss, J. Chem. Phys. 86, 2123 (1987).

161. J. F. Harrison, J. Phys. Chem. 87, 1312 (1983).

162. K. D. Carlson and C. Moser, J. Phys. 46, 35 (1967).

163. K. F. Zmbov and J. L. Margrave, Adv. Chem. Series 72, 267 (1968).

164. P. Pyykkö, J. G. Snijders and E. J. Baerends, Chem. Phys. Lett. 83, 432 (1981).

165. B. C. Laskowski and J. R. Stallcop, J. Chem. Phys. 74, 4883 (1981).

166. G. H. Jeung, J. P. Malrieu and J. P. Daudey, J. Chem. Phys. 77, 3571 (1982).

167. B. C. Laskowski, S. P. Walch and P. A. Christiansen, J. Chem. Phys. 78, 6824 (1983).

168. C. H. Jeung, F. Spiegelmann, J. P. Daudey and J. P. Malrieu, J. Phys. B 16, 2659 (1983).

169. T. Ziegler, J. G. Snijders and E. J. Baerends, J. Chem. Phys. 74, 1271 (1981).

170. R. E. Olsen, M. Kimura and H. Sato, Phys. Rev. A 30, 1692 (1984).

171. M. Pèlissier and E. R. Davidson, Int. J. Quantum Chem. 25, 723 (1984).

172. B. C. Laskowski, S. R. Langhoff and P. E. M. Siegbahn, Int. J. Quantum Chem. 23, 483 (1983).

173. S. R. Langhoff and C. W. Bauschlicher, Jr., in "Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules," R. J. Bartlett, ed., D. Reidel Publishing Company, pp. 357-??, 1985.

174. S. P. Walch and C. W. Bauschlicher, Jr., E. M. Siegbahn and H. Partridge, Chem. Phys. Lett. 92, 54 (1982).

175. B. C. Laskowski and S. R. Langhoff, Chem. Phys. Lett. 92, 49 (1982).

176. H. Gollisch, J. Phys. B 15, 2569 (1982).

177. L. Von Szentpaly, P. Fuentealba, H. Preuss and H. Stoll, Chem. Phys. Lett. 93, 555 (1982).

178. D. Hohl and N. Rösch, Inorg. Chem. 25, 2711 (1986).

179. C. J. Nelin and C. W. Bauschlicher, Chem. Phys. Lett. 118, 221 (1985).

180. T. Ziegler, J. Am. Chem. Soc. 105, 7543 (1983).

181. T. Ziegler, J. Am. Chem. Soc. 106, 5901 (1984).

182. T. Ziegler, J. Am. Chem. Soc. 107, 4453, (1985).

183. C. Y. Yang, R. Arratia-Perez and J. P. Lopez, Chem. Phys. Lett. 107, 112 (1984).

184. H. Chermette, G. Hollinger and P. Pertosa, Chem. Phys. Lett. 86, 170 (1982).

185. M. D. Braydich, B. E. Bursten, M. H. Chisholm and D. L. Clark, J. Am. Chem. Soc. 107, 4459 (1985).

186. A. Rosén, B. Fricke, T. Morovic and D. E. Ellis, J. Physique Coll.C4 40, 218 (1979).

187. S. W. Wang and K. S. Pitzer, J. Chem. Phys. 79, 3851 (1983).

188. C. M. Rohlfing, P. J. Hay and R. L. Martin, J. Chem. Phys. 85, 1447 (1986).

189. H. Basch, D. Cohen and S. Topiol, Isr. J. Chem. 19, 233 (1980).

190. J. J. Low and W. A. Goddard III, J. Am. Chem. Soc. 106, 6928 (1984).

191. H. Basch, Faraday Symp. Chem. Soc. 14 (Diatomic Met. Met. Clusters), 149 (1980).

192. E. Miyoshi, Y. Sakai and S. MOri, Chem. Phys. Lett. 113, 457 (1985).

193. B. Bigot and C. Minot, J. Am. Chem. Soc. 106, 6601 (1984).

194. H. Basch and D. Cohen, J. Am. Chem. Soc. 105, 3856 (1983).

195. H. Basch, Chem. Phys. Lett. 116, 58, (1985).

196. C. W. Bauschlicher, Jr., Chem. Phys. Lett. 115, 535, (1985).

197. C. M. Rohlfing and P. J. Hay, J. Chem. Phys. 83, 4641 (1985).

198. K. Kitaura, S. Obara and K. Morokuma, J. Am. Chem. Soc. 103, 2891 (1981).

199. S. Obara, K. Kitaura and K. Morokuma, J. Am. Chem. Soc. 106, 7482 (1984).

200. T. Ziegler, Inorg. Chem. 24, 1547 (1985).

201. J. O. Noell and P. J. Hay, J. Am. Chem. Soc. 104, 4578 (1982).

202. K. Kitaura, S. Obara and K. Morokuma, Chem. Phys. Lett. 77, 452 (1981).

203. J. O. Noell and P. J. Hay, Inorg. Chem. 21, 14 (1982).

204. P. J. Hay, J. Am. Chem. Soc. 103, 1390 (1981).

205. P. J. Hay, in "Relativistic Effects in Atoms, Molecules and Solids," G. L. Malli,Ed., Plenum Press, New York, pp. 383-401, 1983.

206. S. Larsson, L. F. Olsson and A. Rosén, Int. J. Quantum Chem. 25, 201 (1984).

207. I. B. Bersuker, S. S. Budnikov and B. A. Leizerov, Int. J. Quantum Chem. 11, 543 (1977).

208. H. Basch, P. S. Julienne, M. Krauss and M. E. Rosenkrantz, J. Chem. Phys. 73, 6247 (1980).

209. P. J. Hay, W. R. Wadt, L. R. Kahn and F. W. Bobrowicz, J. Chem. Phys. 69, 984 (1978).

210. M. Krauss, W. J. Stevens and H. Basch, J. Comput. Chem. 6, 287 (1985).

211. K. S. Pitzer, Int. J. Quantum Chem. 25, 131 (1984).

212. R. B. Ross and W. C. Ermler, J. Phys. Chem. 89, 5202 (1985).

213. P. A. Christiansen and W. C. Ermler, Mol. Phys. 55, 1109 (1985).

214. T. Ziegler, J. G. Snijders and E. J. Baerends, Chem. Phys. Lett. 75, 1 (1980).

215. S. P. Walch, C. W. Bauschlicher, Jr. and S. R. Langhoff, J. Chem. Phys. 85, 5900 (1986).

216. M. G. Ruffolo, S. Ossicini and F. Forstmann, J. Chem. Phys. 82, 3988 (1985).

217. T. Ziegler, in "Relativistic Effects in Atoms, Molecules and Solids," G. L. Malli, ed., Plenum, New York, pp. 421-436, 1983.

218. D. A. Kleier and W. R. Wadt, J. Am. Chem. Soc. 102, 6909 (1980).

219. W. R. Wadt, Appl. Phys. Lett. 34, 658 (1979).

220. P. S. Julienne, D. D. Konowalow, M. Krauss, M. E. Rosenkrantz and W. J. Stevens, Appl. Phys. Lett. 36, 132 (1980).

221. W. R. Wadt, J. Chem. Phys. 72, 2469 (1980).

222. J. G. Snijders, E. J. Baerends and P. Ros, Mol. Phys. 38, 1909 (1979).

223. K. C. Celestino and W. C. Ermler, J. Chem. Phys. 81, 1872 (1984).

224. P. J. Hay, T. H. Dunning, Jr. and R. C. Raffenetti, J. Chem. Phys. 65, 2679 (1976).

225. K. S. Pitzer and P. A. Christiansen, Chem. Phys. Lett. 77, 589 (1981).

226. E. Canadell, O. Eisenstein and J. Rubio, Organometallics 3, 759 (1984).

227. H. Basch, P. S. Julienne, M. Krauss and M. E. Rosenkrantz, J. Chem. Phys. 73, 6247 (1980).

228. H. Basch, W. J. Stevens and M. Krauss, J. Chem. Phys. 74, 2416 (1981).

229. G. Trinquier and R. Hoffmann, J. Phys. Chem. 88, 6696 (1984).

230. K. S. Pitzer and K. Balasubramanian, J. Phys. Chem. 86, 3068 (1982).

231. G. Pacchioni, Mol. Phys. 55, 211 (1985).

232. R. G. Egdell, M. Hotokka, L. Laaksonen, P. Pyykkö and J. G. Snijders, Chem. Phys. 72, 237 (1982).

233. W. R. Wadt, J. Am. Chem. Soc. 103, 6053 (1981).

234. M. Krauss and W. J. Stevens, J. Comput. Chem. 4, 127 (1983).

235. M. Krauss and W. J. Stevens, Chem. Phys. Lett. 99, 417 (1983).

236. I. A. Topol, B. I. Zhilinskii, Teor. Eksp. Khim. 20, 406 (1984).

237. W. R. Wadt and P. J. Hay, J. Am. Chem. Soc. 101, 5198 (1979).

238. A. Rosén and B. Fricke, Chem. Phys. Lett. 61, 75 (1979).

239. P. J. Hay, J. Chem. Phys. 79, 5469 (1983).

240. M. Boring and J. H. Wood, J. Chem. Phys. 71, 32 (1979).

241. M. Boring and J. H. Wood, J. Chem. Phys. 71, 392 (1979).

242. S. Larsson, J. S. Tse, J. L. Esquivel and A. Tang Kai, Chem. Phys. 89, 43 (1984).

243. C. R. A. Catlow and N. C. Pyper, J. Nucl. Mater 80, 110 (1979).

244. J. H. Wood, M. Boring and S. B. Woodruff, J. Chem. Phys. 74, 5225 (1981).

245. R. L. DeKock, E. J. Baerends, P. M. Boerrigter and J. G.

246. K. Tasumi and R. Hoffmann, Inorg. Chem. 19, 2656 (1980).

247. D. Hohl, D. E. Ellis and N. Rösch, Inorg. Chem. 127, 195 (1987).

248. R. G. Hayes and N. Edelstein, J. Am. Chem. Soc. 94, 8688 (1972).

249. P. Pyykkö and J. P. Desclaux, Chem. Phys. Lett. 50, 503, (1977).

250. R. Kugel, C. Williams, M. Fred, J. G. Malm, W. T. Carnall, J. C. Hindman, W. J. Child and L. S. Goodman, J. Chem. Phys. 65, 3486 (1976).

251. P. Pyykkö and J. P. Desclaux, Chem. Phys. 34, 261 (1978).

APPENDICES

APPENDIX A

TABLE XXVIII

PREVIOUS CALCULATIONS ON HEAVY ELEMENTS

Element (AN)	Compound	References
Cs (55)	CsH	164,165,166,167,168,169,170,171
	CsO	172,173
	CsOH	173
	CsF	173
	CsCl	169,173
	Cs_2	166,168,169,174,175,176
	Cs_2^+	166,177
	CsH^+	177
Ba (56)	BaH^+	164
	BaOH	173
	BaO	173
	BaCN	173
	BaNC	173
La (57)	LaH	74
Tm (69)	TmH	74

TABLE XXVIII (continued)

Element (AN)	Compound	References
Lu (71)	LuH	74
Hf (72)	HfX_4 (X = H, Cl)	164
	$Hf(BH_4)_4$	178
W (74)	WO	179
	$H_3W{\equiv}WH_3$	180
	$W_2Cl_4(PH_3)_4$	181
	$W_2(CO_2H)_4$	182
	$W_2(CO_2CF_3)_4$	182
	$W_2(PH_3)Cl_4$	182
	$W(CO)_6$	183
	$W(CO)_6^{6-}$	184
	$W_2(O_2CH)_4$	185
	WF_6	186
Pt (78)	PtH	50,187,188,189,190
	PtH^+	187
	Pt_2	189,191
	Pt_4	192
	Pt_n (n = 2-13)	193
	Pt(CO)	194,195,196,197
	$Pt(CO)_4$	197

TABLE XXVIII (continued)

Element (AN)	Compound	References
	$Pt(PH_3)_2$	190,198,199,200,201
	$PtH_2(PH_3)_2$	190,198,199,201,202
	$Pt(H)(CH_3)(PH_3)_2$	199
	$Pt[P(CH_3)_3]_2$	201
	$Pt[P(CH_3)_3]_2H_2$	201
	$Pt(PH_3)_2XY$ (X,Y = H,Cl)	203
	$PtCl_3(C_2H_4)^-$	204
	$PtCl_4^{2-}$	205,206
	$PtCl_6^{2-}$	207
	$Pt(NH_3)_2^{2+}$	208
	$Pt(NH_3)_2Cl_2$	208
	$Pt(NH_3)_3X$ (X = H_2O)	208
	$Pt(NH_3)_2XY$ (X Y = H_2O,OH^-)	208
Au (79)	AuH	169,209,210,211,212,213
	Au_2	44,45,214,169,176,191, 211,212,213,215
	Au_2^+	51,137
	AuCl	50,169,209,212
	AgAu	191,212
	AuRg (Rg = Ar, Kr, Xe)	216
	AuCs	169,176

TABLE XXVIII (continued)

Element (AN)	Compound	References
	$AuCu_2$	212
	$AuCH_3$	217
Hg (80)	HgH	209
	HgF	218
	Hg_2F_2	218
	HgCl	219,220
	$HgCl_2$	50,137,169,209,221
	Hg_2Cl_2	218
	HgBr	219
	$HgBr_2$	221
	HgI_2	222
	Hg_2	223,224
	Hg_2^+	169,223
	Hg_2^{+2}	169
	HgH^+	169
Tl (81)	TlH	51,52,54,124,225
	TlF	63
	Tl_2	53, 55,137
	Tl_2^+	53
	TlHg	223
	TlC_5H_5	226

TABLE XXVIII (continued)

Element (AN)	Compound	References
Pb (82)	PbH	60
	PbHe	208,227
	$PbHe^+$	208,227
	PbF	64
	PbO	49,57,228,229
	PbO^+	62
	PbS	51,68
	PbS^+	62
	PbSe	51
	$PbSe^+$	62
	PbXe	208
	$PbXe^+$	208
	Pb_2	56,137,230,231
	PbH_2	137
	$PbCl_2$	137
Bi (83)	BiH	65,69
	BiF	71
	Bi_2	59
	BiX_3 (X = Cl, Br, Cl)	232
Ac (89)	AcH	74

TABLE XXVIII (continued)

Element (AN)	Compound	References
Th (90)	ThO_2	233
	$Th(BH_4)_4$	178
U (92)	UH	234
	UH^-	234
	UH^+	234
	UF	234
	UF^-	234
	UO	235
	UO^+	235
	UF_4	236
	UF_5	237,238
	UF_6	48,239,240,241,242
	UF_6^+	48,239
	UF_6^-	48,239
	UO_2	243,244
	UO_2^+	244
	UO_2^{++}	233,240,241,244,245,246
	$U(BH_4)_4$	247
	$U(C_8H_8)_2$	248
Np (93)	$Np(C_8H_8)_2$	248

TABLE XXVIII (continued)

Element (AN)	Compound	References
Pu (94)	$Pu(C_8H_8)_2$	248
	PuO_2	243
	PuF_6	75,249
Lr (103)	LrH	74
element 104	$(104)H_4$	250
element 106	$(106)F_6$	186
	$(106)H_6$	251

** AN = Atomic number

APPENDIX B

NUMERICAL RELATIVISTIC EFFECTIVE POTENTIAL OF LUTETIUM (Z=71) WITH 3 ELECTRONS (6S2 5D1) IN THE VALENCE

POTENTIALS -1

-0.2211968D+00	0.5000000D-01	0.1408451D-03	259
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-1; from a grid point #1 to a grid point # 259

0.1513038D+09	0.1369015D+09	0.1238712D+09	0.1120945D+09	0.1014270D+09
0.9177514D+08	0.8304833D+08	0.7514111D+08	0.6799927D+08	0.6152535D+08
0.5567473D+08	0.5037863D+08	0.4558471D+08	0.4124996D+08	0.3732485D+08
0.3377546D+08	0.3056219D+08	0.2765522D+08	0.2502433D+08	0.2264596D+08
0.2048948D+08	0.1854303D+08	0.1677866D+08	0.1518248D+08	0.1373929D+08
0.1243242D+08	0.1125034D+08	0.1018045D+08	0.9212565D+07	0.8336545D+07
0.7543944D+07	0.6826708D+07	0.6177713D+07	0.5590316D+07	0.5059344D+07
0.4577993D+07	0.4142909D+07	0.3749401D+07	0.3392932D+07	0.3070450D+07
0.2778784D+07	0.2514740D+07	0.2275822D+07	0.2059596D+07	0.1863977D+07
0.1686946D+07	0.1526693D+07	0.1381734D+07	0.1250583D+07	0.1131681D+07
0.1024492D+07	0.9270333D+06	0.8391713D+06	0.7595220D+06	0.6874294D+06
0.6222312D+06	0.5632122D+06	0.5097940D+06	0.4614600D+06	0.4177130D+06
0.3781136D+06	0.3422906D+06	0.3098574D+06	0.2804988D+06	0.2539581D+06
0.2298878D+06	0.2081364D+06	0.1884402D+06	0.1706188D+06	0.1544772D+06
0.1398758D+06	0.1266514D+06	0.1146886D+06	0.1038527D+06	0.9405132D+05
0.8517429D+05	0.7713722D+05	0.6986585D+05	0.6327893D+05	0.5731886D+05
0.5192010D+05	0.4703394D+05	0.4261092D+05	0.3860389D+05	0.3497854D+05
0.3169170D+05	0.2871997D+05	0.2602564D+05	0.2358766D+05	0.2137852D+05
0.1937859D+05	0.1756689D+05	0.1592592D+05	0.1443956D+05	0.1309284D+05
0.1187470D+05	0.1076794D+05	0.9767522D+04	0.8860842D+04	0.8038367D+04
0.7294053D+04	0.6618785D+04	0.6007409D+04	0.5452614D+04	0.4950126D+04
0.4494606D+04	0.4081364D+04	0.3706903D+04	0.3367243D+04	0.3059146D+04
0.2779931D+04	0.2526309D+04	0.2296397D+04	0.2087930D+04	0.1898491D+04
0.1726741D+04	0.1570781D+04	0.1429168D+04	0.1300673D+04	0.1183891D+04
0.1077861D+04	0.9815607D+03	0.8940104D+03	0.8144939D+03	0.7422021D+03
0.6764588D+03	0.6167198D+03	0.5623477D+03	0.5129117D+03	0.4679021D+03
0.4269570D+03	0.3896873D+03	0.3557291D+03	0.3248176D+03	0.2966453D+03
0.2709723D+03	0.2475764D+03	0.2262376D+03	0.2067751D+03	0.1890215D+03
0.1728293D+03	0.1580238D+03	0.1445217D+03	0.1321828D+03	0.1209168D+03
0.1106077D+03	0.1011898D+03	0.9257472D+02	0.8469454D+02	0.7748385D+02
0.7088208D+02	0.6483914D+02	0.5930146D+02	0.5423643D+02	0.4958428D+02
0.4532797D+02	0.4142392D+02	0.3784392D+02	0.3456107D+02	0.3154959D+02
0.2878673D+02	0.2625191D+02	0.2392549D+02	0.2179102D+02	0.1983158D+02
0.1803366D+02	0.1638348D+02	0.1486824D+02	0.1347933D+02	0.1220344D+02
0.1103338D+02	0.9959957D+01	0.8975490D+01	0.8072855D+01	0.7245560D+01
0.6487384D+01	0.5793053D+01	0.5157477D+01	0.4575873D+01	0.4044346D+01
0.3558663D+01	0.3115873D+01	0.2712189D+01	0.2344992D+01	0.2012062D+01
0.1710574D+01	0.1438638D+01	0.1194528D+01	0.9765996D+00	0.7833286D+00
0.6135775D+00	0.4663274D+00	0.3405601D+00	0.2355551D+00	0.1505427D+00
0.8476613D-01	0.3718872D-01	0.6365462D-02	-0.9979213D-02	-0.1517637D-01
-0.1367747D-01	-0.1022998D-01	-0.7405013D-02	-0.5335848D-02	-0.3827114D-02
-0.2722902D-02	-0.1929050D-02	-0.1361534D-02	-0.9503302D-03	-0.6666973D-03
-0.4615478D-03	-0.3232643D-03	-0.2213423D-03	-0.1534620D-03	-0.1067311D-03
-0.7638217D-04	-0.4980517D-04	-0.3964351D-04	-0.2653020D-04	-0.1903770D-04

-0.1436333D-04	-0.1031422D-04	-0.8182712D-05	-0.4682056D-05	-0.3120236D-05
-0.1258533D-05	0.1261260D-05	0.3725159D-05	0.4490375D-05	0.8043329D-05
0.9411301D-05	0.1035069D-04	0.9370448D-05	0.6389034D-05	-0.5899105D-06
-0.1459367D-04	-0.3754414D-04	-0.7405322D-04	-0.1283511D-03	-0.2100822D-03
-0.3245849D-03	-0.4843072D-03	-0.7061268D-03	-0.9979397D-03	-0.1397241D-02
-0.1892661D-02	-0.2556041D-02	-0.3394811D-02	-0.4467885D-02	-0.5725862D-02
-0.7392725D-02	-0.9337436D-02	-0.1097570D-01	-0.1836148D-01	0.2583424D-02
-0.1774659D-01	-0.2015690D+00	-0.2025259D+00	-0.2034360D+00	

POTENTIALS 1

-0.1769989D+00	0.5000000D-01	0.1408451D-03	261
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j= 1; from a grid point #1 to a grid point # 261

0.2520380D+09	0.2280511D+09	0.2063474D+09	0.1867135D+09	0.1689387D+09
0.1528646D+09	0.1383178D+09	0.1251559D+09	0.1132439D+09	0.1024646D+09
0.9271721D+08	0.8389139D+08	0.7590879D+08	0.6868415D+08	0.6214799D+08
0.5623270D+08	0.5088247D+08	0.4603955D+08	0.4165838D+08	0.3769269D+08
0.3410627D+08	0.3086066D+08	0.2792336D+08	0.2526594D+08	0.2286157D+08
0.2068539D+08	0.1871763D+08	0.1693471D+08	0.1532449D+08	0.1386538D+08
0.1254563D+08	0.1135207D+08	0.1027128D+08	0.9293872D+07	0.8409369D+07
0.7608876D+07	0.6884757D+07	0.6229508D+07	0.5636676D+07	0.5099910D+07
0.4614777D+07	0.4175384D+07	0.3778102D+07	0.3418382D+07	0.3093047D+07
0.2798624D+07	0.2532269D+07	0.2291198D+07	0.2073130D+07	0.1875772D+07
0.1697259D+07	0.1535623D+07	0.1389483D+07	0.1257223D+07	0.1137522D+07
0.1029227D+07	0.9312643D+06	0.8425852D+06	0.7623854D+06	0.6897917D+06
0.6241193D+06	0.5647060D+06	0.5109187D+06	0.4622879D+06	0.4182734D+06
0.3784308D+06	0.3423976D+06	0.3098011D+06	0.2802917D+06	0.2535986D+06
0.2294501D+06	0.2075927D+06	0.1878229D+06	0.1699296D+06	0.1537480D+06
0.1391000D+06	0.1258472D+06	0.1138615D+06	0.1030088D+06	0.9319774D+05
0.8431588D+05	0.7628077D+05	0.6901208D+05	0.6243441D+05	0.5648362D+05
0.5110041D+05	0.4622668D+05	0.4182156D+05	0.3783382D+05	0.3422534D+05
0.3096149D+05	0.2800912D+05	0.2533668D+05	0.2291995D+05	0.2073297D+05
0.1875473D+05	0.1696447D+05	0.1534536D+05	0.1388069D+05	0.1255491D+05
0.1135592D+05	0.1027139D+05	0.9290200D+04	0.8402362D+04	0.7599277D+04
0.6872949D+04	0.6215693D+04	0.5621323D+04	0.5083459D+04	0.4596956D+04
0.4157072D+04	0.3759047D+04	0.3398992D+04	0.3073305D+04	0.2778811D+04
0.2512374D+04	0.2271410D+04	0.2053465D+04	0.1856351D+04	0.1678087D+04
0.1516825D+04	0.1371093D+04	0.1239191D+04	0.1119923D+04	0.1012139D+04
0.9146133D+03	0.8264579D+03	0.7467390D+03	0.6746498D+03	0.6094949D+03
0.5505697D+03	0.4973056D+03	0.4491624D+03	0.4056322D+03	0.3662900D+03
0.3307197D+03	0.2985873D+03	0.2695425D+03	0.2432852D+03	0.2195667D+03
0.1981347D+03	0.1787691D+03	0.1612748D+03	0.1454707D+03	0.1311964D+03
0.1183029D+03	0.1066567D+03	0.9614591D+02	0.8665473D+02	0.7808121D+02
0.7034749D+02	0.6336660D+02	0.5706588D+02	0.5138208D+02	0.4625440D+02
0.4163024D+02	0.3745998D+02	0.3369906D+02	0.3031223D+02	0.2725778D+02
0.2450624D+02	0.2202893D+02	0.1979752D+02	0.1778914D+02	0.1598249D+02
0.1435668D+02	0.1289492D+02	0.1158101D+02	0.1040064D+02	0.9339089D+01
0.8387923D+01	0.7532401D+01	0.6765678D+01	0.6077169D+01	0.5459838D+01
0.4905970D+01	0.4408945D+01	0.3962689D+01	0.3561822D+01	0.3201225D+01
0.2876355D+01	0.2583010D+01	0.2317389D+01	0.2076043D+01	0.1855789D+01
0.1654170D+01	0.1468116D+01	0.1296258D+01	0.1136183D+01	0.9869565D+00
0.8472440D+00	0.7166189D+00	0.5946538D+00	0.4816401D+00	0.3780557D+00
0.2847774D+00	0.2029823D+00	0.1339831D+00	0.7902575D-01	0.3894078D-01
0.1360386D-01	0.1286309D-02	-0.1951365D-02	-0.1477356D-02	-0.8356340D-03
-0.4146492D-03	-0.1514506D-03	0.1638860D-04	0.1173648D-03	0.1697686D-03
0.1982835D-03	0.2039151D-03	0.1976111D-03	0.1872120D-03	0.1731574D-03
0.1573490D-03	0.1420652D-03	0.1235084D-03	0.1118768D-03	0.9869761D-04
0.8432487D-04	0.7369117D-04	0.6581783D-04	0.5549139D-04	0.4894444D-04
0.4211287D-04	0.3679732D-04	0.3277371D-04	0.2926024D-04	0.2589418D-04
0.2483918D-04	0.2286383D-04	0.2279473D-04	0.2148765D-04	0.2038955D-04

0.1839416D-04	0.1324820D-04	0.5476414D-05	-0.8983770D-05	-0.3196418D-04
-0.6662241D-04	-0.1195690D-03	-0.1953516D-03	-0.3030749D-03	-0.4524531D-03
-0.6560556D-03	-0.9297014D-03	-0.1288777D-02	-0.1753824D-02	-0.2372880D-02
-0.3124534D-02	-0.3980569D-02	-0.5433029D-02	-0.7078893D-02	-0.6084820D-02
-0.1505598D-01	0.1569090D-01	0.1201242D-01	-0.1595708D+00	-0.1604124D+00
-0.1612081D+00				

POTENTIALS -2

-0.1618204D+00	0.5000000D-01	0.1408451D-03	263
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-2; from a grid point #1 to a grid point # 263

0.2520382D+09	0.2280476D+09	0.2063444D+09	0.1867040D+09	0.1689438D+09
0.1528612D+09	0.1383155D+09	0.1251491D+09	0.1132443D+09	0.1024641D+09
0.9271231D+08	0.8389149D+08	0.7590569D+08	0.6868280D+08	0.6214591D+08
0.5623197D+08	0.5088032D+08	0.4603801D+08	0.4165687D+08	0.3769201D+08
0.3410496D+08	0.3085885D+08	0.2792259D+08	0.2526483D+08	0.2286038D+08
0.2068461D+08	0.1871603D+08	0.1693520D+08	0.1532224D+08	0.1386513D+08
0.1254506D+08	0.1135095D+08	0.1027091D+08	0.9293029D+07	0.8408827D+07
0.7608233D+07	0.6884225D+07	0.6228953D+07	0.5636006D+07	0.5099632D+07
0.4614241D+07	0.4174981D+07	0.3777638D+07	0.3417957D+07	0.3092728D+07
0.2798230D+07	0.2531936D+07	0.2290872D+07	0.2072810D+07	0.1875484D+07
0.1696947D+07	0.1535369D+07	0.1389240D+07	0.1256989D+07	0.1137259D+07
0.1029031D+07	0.9310455D+06	0.8423947D+06	0.7621888D+06	0.6896171D+06
0.6239471D+06	0.5645280D+06	0.5107948D+06	0.4621211D+06	0.4181279D+06
0.3783058D+06	0.3422719D+06	0.3096783D+06	0.2801750D+06	0.2534931D+06
0.2293413D+06	0.2074969D+06	0.1877288D+06	0.1698440D+06	0.1536566D+06
0.1390210D+06	0.1257698D+06	0.1137884D+06	0.1029386D+06	0.9313228D+05
0.8425161D+05	0.7622094D+05	0.6895522D+05	0.6237955D+05	0.5643202D+05
0.5105088D+05	0.4618033D+05	0.4177602D+05	0.3779194D+05	0.3418448D+05
0.3092387D+05	0.2797188D+05	0.2530195D+05	0.2288698D+05	0.2070135D+05
0.1872474D+05	0.1693593D+05	0.1531785D+05	0.1385482D+05	0.1253060D+05
0.1133239D+05	0.1024898D+05	0.9268899D+04	0.8382128D+04	0.7580124D+04
0.6854511D+04	0.6198298D+04	0.5604564D+04	0.5067636D+04	0.4582139D+04
0.4142478D+04	0.3745499D+04	0.3385890D+04	0.3060959D+04	0.2766954D+04
0.2501146D+04	0.2260695D+04	0.2043247D+04	0.1846621D+04	0.1668832D+04
0.1507991D+04	0.1362642D+04	0.1231173D+04	0.1112325D+04	0.1004824D+04
0.9076667D+03	0.8198349D+03	0.7404179D+03	0.6686318D+03	0.6037495D+03
0.5451086D+03	0.4920575D+03	0.4441797D+03	0.4008774D+03	0.3617550D+03
0.3263893D+03	0.2944497D+03	0.2655942D+03	0.2395205D+03	0.2159674D+03
0.1946999D+03	0.1754883D+03	0.1581442D+03	0.1424680D+03	0.1283434D+03
0.1155637D+03	0.1040498D+03	0.9364885D+02	0.8426765D+02	0.7580175D+02
0.6816821D+02	0.6128256D+02	0.5507416D+02	0.4947806D+02	0.4443514D+02
0.3989085D+02	0.3579887D+02	0.3211117D+02	0.2879687D+02	0.2580893D+02
0.2312599D+02	0.2071126D+02	0.1854226D+02	0.1659404D+02	0.1484506D+02
0.1327636D+02	0.1187013D+02	0.1061034D+02	0.9483231D+01	0.8475125D+01
0.7574630D+01	0.6771987D+01	0.6055566D+01	0.5418436D+01	0.4852341D+01
0.4349579D+01	0.3903826D+01	0.3509135D+01	0.3159839D+01	0.2851066D+01
0.2577825D+01	0.2335732D+01	0.2120804D+01	0.1929053D+01	0.1756799D+01
0.1600711D+01	0.1457643D+01	0.1324572D+01	0.1199236D+01	0.1079206D+01
0.9629596D+00	0.8493258D+00	0.7378372D+00	0.6284494D+00	0.5220305D+00
0.4199513D+00	0.3240739D+00	0.2368078D+00	0.1606713D+00	0.9815842D-01
0.5122851D-01	0.2058321D-01	0.4921212D-02	0.1005772D-03	-0.7774941D-04
0.1790650D-03	0.3138693D-03	0.3744363D-03	0.4011855D-03	0.3973619D-03
0.3776626D-03	0.3521676D-03	0.3180813D-03	0.2878336D-03	0.2551873D-03
0.2233253D-03	0.1964168D-03	0.1725557D-03	0.1480098D-03	0.1280798D-03
0.1121386D-03	0.9250868D-04	0.8195921D-04	0.6799459D-04	0.5951640D-04
0.4996154D-04	0.4232822D-04	0.3678556D-04	0.3128449D-04	0.2729709D-04
0.2454988D-04	0.2260575D-04	0.2057127D-04	0.1994834D-04	0.1881993D-04
0.1750680D-04	0.1522751D-04	0.1003936D-04	0.2559348D-05	-0.1118542D-04

-0.3307115D-04	-0.6581546D-04	-0.1152651D-03	-0.1862019D-03	-0.2864366D-03
-0.4252954D-03	-0.6144730D-03	-0.8671168D-03	-0.1200543D-02	-0.1633871D-02
-0.2190147D-02	-0.2892597D-02	-0.3774870D-02	-0.4872453D-02	-0.6182101D-02
-0.7725629D-02	-0.9826093D-02	-0.1436885D-01	-0.2199314D-02	0.1500541D-01
-0.1460296D+00	-0.1467878D+00	-0.1475101D+00		

POTENTIALS 2

-0.1930510D+00	0.5000000D-01	0.1408451D-03	261
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=2; from a grid point #1 to a grid point # 261

0.3528073D+09	0.3192225D+09	0.2888443D+09	0.2613533D+09	0.2364864D+09
0.2139629D+09	0.1936174D+09	0.1751803D+09	0.1585117D+09	0.1434230D+09
0.1297740D+09	0.1174236D+09	0.1062462D+09	0.9613421D+08	0.8698615D+08
0.7870462D+08	0.7121478D+08	0.6443620D+08	0.5830296D+08	0.5275432D+08
0.4773278D+08	0.4318902D+08	0.3907850D+08	0.3535788D+08	0.3199352D+08
0.2894797D+08	0.2619133D+08	0.2369947D+08	0.2144241D+08	0.1940187D+08
0.1755462D+08	0.1588357D+08	0.1437141D+08	0.1300334D+08	0.1176519D+08
0.1064526D+08	0.9631751D+07	0.8714600D+07	0.7884998D+07	0.7134143D+07
0.6454878D+07	0.5840376D+07	0.5283900D+07	0.4781108D+07	0.4325555D+07
0.3913749D+07	0.3540989D+07	0.3203749D+07	0.2898601D+07	0.2622509D+07
0.2372725D+07	0.2146739D+07	0.1942127D+07	0.1757219D+07	0.1589753D+07
0.1438310D+07	0.1301234D+07	0.1177260D+07	0.1065060D+07	0.9635600D+06
0.8717313D+06	0.7886124D+06	0.7134623D+06	0.6454352D+06	0.5838998D+06
0.5282214D+06	0.4778447D+06	0.4322761D+06	0.3910431D+06	0.3537380D+06
0.3199834D+06	0.2894660D+06	0.2618226D+06	0.2368459D+06	0.2142283D+06
0.1937766D+06	0.1752722D+06	0.1585316D+06	0.1433882D+06	0.1296839D+06
0.1172939D+06	0.1060799D+06	0.9593765D+05	0.8676395D+05	0.7846224D+05
0.7095525D+05	0.6416395D+05	0.5802034D+05	0.5246506D+05	0.4743614D+05
0.4289223D+05	0.3877839D+05	0.3506007D+05	0.3169602D+05	0.2865305D+05
0.2590160D+05	0.2341285D+05	0.2116203D+05	0.1912725D+05	0.1728585D+05
0.1562191D+05	0.1411627D+05	0.1275546D+05	0.1152488D+05	0.1041194D+05
0.9406015D+04	0.8496367D+04	0.7673914D+04	0.6930574D+04	0.6258564D+04
0.5651075D+04	0.5101864D+04	0.4605645D+04	0.4157017D+04	0.3751671D+04
0.3385347D+04	0.3054220D+04	0.2755200D+04	0.2484926D+04	0.2240796D+04
0.2020222D+04	0.1821056D+04	0.1641101D+04	0.1478620D+04	0.1331900D+04
0.1199419D+04	0.1079807D+04	0.9718713D+03	0.8744024D+03	0.7864809D+03
0.7071193D+03	0.6355416D+03	0.5709625D+03	0.5127291D+03	0.4602116D+03
0.4128745D+03	0.3701910D+03	0.3317351D+03	0.2970900D+03	0.2658837D+03
0.2377791D+03	0.2124742D+03	0.1897087D+03	0.1692176D+03	0.1507966D+03
0.1342209D+03	0.1193397D+03	0.1059578D+03	0.9394892D+02	0.8316736D+02
0.7349449D+02	0.6482483D+02	0.5705306D+02	0.5009560D+02	0.4386906D+02
0.3830165D+02	0.3333016D+02	0.2888753D+02	0.2493329D+02	0.2140627D+02
0.1827299D+02	0.1548868D+02	0.1302040D+02	0.1083708D+02	0.8908531D+01
0.7210876D+01	0.5720311D+01	0.4416837D+01	0.3281495D+01	0.2298354D+01
0.1453374D+01	0.7316844D+00	0.1241721D+00	-0.3810194D+00	-0.7920703D+00
-0.1116909D+01	-0.1362613D+01	-0.1535061D+01	-0.1639696D+01	-0.1681931D+01
-0.1666628D+01	-0.1599074D+01	-0.1485771D+01	-0.1334216D+01	-0.1154018D+01
-0.9574989D+00	-0.7590817D+00	-0.5749066D+00	-0.4201932D+00	-0.3057735D+00
-0.2335808D+00	-0.1941708D+00	-0.1693335D+00	-0.1423805D+00	-0.1120107D+00
-0.8609176D-01	-0.6568654D-01	-0.4970477D-01	-0.3726824D-01	-0.2771062D-01
-0.2040496D-01	-0.1487515D-01	-0.1074456D-01	-0.7668124D-02	-0.5405234D-02
-0.3755822D-02	-0.2565395D-02	-0.1717680D-02	-0.1120825D-02	-0.6970647D-03
-0.4199621D-03	-0.2231524D-03	-0.9764388D-04	-0.1331395D-04	0.3701383D-04
0.5675700D-04	0.8186270D-04	0.8190125D-04	0.8336773D-04	0.7903904D-04
0.7331250D-04	0.6667371D-04	0.6081590D-04	0.5295159D-04	0.4759344D-04
0.4298362D-04	0.3729405D-04	0.3302473D-04	0.2979230D-04	0.2778171D-04
0.2512168D-04	0.2243785D-04	0.2064844D-04	0.1732479D-04	0.1361695D-04
0.5422477D-05	-0.6801445D-05	-0.2649849D-04	-0.5615414D-04	-0.1001566D-03
-0.1628215D-03	-0.2532314D-03	-0.3769804D-03	-0.5479841D-03	-0.7779301D-03

-0.1082654D-02	-0.1483994D-02	-0.1999749D-02	-0.2659358D-02	-0.3513850D-02
-0.4533502D-02	-0.5727611D-02	-0.7632982D-02	-0.9638753D-02	-0.8786092D-02
-0.1919722D-01	0.1603959D-01	0.7603232D-02	-0.1762550D+00	-0.1770338D+00
-0.1777753D+00				

POTENTIALS -3

-0.1860680D+00	0.5000000D-01	0.1408451D-03	261
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-3; from a grid point #1 to a grid point # 261

0.3528173D+09	0.3192218D+09	0.2888443D+09	0.2613541D+09	0.2364805D+09
0.2139738D+09	0.1936104D+09	0.1751855D+09	0.1585078D+09	0.1434269D+09
0.1297737D+09	0.1174224D+09	0.1062479D+09	0.9613462D+08	0.8698461D+08
0.7870717D+08	0.7121311D+08	0.6443770D+08	0.5830391D+08	0.5275367D+08
0.4773295D+08	0.4318951D+08	0.3907858D+08	0.3535820D+08	0.3199411D+08
0.2894699D+08	0.2619258D+08	0.2369902D+08	0.2144310D+08	0.1940170D+08
0.1755483D+08	0.1588378D+08	0.1437151D+08	0.1300320D+08	0.1176575D+08
0.1064509D+08	0.9631964D+07	0.8714747D+07	0.7884981D+07	0.7134307D+07
0.6454949D+07	0.5840317D+07	0.5284317D+07	0.4780850D+07	0.4325837D+07
0.3913763D+07	0.3541010D+07	0.3203853D+07	0.2898641D+07	0.2622580D+07
0.2372784D+07	0.2146755D+07	0.1942219D+07	0.1757266D+07	0.1589768D+07
0.1438351D+07	0.1301298D+07	0.1177281D+07	0.1065106D+07	0.9635908D+06
0.8717620D+06	0.7886536D+06	0.7134775D+06	0.6454801D+06	0.5839170D+06
0.5282437D+06	0.4778770D+06	0.4322948D+06	0.3910642D+06	0.3537583D+06
0.3200101D+06	0.2894728D+06	0.2618519D+06	0.2368575D+06	0.2142465D+06
0.1937933D+06	0.1752852D+06	0.1585459D+06	0.1434006D+06	0.1296979D+06
0.1173081D+06	0.1060879D+06	0.9595163D+05	0.8677214D+05	0.7847310D+05
0.7096486D+05	0.6417299D+05	0.5802898D+05	0.5247275D+05	0.4744486D+05
0.4289809D+05	0.3878652D+05	0.3506644D+05	0.3170219D+05	0.2865949D+05
0.2590718D+05	0.2341840D+05	0.2116776D+05	0.1913152D+05	0.1729081D+05
0.1562627D+05	0.1412077D+05	0.1275949D+05	0.1152865D+05	0.1041580D+05
0.9409446D+04	0.8499556D+04	0.7677493D+04	0.6933460D+04	0.6261397D+04
0.5653860D+04	0.5104567D+04	0.4608057D+04	0.4159445D+04	0.3753943D+04
0.3387475D+04	0.3056369D+04	0.2757095D+04	0.2486803D+04	0.2242595D+04
0.2021929D+04	0.1822679D+04	0.1642643D+04	0.1480098D+04	0.1333299D+04
0.1200784D+04	0.1081068D+04	0.9730917D+03	0.8755725D+03	0.7875718D+03
0.7081990D+03	0.6365445D+03	0.5719277D+03	0.5136536D+03	0.4610899D+03
0.4137099D+03	0.3709969D+03	0.3325121D+03	0.2978170D+03	0.2665880D+03
0.2384462D+03	0.2131174D+03	0.1903215D+03	0.1698058D+03	0.1513547D+03
0.1347677D+03	0.1198492D+03	0.1064518D+03	0.9442475D+02	0.8361920D+02
0.7393166D+02	0.6524040D+02	0.5745501D+02	0.5047996D+02	0.4423905D+02
0.3865570D+02	0.3367204D+02	0.2921583D+02	0.2524861D+02	0.2171046D+02
0.1856508D+02	0.1576984D+02	0.1329181D+02	0.1109796D+02	0.9160068D+01
0.7453178D+01	0.5953821D+01	0.4641456D+01	0.3497932D+01	0.2506526D+01
0.1653208D+01	0.9240174D+00	0.3075903D+00	-0.2055099D+00	-0.6251640D+00
-0.9589178D+00	-0.1213963D+01	-0.1396420D+01	-0.1512041D+01	-0.1566084D+01
-0.1563689D+01	-0.1510377D+01	-0.1412478D+01	-0.1277366D+01	-0.1114328D+01
-0.9348635D+00	-0.7523063D+00	-0.5813751D+00	-0.4359002D+00	-0.3257139D+00
-0.2528540D+00	-0.2095303D+00	-0.1801943D+00	-0.1505525D+00	-0.1191797D+00
-0.9254327D-01	-0.7140875D-01	-0.5471047D-01	-0.4159080D-01	-0.3137008D-01
-0.2347817D-01	-0.1743747D-01	-0.1282017D-01	-0.9351276D-02	-0.6745456D-02
-0.4812402D-02	-0.3386262D-02	-0.2354830D-02	-0.1600248D-02	-0.1062611D-02
-0.6928338D-03	-0.4264319D-03	-0.2478419D-03	-0.1248741D-03	-0.5130977D-04
0.1132242D-05	0.3268045D-04	0.4434855D-04	0.5347965D-04	0.5684181D-04
0.5420348D-04	0.5144655D-04	0.4717072D-04	0.4314588D-04	0.3718602D-04
0.3540602D-04	0.2916825D-04	0.2788561D-04	0.2508670D-04	0.2249832D-04
0.2065795D-04	0.1942259D-04	0.1699770D-04	0.1413132D-04	0.1015440D-04
0.2777475D-05	-0.7912539D-05	-0.2437821D-04	-0.5139923D-04	-0.8969247D-04
-0.1455401D-03	-0.2239639D-03	-0.3342777D-03	-0.4840580D-03	-0.6862773D-03
-0.9557570D-03	-0.1308255D-02	-0.1767604D-02	-0.2354980D-02	-0.3087596D-02

-0.4025920D-02 -0.5228703D-02 -0.6477860D-02 -0.8010619D-02 -0.1147063D-01
-0.1471275D-01 -0.8682421D-02 0.1840756D-01 -0.1692738D+00 -0.1700508D+00
-0.1707923D+00

POTENTIALS 3

-0.3148216D-01	0.5000000D-01	0.1408451D-03	279
(ε_j)	(step size)	(r_0)	(#grid points)

U^{REP} for j=3; from a grid point #1 to a grid point # 279

-0.1512163D+09 -0.1368308D+09 -0.1238097D+09 -0.1120259D+09 -0.1013673D+09
-0.9171798D+08 -0.8298998D+08 -0.7509731D+08 -0.6794246D+08 -0.6148029D+08
-0.5563210D+08 -0.5033404D+08 -0.4554390D+08 -0.4121263D+08 -0.3728823D+08
-0.3374013D+08 -0.3052900D+08 -0.2762399D+08 -0.2499471D+08 -0.2261622D+08
-0.2046375D+08 -0.1851660D+08 -0.1675396D+08 -0.1515884D+08 -0.1371751D+08
-0.1241106D+08 -0.1123070D+08 -0.1016107D+08 -0.9194330D+07 -0.8319124D+07
-0.7527785D+07 -0.6810865D+07 -0.6162938D+07 -0.5576227D+07 -0.5045591D+07
-0.4565355D+07 -0.4130969D+07 -0.3737537D+07 -0.3381927D+07 -0.3060074D+07
-0.2768675D+07 -0.2505322D+07 -0.2266773D+07 -0.2051068D+07 -0.1855800D+07
-0.1679143D+07 -0.1519336D+07 -0.1374709D+07 -0.1243849D+07 -0.1125452D+07
-0.1018328D+07 -0.9213682D+06 -0.8337033D+06 -0.7542450D+06 -0.6825401D+06
-0.6175387D+06 -0.5587126D+06 -0.5055530D+06 -0.4574086D+06 -0.4138742D+06
-0.3744488D+06 -0.3388132D+06 -0.3065432D+06 -0.2773624D+06 -0.2509441D+06
-0.2270568D+06 -0.2054267D+06 -0.1858741D+06 -0.1681612D+06 -0.1521463D+06
-0.1376680D+06 -0.1245487D+06 -0.1126804D+06 -0.1019553D+06 -0.9223898D+05
-0.8345432D+05 -0.7550252D+05 -0.6830835D+05 -0.6180042D+05 -0.5591271D+05
-0.5058389D+05 -0.4576300D+05 -0.4140307D+05 -0.3745320D+05 -0.3388817D+05
-0.3065306D+05 -0.2773491D+05 -0.2508661D+05 -0.2269638D+05 -0.2053189D+05
-0.1857337D+05 -0.1680134D+05 -0.1519905D+05 -0.1374862D+05 -0.1243682D+05
-0.1124950D+05 -0.1017608D+05 -0.9204379D+04 -0.8325730D+04 -0.7530494D+04
-0.6810876D+04 -0.6160567D+04 -0.5571680D+04 -0.5039402D+04 -0.4557324D+04
-0.4121754D+04 -0.3727405D+04 -0.3370851D+04 -0.3048266D+04 -0.2756445D+04
-0.2492458D+04 -0.2253783D+04 -0.2037749D+04 -0.1842446D+04 -0.1665746D+04
-0.1506025D+04 -0.1361337D+04 -0.1230722D+04 -0.1112458D+04 -0.1005577D+04
-0.9088080D+03 -0.8214166D+03 -0.7422889D+03 -0.6708151D+03 -0.6061188D+03
-0.5476571D+03 -0.4947769D+03 -0.4469771D+03 -0.4037515D+03 -0.3646709D+03
-0.3293408D+03 -0.2974034D+03 -0.2685363D+03 -0.2424275D+03 -0.2188431D+03
-0.1975228D+03 -0.1782525D+03 -0.1608347D+03 -0.1451009D+03 -0.1308785D+03
-0.1180293D+03 -0.1064209D+03 -0.9593334D+02 -0.8646013D+02 -0.7790290D+02
-0.7017631D+02 -0.6319100D+02 -0.5689832D+02 -0.5119969D+02 -0.4606538D+02
-0.4142995D+02 -0.3724404D+02 -0.3346741D+02 -0.3006037D+02 -0.2698473D+02
-0.2421386D+02 -0.2171206D+02 -0.1945761D+02 -0.1742553D+02 -0.1559372D+02
-0.1394324D+02 -0.1245624D+02 -0.1111807D+02 -0.9912920D+01 -0.8826967D+01
-0.7852474D+01 -0.6974835D+01 -0.6185736D+01 -0.5477998D+01 -0.4841359D+01
-0.4270988D+01 -0.3759483D+01 -0.3300972D+01 -0.2891068D+01 -0.2524341D+01
-0.2197111D+01 -0.1905363D+01 -0.1645708D+01 -0.1415007D+01 -0.1210845D+01
-0.1030071D+01 -0.8709785D+00 -0.7313329D+00 -0.6091389D+00 -0.5028184D+00
-0.4109068D+00 -0.3318759D+00 -0.2645131D+00 -0.2075399D+00 -0.1599584D+00
-0.1206321D+00 -0.8871908D-01 -0.6322931D-01 -0.4335673D-01 -0.2831583D-01
-0.1730862D-01 -0.9653670D-02 -0.4687390D-02 -0.1746358D-02 -0.2922872D-03
0.1897690D-03 0.1145191D-03 -0.1268888D-03 -0.3957348D-03 -0.4990791D-03
-0.4516746D-03 -0.3279340D-03 -0.1953593D-03 -0.1176727D-03 -0.6807296D-04
-0.3910295D-04 -0.2360222D-04 -0.1590429D-04 -0.8788899D-05 -0.7584884D-05
-0.4662117D-05 -0.2667880D-05 -0.8557260D-05 0.4453552D-06 -0.4008995D-05
-0.1864176D-05 -0.3825155D-05 -0.2644935D-05 -0.1686857D-05 -0.2771599D-05
-0.9833688D-06 -0.3161573D-05 -0.6350133D-06 -0.2046518D-05 -0.1470982D-05
-0.1839776D-05 -0.9374345D-06 -0.1648492D-05 -0.1653900D-05 -0.9782842D-06
-0.1113276D-05 -0.1167045D-05 -0.5798783D-06 -0.1070534D-05 -0.7857202D-06
-0.5803872D-06 -0.8983915D-06 -0.6322979D-06 -0.7453110D-06 -0.5442158D-06
-0.1057440D-05 -0.8143055D-06 -0.9718775D-06 -0.9968241D-06 -0.1001711D-05
-0.9239423D-06 -0.8071675D-06 -0.5098823D-06 0.3303124D-07 0.5434778D-06

0.1258054D-05	0.1997035D-05	0.2653876D-05	0.2775301D-05	0.2217098D-05
0.1556145D-06	-0.4357016D-05	-0.1228715D-04	-0.2552826D-04	-0.4658672D-04
-0.7719120D-04	-0.1191592D-03	-0.1884040D-03	-0.2727519D-03	-0.3352435D-03
-0.5909786D-03	-0.9178821D-03	0.7352494D-04	-0.2922934D-02	0.1026792D-01
0.5276246D-02	-0.2458317D-01	-0.2490516D-01	-0.2521283D-01	

POTENTIALS -4

-0.3148216D-01	0.5000000D-01	0.1408451D-03	279
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-4; from a grid point #1 to a grid point # 279

-0.1512135D+09	-0.1368324D+09	-0.1238102D+09	-0.1120279D+09	-0.1013651D+09
-0.9172167D+08	-0.8299148D+08	-0.7509083D+08	-0.6795015D+08	-0.6147840D+08
-0.5562925D+08	-0.5033696D+08	-0.4554648D+08	-0.4120943D+08	-0.3728993D+08
-0.3374062D+08	-0.3052907D+08	-0.2762436D+08	-0.2499495D+08	-0.2261638D+08
-0.2046422D+08	-0.1851587D+08	-0.1675541D+08	-0.1515877D+08	-0.1371721D+08
-0.1241213D+08	-0.1122990D+08	-0.1016166D+08	-0.9194574D+07	-0.8319204D+07
-0.7527842D+07	-0.6811165D+07	-0.6162940D+07	-0.5576422D+07	-0.5045721D+07
-0.4565401D+07	-0.4130925D+07	-0.3737876D+07	-0.3382009D+07	-0.3059978D+07
-0.2769045D+07	-0.2505275D+07	-0.2266811D+07	-0.2051138D+07	-0.1855909D+07
-0.1679220D+07	-0.1519399D+07	-0.1374762D+07	-0.1243903D+07	-0.1125519D+07
-0.1018369D+07	-0.9214260D+06	-0.8337200D+06	-0.7543470D+06	-0.6825465D+06
-0.6175921D+06	-0.5587446D+06	-0.5056077D+06	-0.4574249D+06	-0.4139130D+06
-0.3744871D+06	-0.3388397D+06	-0.3065741D+06	-0.2773881D+06	-0.2509751D+06
-0.2270743D+06	-0.2054573D+06	-0.1858947D+06	-0.1681763D+06	-0.1521809D+06
-0.1376746D+06	-0.1245745D+06	-0.1126955D+06	-0.1019732D+06	-0.9225564D+05
-0.8346596D+05	-0.7551961D+05	-0.6832199D+05	-0.6181354D+05	-0.5592428D+05
-0.5059669D+05	-0.4577391D+05	-0.4141148D+05	-0.3746817D+05	-0.3389374D+05
-0.3066547D+05	-0.2774133D+05	-0.2509599D+05	-0.2270420D+05	-0.2053940D+05
-0.1858033D+05	-0.1680849D+05	-0.1520524D+05	-0.1375503D+05	-0.1244235D+05
-0.1125535D+05	-0.1018137D+05	-0.9209379D+04	-0.8330352D+04	-0.7534968D+04
-0.6815542D+04	-0.6164772D+04	-0.5575471D+04	-0.5042923D+04	-0.4561095D+04
-0.4125071D+04	-0.3730578D+04	-0.3373994D+04	-0.3051042D+04	-0.2759241D+04
-0.2495117D+04	-0.2256230D+04	-0.2040128D+04	-0.1844750D+04	-0.1667736D+04
-0.1508173D+04	-0.1363267D+04	-0.1232528D+04	-0.1114188D+04	-0.1007228D+04
-0.9104224D+03	-0.8228674D+03	-0.7437463D+03	-0.6721335D+03	-0.6074275D+03
-0.5488574D+03	-0.4959411D+03	-0.4480722D+03	-0.4047953D+03	-0.3656625D+03
-0.3302766D+03	-0.2983038D+03	-0.2693656D+03	-0.2432427D+03	-0.2196112D+03
-0.1982416D+03	-0.1789361D+03	-0.1614900D+03	-0.1457132D+03	-0.1314632D+03
-0.1185861D+03	-0.1069449D+03	-0.9642981D+02	-0.8693214D+02	-0.7835000D+02
-0.7059134D+02	-0.6359993D+02	-0.5726835D+02	-0.5156030D+02	-0.4640046D+02
-0.4174985D+02	-0.3754298D+02	-0.3375062D+02	-0.3032744D+02	-0.2723651D+02
-0.2444988D+02	-0.2193488D+02	-0.1966661D+02	-0.1762193D+02	-0.1577727D+02
-0.1411566D+02	-0.1261709D+02	-0.1126903D+02	-0.1005160D+02	-0.8958787D+01
-0.7973108D+01	-0.7086874D+01	-0.6289824D+01	-0.5573185D+01	-0.4929717D+01
-0.4351355D+01	-0.3833060D+01	-0.3367908D+01	-0.2951573D+01	-0.2578955D+01
-0.2245892D+01	-0.1948792D+01	-0.1684091D+01	-0.1448644D+01	-0.1240025D+01
-0.1055242D+01	-0.8920517D+00	-0.7491051D+00	-0.6237359D+00	-0.5144822D+00
-0.4200937D+00	-0.3387751D+00	-0.2694923D+00	-0.2109137D+00	-0.1619383D+00
-0.1216038D+00	-0.8883931D-01	-0.6278056D-01	-0.4253015D-01	-0.2727471D-01
-0.1622681D-01	-0.8623550D-02	-0.3787757D-02	-0.1025360D-02	0.2256327D-03
0.4972079D-03	0.2980897D-03	-0.1007517D-03	-0.4245245D-03	-0.5630381D-03
-0.5258541D-03	-0.3818844D-03	-0.2253525D-03	-0.1368809D-03	-0.8154099D-04
-0.4640580D-04	-0.2825721D-04	-0.1719347D-04	-0.1184872D-04	-0.7524944D-05
-0.5598728D-05	-0.7737066D-05	0.1570612D-05	-0.6811171D-05	-0.3471502D-05
-0.1746829D-05	-0.3847617D-05	-0.7851518D-06	-0.4456947D-05	-0.1309247D-05
-0.2001116D-05	-0.2168859D-05	-0.1347267D-05	-0.1956609D-05	-0.1440916D-05
-0.1821430D-05	-0.9854303D-06	-0.9394411D-06	-0.1401111D-05	-0.1058594D-05
-0.8632661D-06	-0.1221557D-05	-0.6250611D-06	-0.8408617D-06	-0.1061689D-05
-0.5817264D-06	-0.9033871D-06	-0.8693704D-06	-0.9685091D-06	-0.7903799D-06

-0.1075460D-05	-0.9447160D-06	-0.1046672D-05	-0.9709699D-06	-0.9281050D-06
-0.7175415D-06	-0.5389197D-06	-0.5485651D-07	0.3083564D-06	0.1101599D-05
0.1709242D-05	0.2388457D-05	0.2794693D-05	0.2735290D-05	0.1685278D-05
-0.9751975D-06	-0.6171522D-05	-0.1517612D-04	-0.2961026D-04	-0.5167907D-04
-0.8412606D-04	-0.1303097D-03	-0.1941609D-03	-0.2804677D-03	-0.3973189D-03
-0.5496792D-03	-0.7100644D-03	-0.9016154D-03	-0.2456127D-02	0.3941723D-02
0.7644707D-02	-0.2458317D-01	-0.2490516D-01	-0.2521283D-01	

POTENTIALS 4

-0.2000380D-01	0.5000000D-01	0.1408451D-03	285
(ε_j)	(step size)	(r_0)	(#grid points)

U^{REP} for j=4; from a grid point #1 to a grid point # 285

-0.1956563D+09	-0.1765373D+09	-0.1592485D+09	-0.1436352D+09	-0.1295237D+09
-0.1167709D+09	-0.1053051D+09	-0.9491118D+08	-0.8553658D+08	-0.7706838D+08
-0.6943496D+08	-0.6253726D+08	-0.5631687D+08	-0.5070218D+08	-0.4563863D+08
-0.4107106D+08	-0.3695135D+08	-0.3323776D+08	-0.2988690D+08	-0.2687078D+08
-0.2414905D+08	-0.2169841D+08	-0.1949102D+08	-0.1750207D+08	-0.1571188D+08
-0.1410029D+08	-0.1264929D+08	-0.1134457D+08	-0.1017013D+08	-0.9115201D+07
-0.8165794D+07	-0.7313101D+07	-0.6546467D+07	-0.5858714D+07	-0.5240740D+07
-0.4686266D+07	-0.4188710D+07	-0.3742555D+07	-0.3342562D+07	-0.2984127D+07
-0.2663056D+07	-0.2375444D+07	-0.2118353D+07	-0.1887968D+07	-0.1682210D+07
-0.1498156D+07	-0.1333799D+07	-0.1187008D+07	-0.1055986D+07	-0.9390914D+06
-0.8348243D+06	-0.7420029D+06	-0.6591674D+06	-0.5854485D+06	-0.5199179D+06
-0.4615463D+06	-0.4096377D+06	-0.3635440D+06	-0.3225654D+06	-0.2861958D+06
-0.2538790D+06	-0.2252830D+06	-0.1998084D+06	-0.1773080D+06	-0.1573395D+06
-0.1396308D+06	-0.1239742D+06	-0.1100833D+06	-0.9779593D+05	-0.8691842D+05
-0.7729408D+05	-0.6875422D+05	-0.6123233D+05	-0.5453835D+05	-0.4864301D+05
-0.4340525D+05	-0.3877585D+05	-0.3467469D+05	-0.3104096D+05	-0.2782043D+05
-0.2496422D+05	-0.2243500D+05	-0.2018177D+05	-0.1818779D+05	-0.1640990D+05
-0.1483120D+05	-0.1342467D+05	-0.1216893D+05	-0.1105008D+05	-0.1004966D+05
-0.9153697D+04	-0.8353629D+04	-0.7632410D+04	-0.6987538D+04	-0.6404358D+04
-0.5880819D+04	-0.5406903D+04	-0.4978996D+04	-0.4590834D+04	-0.4238775D+04
-0.3918304D+04	-0.3627042D+04	-0.3360240D+04	-0.3116968D+04	-0.2893969D+04
-0.2689378D+04	-0.2501264D+04	-0.2328064D+04	-0.2168262D+04	-0.2020716D+04
-0.1884291D+04	-0.1757496D+04	-0.1640534D+04	-0.1531201D+04	-0.1430129D+04
-0.1335554D+04	-0.1247765D+04	-0.1165744D+04	-0.1089214D+04	-0.1017754D+04
-0.9509929D+03	-0.8885205D+03	-0.8301836D+03	-0.7754520D+03	-0.7243148D+03
-0.6763713D+03	-0.6314898D+03	-0.5893940D+03	-0.5499338D+03	-0.5129286D+03
-0.4782070D+03	-0.4456269D+03	-0.4150451D+03	-0.3863184D+03	-0.3593599D+03
-0.3340570D+03	-0.3102905D+03	-0.2879842D+03	-0.2670731D+03	-0.2474732D+03
-0.2291045D+03	-0.2119223D+03	-0.1958635D+03	-0.1808620D+03	-0.1668694D+03
-0.1538295D+03	-0.1416792D+03	-0.1303833D+03	-0.1198598D+03	-0.1100751D+03
-0.1009757D+03	-0.9250238D+02	-0.8461422D+02	-0.7726475D+02	-0.7042141D+02
-0.6404187D+02	-0.5810027D+02	-0.5257183D+02	-0.4743309D+02	-0.4266717D+02
-0.3825822D+02	-0.3419184D+02	-0.3045654D+02	-0.2703639D+02	-0.2392171D+02
-0.2109485D+02	-0.1854335D+02	-0.1624943D+02	-0.1419575D+02	-0.1236540D+02
-0.1073935D+02	-0.9299121D+01	-0.8027316D+01	-0.6906833D+01	-0.5921250D+01
-0.5056242D+01	-0.4298280D+01	-0.3635842D+01	-0.3057655D+01	-0.2555944D+01
-0.2120928D+01	-0.1746809D+01	-0.1426646D+01	-0.1154492D+01	-0.9252791D+00
-0.7339926D+00	-0.5759794D+00	-0.4468433D+00	-0.3426196D+00	-0.2594911D+00
-0.1940583D+00	-0.1432217D+00	-0.1043378D+00	-0.7487365D-01	-0.5300061D-01
-0.3691525D-01	-0.2532334D-01	-0.1707338D-01	-0.1131496D-01	-0.7381942D-02
-0.4729775D-02	-0.2989008D-02	-0.1855767D-02	-0.1130372D-02	-0.6878388D-03
-0.4178925D-03	-0.2361262D-03	-0.1506230D-03	-0.8255771D-04	-0.5270094D-04
-0.3120471D-04	-0.2030772D-04	-0.1353544D-04	-0.9865071D-05	-0.9646782D-05
-0.3284698D-05	-0.4395570D-05	-0.4049894D-05	-0.5742949D-05	-0.2630126D-05
-0.2434044D-05	-0.3749687D-05	-0.2155509D-05	-0.2780350D-05	-0.2467567D-05
-0.2409150D-05	-0.2358582D-05	-0.1886620D-05	-0.1945972D-05	-0.1624819D-05
-0.2346623D-05	-0.7981716D-06	-0.2310485D-05	-0.9657268D-06	-0.1134846D-05

-0.1140030D-05	-0.1123544D-05	-0.1317971D-05	-0.5597072D-06	-0.9959322D-06
-0.8390950D-06	-0.5991546D-06	-0.9090661D-06	-0.7294946D-06	-0.7236457D-06
-0.6849225D-06	-0.7910530D-06	-0.5272924D-06	-0.7324295D-06	-0.6951402D-06
0.9266309D-07	-0.3620920D-06	-0.5971612D-06	-0.5460140D-06	-0.6678985D-06
-0.7211463D-06	-0.7762459D-06	-0.7166561D-06	-0.6719120D-06	-0.3683806D-06
-0.6055919D-07	0.4810540D-06	0.1073995D-05	0.1701874D-05	0.2127751D-05
0.2206181D-05	0.1269830D-05	-0.1111153D-05	-0.5963439D-05	-0.1441691D-04
-0.2850044D-04	-0.4938264D-04	-0.7934702D-04	-0.1279659D-03	-0.1861358D-03
-0.2404035D-03	-0.4214318D-03	-0.6122792D-03	-0.2493704D-04	-0.2080625D-02
0.7651398D-02	0.3584632D-02	-0.1494715D-01	-0.1518052D-01	-0.1540378D-01

POTENTIALS -5

-0.2000379D-01	0.5000000D-01	0.1408451D-03	285
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-5; from a grid point #1 to a grid point # 285

-0.6558377D+07	-0.5971729D+07	-0.5415694D+07	-0.4918823D+07	-0.4504560D+07
-0.4078030D+07	-0.3703510D+07	-0.3366773D+07	-0.3066153D+07	-0.2785811D+07
-0.2534979D+07	-0.2306897D+07	-0.2101083D+07	-0.1911702D+07	-0.1742505D+07
-0.1586359D+07	-0.1445322D+07	-0.1319727D+07	-0.1202297D+07	-0.1096742D+07
-0.1000400D+07	-0.9138512D+06	-0.8340108D+06	-0.7623055D+06	-0.6966573D+06
-0.6364224D+06	-0.5830342D+06	-0.5323957D+06	-0.4880513D+06	-0.4469528D+06
-0.4091650D+06	-0.3753445D+06	-0.3442142D+06	-0.3157615D+06	-0.2899199D+06
-0.2663408D+06	-0.2445896D+06	-0.2251288D+06	-0.2069859D+06	-0.1904336D+06
-0.1755451D+06	-0.1616869D+06	-0.1490741D+06	-0.1375527D+06	-0.1270280D+06
-0.1171413D+06	-0.1084659D+06	-0.1001754D+06	-0.9271967D+05	-0.8585831D+05
-0.7950559D+05	-0.7372404D+05	-0.6835787D+05	-0.6344175D+05	-0.5891133D+05
-0.5475265D+05	-0.5084874D+05	-0.4735379D+05	-0.4403466D+05	-0.4103543D+05
-0.3821067D+05	-0.3563781D+05	-0.3323377D+05	-0.3102128D+05	-0.2895873D+05
-0.2706104D+05	-0.2528879D+05	-0.2364967D+05	-0.2212681D+05	-0.2071196D+05
-0.1939121D+05	-0.1816815D+05	-0.1703061D+05	-0.1596081D+05	-0.1497478D+05
-0.1404982D+05	-0.1318805D+05	-0.1238331D+05	-0.1163149D+05	-0.1092861D+05
-0.1027018D+05	-0.9657548D+04	-0.9078024D+04	-0.8541578D+04	-0.8034554D+04
-0.7560179D+04	-0.7117984D+04	-0.6699189D+04	-0.6308209D+04	-0.5940312D+04
-0.5594815D+04	-0.5270313D+04	-0.4964713D+04	-0.4678002D+04	-0.4407333D+04
-0.4153062D+04	-0.3913677D+04	-0.3688092D+04	-0.3475630D+04	-0.3275229D+04
-0.3086574D+04	-0.2908243D+04	-0.2740878D+04	-0.2581763D+04	-0.2432722D+04
-0.2291344D+04	-0.2158324D+04	-0.2032298D+04	-0.1913573D+04	-0.1801370D+04
-0.1695298D+04	-0.1595177D+04	-0.1500571D+04	-0.1411002D+04	-0.1326733D+04
-0.1246902D+04	-0.1171439D+04	-0.1100322D+04	-0.1033082D+04	-0.9695986D+03
-0.9096919D+03	-0.8531338D+03	-0.7998247D+03	-0.7494746D+03	-0.7020400D+03
-0.6573038D+03	-0.6151143D+03	-0.5753939D+03	-0.5379189D+03	-0.5026358D+03
-0.4693932D+03	-0.4380707D+03	-0.4085648D+03	-0.3808055D+03	-0.3546451D+03
-0.3300084D+03	-0.3068524D+03	-0.2850712D+03	-0.2645952D+03	-0.2453708D+03
-0.2273329D+03	-0.2104277D+03	-0.1946019D+03	-0.1798005D+03	-0.1659744D+03
-0.1530736D+03	-0.1410434D+03	-0.1298393D+03	-0.1194026D+03	-0.1096841D+03
-0.1006388D+03	-0.9221592D+02	-0.8437055D+02	-0.7705934D+02	-0.7024946D+02
-0.6390050D+02	-0.5798770D+02	-0.5248476D+02	-0.4737007D+02	-0.4262501D+02
-0.3823485D+02	-0.3418460D+02	-0.3046154D+02	-0.2705383D+02	-0.2394442D+02
-0.2112456D+02	-0.1857564D+02	-0.1628236D+02	-0.1422904D+02	-0.1239730D+02
-0.1076882D+02	-0.9326773D+01	-0.8052508D+01	-0.6929877D+01	-0.5942614D+01
-0.5076279D+01	-0.4317297D+01	-0.3654054D+01	-0.3075663D+01	-0.2573092D+01
-0.2138156D+01	-0.1763413D+01	-0.1442442D+01	-0.1169686D+01	-0.9394033D+00
-0.7470910D+00	-0.5877219D+00	-0.4573263D+00	-0.3517259D+00	-0.2672808D+00
-0.2005770D+00	-0.1486251D+00	-0.1086148D+00	-0.7828409D-01	-0.5565972D-01
-0.3893774D-01	-0.2679903D-01	-0.1817033D-01	-0.1210420D-01	-0.7920340D-02
-0.5108437D-02	-0.3238967D-02	-0.2011061D-02	-0.1262863D-02	-0.7440940D-03
-0.4468727D-03	-0.2746622D-03	-0.1563660D-03	-0.9296024D-04	-0.5899433D-04
-0.3093168D-04	-0.2105783D-04	-0.1486311D-04	-0.7919453D-05	-0.9564138D-05
-0.7101435D-06	-0.8258134D-05	-0.1180685D-05	-0.3779923D-05	-0.2735778D-05

-0.2586524D-05	-0.1856163D-05	-0.3130248D-05	-0.1675014D-05	-0.2628597D-05
-0.2152053D-05	-0.2187949D-05	-0.1729956D-05	-0.2122750D-05	-0.2255044D-05
-0.1264213D-05	-0.1817479D-05	-0.1471146D-05	-0.1565168D-05	-0.1565942D-05
-0.1069657D-05	-0.1114563D-05	-0.9500819D-06	-0.1079485D-05	-0.9318726D-06
-0.8022325D-06	-0.7821728D-06	-0.5599113D-06	-0.7579500D-06	-0.5947368D-06
-0.5861863D-06	-0.5621000D-06	-0.5701560D-06	-0.5167653D-06	-0.5810509D-06
-0.3843427D-06	-0.7041481D-06	-0.5047149D-06	-0.7672550D-06	-0.7337182D-06
-0.7364234D-06	-0.7082193D-06	-0.5521111D-06	-0.3500754D-06	-0.9877768D-07
0.4630863D-06	0.8930256D-06	0.1509614D-05	0.2052356D-05	0.2285341D-05
0.2022765D-05	0.6850982D-06	-0.2305930D-05	-0.7961029D-05	-0.1741816D-04
-0.3238339D-04	-0.5486627D-04	-0.8741186D-04	-0.1329874D-03	-0.1951713D-03
-0.2792261D-03	-0.3888820D-03	-0.5103147D-03	-0.6618522D-03	-0.1647442D-02
0.2836533D-02	0.5643810D-02	-0.1494714D-01	-0.1518051D-01	-0.1540377D-01

APPENDIX C

NUMERICAL RELATIVISTIC EFFECTIVE POTENTIAL OF LAWRENCIUM (Z=103) WITH 3 ELECTRONS (7S2 6D1) IN THE VALENCE

POTENTIALS -1

-0.2438858D+00	0.5000000D-01	0.1121395D-03	262
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-1; from a grid point #1 to a grid point # 262

0.4771094D+09	0.4316997D+09	0.3906193D+09	0.3534451D+09	0.3198092D+09
0.2893697D+09	0.2618417D+09	0.2369223D+09	0.2143688D+09	0.1939726D+09
0.1755116D+09	0.1588081D+09	0.1436985D+09	0.1300193D+09	0.1176484D+09
0.1064514D+09	0.9631905D+08	0.8715741D+08	0.7885754D+08	0.7135696D+08
0.6456369D+08	0.5841946D+08	0.5286103D+08	0.4782904D+08	0.4327818D+08
0.3915882D+08	0.3543258D+08	0.3205998D+08	0.2900894D+08	0.2624830D+08
0.2375033D+08	0.2148979D+08	0.1944472D+08	0.1759397D+08	0.1591956D+08
0.1440453D+08	0.1303346D+08	0.1179307D+08	0.1067072D+08	0.9654924D+07
0.8736233D+07	0.7904806D+07	0.7152173D+07	0.6471672D+07	0.5855577D+07
0.5298249D+07	0.4793999D+07	0.4337684D+07	0.3924805D+07	0.3551235D+07
0.3213214D+07	0.2907302D+07	0.2630664D+07	0.2380185D+07	0.2153688D+07
0.1948592D+07	0.1763123D+07	0.1595304D+07	0.1443423D+07	0.1306020D+07
0.1181684D+07	0.1069186D+07	0.9673980D+06	0.8752796D+06	0.7919701D+06
0.7165577D+06	0.6483451D+06	0.5865908D+06	0.5307468D+06	0.4802086D+06
0.4344817D+06	0.3931084D+06	0.3556732D+06	0.3217988D+06	0.2911488D+06
0.2634272D+06	0.2383362D+06	0.2156297D+06	0.1950960D+06	0.1765080D+06
0.1596932D+06	0.1444810D+06	0.1307157D+06	0.1182613D+06	0.1069915D+06
0.9679973D+05	0.8757005D+05	0.7922724D+05	0.7167416D+05	0.6484454D+05
0.5866220D+05	0.5306861D+05	0.4800964D+05	0.4343193D+05	0.3928948D+05
0.3554281D+05	0.3215239D+05	0.2908449D+05	0.2631138D+05	0.2379872D+05
0.2152916D+05	0.1947300D+05	0.1761507D+05	0.1593263D+05	0.1441135D+05
0.1303494D+05	0.1178985D+05	0.1066319D+05	0.9644297D+04	0.8722425D+04
0.7888587D+04	0.7134037D+04	0.6451624D+04	0.5834589D+04	0.5276030D+04
0.4771018D+04	0.4314086D+04	0.3900915D+04	0.3527093D+04	0.3189027D+04
0.2883171D+04	0.2606775D+04	0.2356459D+04	0.2130290D+04	0.1925719D+04
0.1740635D+04	0.1573345D+04	0.1421993D+04	0.1285173D+04	0.1161420D+04
0.1049546D+04	0.9483637D+03	0.8569111D+03	0.7741684D+03	0.6994308D+03
0.6318056D+03	0.5707167D+03	0.5154711D+03	0.4655282D+03	0.4204013D+03
0.3796018D+03	0.3427381D+03	0.3094181D+03	0.2793100D+03	0.2521065D+03
0.2275196D+03	0.2053153D+03	0.1852584D+03	0.1671287D+03	0.1507632D+03
0.1359813D+03	0.1226306D+03	0.1105765D+03	0.9969519D+02	0.8986990D+02
0.8100265D+02	0.7299907D+02	0.6577857D+02	0.5926121D+02	0.5338228D+02
0.4808164D+02	0.4329902D+02	0.3898741D+02	0.3510085D+02	0.3159595D+02
0.2843807D+02	0.2559236D+02	0.2302800D+02	0.2071793D+02	0.1863713D+02
0.1676260D+02	0.1507409D+02	0.1355368D+02	0.1218343D+02	0.1094914D+02
0.9836408D+01	0.8833432D+01	0.7927866D+01	0.7110747D+01	0.6371874D+01
0.5703159D+01	0.5097103D+01	0.4546805D+01	0.4046158D+01	0.3589677D+01
0.3172371D+01	0.2790536D+01	0.2439481D+01	0.2117009D+01	0.1820181D+01
0.1546663D+01	0.1295260D+01	0.1064771D+01	0.8546807D+00	0.6648494D+00
0.4957503D+00	0.3479884D+00	0.2227736D+00	0.1211763D+00	0.4420748D-01
-0.7788864D-02	-0.3600499D-01	-0.4413515D-01	-0.3911180D-01	-0.3003496D-01
-0.2246111D-01	-0.1675616D-01	-0.1245055D-01	-0.9210569D-02	-0.6787260D-02
-0.4977653D-02	-0.3643935D-02	-0.2653378D-02	-0.1928740D-02	-0.1398091D-02
-0.1008007D-02	-0.7299781D-03	-0.5247242D-03	-0.3773048D-03	-0.2742670D-03
-0.1934406D-03	-0.1424359D-03	-0.1037679D-03	-0.7338118D-04	-0.5232661D-04

-0.3749026D-04	-0.2672862D-04	-0.1767463D-04	-0.9384765D-05	-0.5634204D-05
0.1524879D-05	0.4966467D-05	0.8705280D-05	0.1307444D-04	0.1505209D-04
0.1680776D-04	0.1476435D-04	0.1006280D-04	-0.1767029D-05	-0.2050481D-04
-0.5387637D-04	-0.1025196D-03	-0.1750444D-03	-0.2809852D-03	-0.4303088D-03
-0.6349886D-03	-0.9128282D-03	-0.1283503D-02	-0.1769175D-02	-0.2398860D-02
-0.3210095D-02	-0.4230099D-02	-0.5463344D-02	-0.7127497D-02	-0.9015742D-02
-0.1039208D-01	-0.1867172D-01	0.6365633D-02	0.2138399D-01	-0.2198247D+00
-0.2198915D+00	-0.2200244D+00			

POTENTIALS 1

-0.1759960D+00	0.5000000D-01	0.1121395D-03	266
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=1; from a grid point #1 to a grid point # 266

0.3975769D+09	0.3597426D+09	0.3255000D+09	0.2945263D+09	0.2664987D+09
0.2411291D+09	0.2181937D+09	0.1974241D+09	0.1786329D+09	0.1616361D+09
0.1462524D+09	0.1323336D+09	0.1197387D+09	0.1083450D+09	0.9803351D+08
0.8870325D+08	0.8026167D+08	0.7262368D+08	0.6570951D+08	0.5945886D+08
0.5380052D+08	0.4867709D+08	0.4404670D+08	0.3985394D+08	0.3606093D+08
0.3262886D+08	0.2952331D+08	0.2671386D+08	0.2417038D+08	0.2187117D+08
0.1978883D+08	0.1790601D+08	0.1620086D+08	0.1465936D+08	0.1326404D+08
0.1200134D+08	0.1085934D+08	0.9825499D+07	0.8890375D+07	0.8044114D+07
0.7278286D+07	0.6585869D+07	0.5958553D+07	0.5391518D+07	0.4878254D+07
0.4413905D+07	0.3993748D+07	0.3613564D+07	0.3269475D+07	0.2958295D+07
0.2676651D+07	0.2421752D+07	0.2191351D+07	0.1982546D+07	0.1793836D+07
0.1623092D+07	0.1468483D+07	0.1328697D+07	0.1202153D+07	0.1087697D+07
0.9841044D+06	0.8903920D+06	0.8055975D+06	0.7288650D+06	0.6594564D+06
0.5966548D+06	0.5398019D+06	0.4883992D+06	0.4418645D+06	0.3997716D+06
0.3616920D+06	0.3272264D+06	0.2960497D+06	0.2678386D+06	0.2423145D+06
0.2192231D+06	0.1983351D+06	0.1794203D+06	0.1623269D+06	0.1468438D+06
0.1328504D+06	0.1201805D+06	0.1087207D+06	0.9835134D+05	0.8897220D+05
0.8048355D+05	0.7280621D+05	0.6586076D+05	0.5957335D+05	0.5388743D+05
0.4874615D+05	0.4409059D+05	0.3988121D+05	0.3607215D+05	0.3262636D+05
0.2950956D+05	0.2668978D+05	0.2413858D+05	0.2183043D+05	0.1974430D+05
0.1785491D+05	0.1614630D+05	0.1460219D+05	0.1320352D+05	0.1193959D+05
0.1079593D+05	0.9761347D+04	0.8825887D+04	0.7979498D+04	0.7213872D+04
0.6522105D+04	0.5895397D+04	0.5329455D+04	0.4817150D+04	0.4354044D+04
0.3935295D+04	0.3556408D+04	0.3213898D+04	0.2904249D+04	0.2624125D+04
0.2370947D+04	0.2141954D+04	0.1934991D+04	0.1747820D+04	0.1578642D+04
0.1425664D+04	0.1287432D+04	0.1162450D+04	0.1049497D+04	0.9473947D+03
0.8551235D+03	0.7717454D+03	0.6963909D+03	0.6283142D+03	0.5667964D+03
0.5112313D+03	0.4610047D+03	0.4156798D+03	0.3747108D+03	0.3377280D+03
0.3043204D+03	0.2741648D+03	0.2469349D+03	0.2223575D+03	0.2001758D+03
0.1801555D+03	0.1620928D+03	0.1457952D+03	0.1310966D+03	0.1178427D+03
0.1058884D+03	0.9511611D+02	0.8540248D+02	0.7665592D+02	0.6877272D+02
0.6167579D+02	0.5528632D+02	0.4953687D+02	0.4436038D+02	0.3971257D+02
0.3552834D+02	0.3177310D+02	0.2839905D+02	0.2537058D+02	0.2265633D+02
0.2022185D+02	0.1804280D+02	0.1609223D+02	0.1434876D+02	0.1279199D+02
0.1140297D+02	0.1016592D+02	0.9065298D+01	0.8087727D+01	0.7220464D+01
0.6453522D+01	0.5775410D+01	0.5177291D+01	0.4651087D+01	0.4188454D+01
0.3782539D+01	0.3426419D+01	0.3113811D+01	0.2838945D+01	0.2596162D+01
0.2380263D+01	0.2186088D+01	0.2009228D+01	0.1845136D+01	0.1690281D+01
0.1540823D+01	0.1394682D+01	0.1249653D+01	0.1104595D+01	0.9596122D+00
0.8154167D+00	0.6737111D+00	0.5371667D+00	0.4087557D+00	0.2922551D+00
0.1913137D+00	0.1094311D+00	0.4913869D-01	0.1127897D-01	-0.6296763D-02
-0.9528623D-02	-0.7112035D-02	-0.4800122D-02	-0.3199948D-02	-0.2081588D-02
-0.1317973D-02	-0.7964099D-03	-0.4491060D-03	-0.2227097D-03	-0.8183863D-04
0.1051787D-04	0.5908088D-04	0.8696817D-04	0.9748864D-04	0.1025315D-03
0.9508559D-04	0.8965242D-04	0.8371560D-04	0.7232492D-04	0.6308450D-04
0.5696592D-04	0.4718566D-04	0.4231411D-04	0.3575879D-04	0.3061651D-04

0.2587634D-04	0.2336567D-04	0.1953470D-04	0.1838990D-04	0.1698889D-04
0.1609556D-04	0.1661855D-04	0.1601577D-04	0.1618723D-04	0.1494917D-04
0.1247574D-04	0.6652120D-05	-0.2984054D-05	-0.1988370D-04	-0.4625510D-04
-0.8767483D-04	-0.1469929D-03	-0.2340799D-03	-0.3552898D-03	-0.5228901D-03
-0.7493099D-03	-0.1052545D-02	-0.1447100D-02	-0.1957900D-02	-0.2629106D-02
-0.3442298D-02	-0.4389558D-02	-0.5915295D-02	-0.7598006D-02	-0.6962087D-02
-0.1575918D-01	0.1407751D-01	0.1124626D-01	-0.1589482D+00	-0.1597657D+00
-0.1605446D+00				

POTENTIALS -2

-0.1379856D+00	0.5000000D-01	0.1121395D-03	268
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-2; from a grid point #1 to a grid point # 268

0.3976021D+09	0.3597530D+09	0.3255349D+09	0.2945417D+09	0.2665162D+09
0.2411597D+09	0.2182020D+09	0.1974389D+09	0.1786527D+09	0.1616502D+09
0.1462654D+09	0.1323488D+09	0.1197516D+09	0.1083598D+09	0.9804078D+08
0.8871664D+08	0.8027285D+08	0.7263342D+08	0.6572019D+08	0.5946690D+08
0.5380833D+08	0.4868690D+08	0.4405414D+08	0.3986140D+08	0.3606910D+08
0.3263426D+08	0.2953027D+08	0.2672027D+08	0.2417668D+08	0.2187643D+08
0.1979412D+08	0.1791037D+08	0.1620643D+08	0.1466366D+08	0.1326845D+08
0.1200560D+08	0.1086289D+08	0.9829760D+07	0.8893516D+07	0.8047758D+07
0.7281468D+07	0.6588726D+07	0.5961652D+07	0.5394258D+07	0.4880942D+07
0.4416405D+07	0.3996123D+07	0.3615788D+07	0.3271670D+07	0.2960376D+07
0.2678599D+07	0.2423601D+07	0.2193074D+07	0.1984270D+07	0.1795458D+07
0.1624569D+07	0.1469964D+07	0.1330057D+07	0.1203479D+07	0.1088901D+07
0.9853511D+06	0.8914907D+06	0.8066693D+06	0.7298999D+06	0.6604153D+06
0.5975716D+06	0.5406929D+06	0.4892264D+06	0.4426610D+06	0.4005330D+06
0.3624063D+06	0.3279141D+06	0.2967001D+06	0.2684576D+06	0.2429032D+06
0.2197826D+06	0.1988640D+06	0.1799329D+06	0.1628039D+06	0.1473074D+06
0.1332842D+06	0.1205945D+06	0.1091161D+06	0.9872833D+05	0.8932567D+05
0.8082702D+05	0.7312723D+05	0.6616770D+05	0.5986633D+05	0.5416742D+05
0.4900893D+05	0.4434253D+05	0.4012034D+05	0.3630005D+05	0.3284261D+05
0.2971684D+05	0.2688437D+05	0.2432569D+05	0.2200805D+05	0.1991195D+05
0.1801572D+05	0.1629935D+05	0.1474674D+05	0.1334196D+05	0.1207081D+05
0.1092102D+05	0.9879945D+04	0.8939156D+04	0.8086653D+04	0.7316587D+04
0.6618924D+04	0.5988229D+04	0.5417360D+04	0.4900902D+04	0.4433673D+04
0.4010957D+04	0.3628490D+04	0.3282403D+04	0.2969430D+04	0.2686148D+04
0.2429845D+04	0.2198083D+04	0.1988279D+04	0.1798568D+04	0.1626853D+04
0.1471585D+04	0.1331065D+04	0.1203946D+04	0.1088956D+04	0.9849260D+03
0.8908388D+03	0.8056863D+03	0.7286814D+03	0.6589943D+03	0.5959923D+03
0.5389719D+03	0.4874112D+03	0.4407565D+03	0.3985675D+03	0.3604008D+03
0.3258776D+03	0.2946547D+03	0.2664093D+03	0.2408598D+03	0.2177703D+03
0.1968640D+03	0.1779733D+03	0.1608803D+03	0.1454241D+03	0.1314481D+03
0.1188094D+03	0.1073798D+03	0.9704576D+02	0.8770297D+02	0.7925085D+02
0.7161282D+02	0.6470940D+02	0.5846287D+02	0.5282034D+02	0.4771883D+02
0.4310626D+02	0.3893836D+02	0.3517124D+02	0.3176658D+02	0.2869037D+02
0.2591009D+02	0.2339771D+02	0.2112881D+02	0.1907856D+02	0.1722651D+02
0.1555317D+02	0.1404224D+02	0.1267760D+02	0.1144486D+02	0.1033184D+02
0.9326762D+01	0.8418937D+01	0.7599179D+01	0.6858674D+01	0.6190225D+01
0.5585739D+01	0.5039765D+01	0.4546348D+01	0.4099544D+01	0.3695735D+01
0.3329540D+01	0.2997650D+01	0.2696347D+01	0.2422279D+01	0.2172789D+01
0.1944956D+01	0.1736652D+01	0.1545588D+01	0.1369988D+01	0.1208136D+01
0.1058750D+01	0.9203670D+00	0.7924098D+00	0.6738241D+00	0.5643916D+00
0.4637439D+00	0.3719977D+00	0.2893813D+00	0.2163581D+00	0.1535527D+00
0.1015432D+00	0.6080805D-01	0.3148389D-01	0.1302468D-01	0.3827616D-02
0.9830616D-03	0.7426788D-03	0.7679443D-03	0.7273330D-03	0.6697820D-03
0.6024713D-03	0.5332434D-03	0.4647928D-03	0.4008289D-03	0.3448998D-03
0.2914618D-03	0.2462146D-03	0.2060261D-03	0.1744556D-03	0.1417270D-03
0.1178344D-03	0.9830414D-04	0.7912705D-04	0.6291265D-04	0.5337471D-04

0.4129010D-04	0.3361836D-04	0.2684851D-04	0.2158331D-04	0.1726299D-04
0.1442887D-04	0.1227726D-04	0.1202500D-04	0.9766759D-05	0.1093085D-04
0.1070902D-04	0.1060789D-04	0.1006550D-04	0.8088777D-05	0.3160275D-05
-0.4756460D-05	-0.1918429D-04	-0.4217477D-04	-0.7665259D-04	-0.1284899D-03
-0.2025211D-03	-0.3067033D-03	-0.4498352D-03	-0.6436258D-03	-0.9018490D-03
-0.1239736D-02	-0.1675979D-02	-0.2232681D-02	-0.2941188D-02	-0.3808205D-02
-0.4798774D-02	-0.6106789D-02	-0.1051831D-01	0.3132715D-02	0.1571839D-01
-0.1225342D+00	-0.1232763D+00	-0.1239834D+00		

POTENTIALS 2

-0.1585493D+00	0.5000000D-01	0.1121395D-03	266
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=2; from a grid point #1 to a grid point # 266

0.5565719D+09	0.5036033D+09	0.4556763D+09	0.4123057D+09	0.3730728D+09
0.3375707D+09	0.3054347D+09	0.2763773D+09	0.2500676D+09	0.2262699D+09
0.2047364D+09	0.1852521D+09	0.1676178D+09	0.1516715D+09	0.1372317D+09
0.1241731D+09	0.1123545D+09	0.1016602D+09	0.9198626D+08	0.8323156D+08
0.7530909D+08	0.6814128D+08	0.6165605D+08	0.5578840D+08	0.5047866D+08
0.4567292D+08	0.4132657D+08	0.3739288D+08	0.3383381D+08	0.3061343D+08
0.2769872D+08	0.2506403D+08	0.2267662D+08	0.2051884D+08	0.1856510D+08
0.1679847D+08	0.1519921D+08	0.1375228D+08	0.1244310D+08	0.1125866D+08
0.1018683D+08	0.9217018D+07	0.8339615D+07	0.7545505D+07	0.6827262D+07
0.6177117D+07	0.5589128D+07	0.5056897D+07	0.4575402D+07	0.4139797D+07
0.3745484D+07	0.3388931D+07	0.3066160D+07	0.2774148D+07	0.2509995D+07
0.2270931D+07	0.2054649D+07	0.1858939D+07	0.1681910D+07	0.1521656D+07
0.1376715D+07	0.1245561D+07	0.1126912D+07	0.1019520D+07	0.9224019D+06
0.8345005D+06	0.7549751D+06	0.6830378D+06	0.6179140D+06	0.5590434D+06
0.5057290D+06	0.4575397D+06	0.4139043D+06	0.3744438D+06	0.3387357D+06
0.3064307D+06	0.2772041D+06	0.2507657D+06	0.2268291D+06	0.2051979D+06
0.1856135D+06	0.1678967D+06	0.1518711D+06	0.1373710D+06	0.1242535D+06
0.1123875D+06	0.1016519D+06	0.9193812D+05	0.8315511D+05	0.7520553D+05
0.6801609D+05	0.6151202D+05	0.5562839D+05	0.5030573D+05	0.4549146D+05
0.4113719D+05	0.3719719D+05	0.3363336D+05	0.3041205D+05	0.2749578D+05
0.2485892D+05	0.2247474D+05	0.2031722D+05	0.1836648D+05	0.1660261D+05
0.1500589D+05	0.1356400D+05	0.1225835D+05	0.1107838D+05	0.1001118D+05
0.9046259D+04	0.8173625D+04	0.7384745D+04	0.6671292D+04	0.6026393D+04
0.5443234D+04	0.4916110D+04	0.4439604D+04	0.4008783D+04	0.3619449D+04
0.3267417D+04	0.2949342D+04	0.2661863D+04	0.2402049D+04	0.2167232D+04
0.1955154D+04	0.1763458D+04	0.1590304D+04	0.1433843D+04	0.1292551D+04
0.1164923D+04	0.1049647D+04	0.9455706D+03	0.8515643D+03	0.7667270D+03
0.6900999D+03	0.6209849D+03	0.5585652D+03	0.5022664D+03	0.4514522D+03
0.4056280D+03	0.3642899D+03	0.3270145D+03	0.2934045D+03	0.2631019D+03
0.2358047D+03	0.2111955D+03	0.1890383D+03	0.1690742D+03	0.1511036D+03
0.1349296D+03	0.1203713D+03	0.1072817D+03	0.9550488D+02	0.8492390D+02
0.7541350D+02	0.6687632D+02	0.5920856D+02	0.5232922D+02	0.4616220D+02
0.4063356D+02	0.3568185D+02	0.3125101D+02	0.2728876D+02	0.2374497D+02
0.2058603D+02	0.1776673D+02	0.1525536D+02	0.1302166D+02	0.1103803D+02
0.9278781D+01	0.7722672D+01	0.6348037D+01	0.5138123D+01	0.4076227D+01
0.3147901D+01	0.2339448D+01	0.1641128D+01	0.1040330D+01	0.5298425D+00
0.1003642D+00	-0.2548069D+00	-0.5420649D+00	-0.7668005D+00	-0.9340706D+00
-0.1048317D+01	-0.1113577D+01	-0.1133654D+01	-0.1112881D+01	-0.1055619D+01
-0.9672185D+00	-0.8544310D+00	-0.7253684D+00	-0.5898497D+00	-0.4589380D+00
-0.3434842D+00	-0.2520684D+00	-0.1880707D+00	-0.1477302D+00	-0.1209713D+00
-0.9730172D-01	-0.7436828D-01	-0.5567372D-01	-0.4136320D-01	-0.3048314D-01
-0.2228344D-01	-0.1615816D-01	-0.1160470D-01	-0.8270409D-02	-0.5842424D-02
-0.4081478D-02	-0.2828225D-02	-0.1934751D-02	-0.1308783D-02	-0.8775914D-03
-0.5675857D-03	-0.3700946D-03	-0.2284553D-03	-0.1377117D-03	-0.7640322D-04
-0.4107296D-04	-0.1429526D-04	-0.3511403D-06	0.6337726D-05	0.1082553D-04
0.1262388D-04	0.1169325D-04	0.1200183D-04	0.9309266D-05	0.8462951D-05

0.6852993D-05	0.7263435D-05	0.5492520D-05	0.4653761D-05	0.5105967D-05
0.5928447D-05	0.6382655D-05	0.6513728D-05	0.7206405D-05	0.6817859D-05
0.5928559D-05	0.3393356D-05	-0.2172758D-05	-0.1114361D-04	-0.2732304D-04
-0.5135626D-04	-0.8824854D-04	-0.1424851D-03	-0.2197693D-03	-0.3277815D-03
-0.4761022D-03	-0.6782250D-03	-0.9444019D-03	-0.1288032D-02	-0.1765642D-02
-0.2340140D-02	-0.2915404D-02	-0.4177241D-02	-0.5737660D-02	-0.3275207D-02
-0.1273483D-01	0.2157338D-01	0.1051866D-01	-0.1421035D+00	-0.1428636D+00
-0.1435907D+00				

POTENTIALS -3

-0.1483086D+00	0.5000000D-01	0.1121395D-03	268
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-3; from a grid point #1 to a grid point # 268

0.5565782D+09	0.5036125D+09	0.4556785D+09	0.4123177D+09	0.3730781D+09
0.3375681D+09	0.3054517D+09	0.2763735D+09	0.2500755D+09	0.2262743D+09
0.2047405D+09	0.1852553D+09	0.1676245D+09	0.1516715D+09	0.1372372D+09
0.1241759D+09	0.1123574D+09	0.1016636D+09	0.9198960D+08	0.8323355D+08
0.7531216D+08	0.6814416D+08	0.6165838D+08	0.5579013D+08	0.5048086D+08
0.4567503D+08	0.4132836D+08	0.3739481D+08	0.3383557D+08	0.3061512D+08
0.2770082D+08	0.2506453D+08	0.2267889D+08	0.2051975D+08	0.1856678D+08
0.1679944D+08	0.1520028D+08	0.1375349D+08	0.1244427D+08	0.1125951D+08
0.1018788D+08	0.9217871D+07	0.8340500D+07	0.7546419D+07	0.6827870D+07
0.6178006D+07	0.5589799D+07	0.5057548D+07	0.4576082D+07	0.4140346D+07
0.3746149D+07	0.3389459D+07	0.3066655D+07	0.2774694D+07	0.2510452D+07
0.2271389D+07	0.2055074D+07	0.1859360D+07	0.1682264D+07	0.1522053D+07
0.1377060D+07	0.1245921D+07	0.1127199D+07	0.1019852D+07	0.9226844D+06
0.8347644D+06	0.7552465D+06	0.6832762D+06	0.6181611D+06	0.5592682D+06
0.5059435D+06	0.4577384D+06	0.4141067D+06	0.3746196D+06	0.3389162D+06
0.3065974D+06	0.2773621D+06	0.2509121D+06	0.2269830D+06	0.2053308D+06
0.1857418D+06	0.1680194D+06	0.1519899D+06	0.1374828D+06	0.1243611D+06
0.1124878D+06	0.1017480D+06	0.9203193D+05	0.8324088D+05	0.7528881D+05
0.6809463D+05	0.6158710D+05	0.5569985D+05	0.5037406D+05	0.4555594D+05
0.4119830D+05	0.3725584D+05	0.3369020D+05	0.3046323D+05	0.2754730D+05
0.2490674D+05	0.2252015D+05	0.2036071D+05	0.1840777D+05	0.1664147D+05
0.1504396D+05	0.1359920D+05	0.1229210D+05	0.1111057D+05	0.1004192D+05
0.9075339D+04	0.8201396D+04	0.7411019D+04	0.6696464D+04	0.6050210D+04
0.5465939D+04	0.4937886D+04	0.4460072D+04	0.4028362D+04	0.3638001D+04
0.3285179D+04	0.2966224D+04	0.2677888D+04	0.2417322D+04	0.2181809D+04
0.1968925D+04	0.1776669D+04	0.1602773D+04	0.1445807D+04	0.1303885D+04
0.1175709D+04	0.1059940D+04	0.9553372D+03	0.8608841D+03	0.7755855D+03
0.6985366D+03	0.6290180D+03	0.5662033D+03	0.5095420D+03	0.4583824D+03
0.4122202D+03	0.3705674D+03	0.3329905D+03	0.2990910D+03	0.2685283D+03
0.2409523D+03	0.2161089D+03	0.1937131D+03	0.1735262D+03	0.1553417D+03
0.1389625D+03	0.1242149D+03	0.1109361D+03	0.9898955D+02	0.8823700D+02
0.7857223D+02	0.6987846D+02	0.6206747D+02	0.5505229D+02	0.4875053D+02
0.4309742D+02	0.3802622D+02	0.3347982D+02	0.2940726D+02	0.2576105D+02
0.2249874D+02	0.1958446D+02	0.1697929D+02	0.1465828D+02	0.1258799D+02
0.1074651D+02	0.9110087D+01	0.7658517D+01	0.6373621D+01	0.5238546D+01
0.4238554D+01	0.3360712D+01	0.2592814D+01	0.1924527D+01	0.1346047D+01
0.8492450D+00	0.4266479D+00	0.7171435D-01	-0.2215611D+00	-0.4580503D+00
-0.6421050D+00	-0.7778949D+00	-0.8687280D+00	-0.9179673D+00	-0.9287335D+00
-0.9044317D+00	-0.8488587D+00	-0.7668686D+00	-0.6644509D+00	-0.5492867D+00
-0.4306994D+00	-0.3192222D+00	-0.2249722D+00	-0.1555497D+00	-0.1129651D+00
-0.9176085D-01	-0.8043541D-01	-0.6799118D-01	-0.5300172D-01	-0.4022228D-01
-0.3039446D-01	-0.2280569D-01	-0.1701214D-01	-0.1259841D-01	-0.9256621D-02
-0.6763030D-02	-0.4895979D-02	-0.3520843D-02	-0.2508061D-02	-0.1767468D-02
-0.1243170D-02	-0.8579634D-03	-0.5903596D-03	-0.4000123D-03	-0.2694050D-03
-0.1762259D-03	-0.1124125D-03	-0.7513384D-04	-0.4691371D-04	-0.2590869D-04
-0.1651973D-04	-0.7966581D-05	-0.4355232D-05	-0.1346076D-05	0.8519273D-06

0.7251033D-06	0.1689395D-05	0.1970918D-05	0.2201344D-05	0.4195102D-05
0.2873252D-05	0.4370067D-05	0.5094037D-05	0.5218549D-05	0.5976736D-05
0.5990187D-05	0.3907565D-05	0.7975762D-06	-0.5958386D-05	-0.1696703D-04
-0.3457303D-04	-0.6218572D-04	-0.1023522D-03	-0.1601620D-03	-0.2424299D-03
-0.3556876D-03	-0.5103533D-03	-0.7175805D-03	-0.9904379D-03	-0.1348103D-02
-0.1808048D-02	-0.2384811D-02	-0.3124014D-02	-0.4069392D-02	-0.5080421D-02
-0.6310812D-02	-0.8872239D-02	-0.1193186D-01	-0.4704056D-02	0.1619841D-01
-0.1333500D+00	-0.1340453D+00	-0.1347099D+00		

POTENTIALS 3

-0.3141412D-01	0.5000000D-01	0.1121395D-03	284
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=3; from a grid point #1 to a grid point # 284

-0.2385579D+09	-0.2158475D+09	-0.1952925D+09	-0.1767201D+09	-0.1598999D+09
-0.1446868D+09	-0.1309098D+09	-0.1184553D+09	-0.1071812D+09	-0.9698282D+08
-0.8775058D+08	-0.7940204D+08	-0.7184339D+08	-0.6500743D+08	-0.5882009D+08
-0.5322289D+08	-0.4815813D+08	-0.4357293D+08	-0.3942685D+08	-0.3567558D+08
-0.3227873D+08	-0.2920827D+08	-0.2642798D+08	-0.2391175D+08	-0.2163718D+08
-0.1957744D+08	-0.1771411D+08	-0.1602837D+08	-0.1450265D+08	-0.1312181D+08
-0.1187481D+08	-0.1074202D+08	-0.9721622D+07	-0.8795506D+07	-0.7958403D+07
-0.7200942D+07	-0.6515368D+07	-0.5895513D+07	-0.5334275D+07	-0.4826400D+07
-0.4367135D+07	-0.3951359D+07	-0.3575223D+07	-0.3234923D+07	-0.2927009D+07
-0.2648249D+07	-0.2396373D+07	-0.2168111D+07	-0.1961689D+07	-0.1774965D+07
-0.1606021D+07	-0.1453057D+07	-0.1314759D+07	-0.1189599D+07	-0.1076278D+07
-0.9738593D+06	-0.8810982D+06	-0.7972116D+06	-0.7212925D+06	-0.6526221D+06
-0.5904362D+06	-0.5342880D+06	-0.4833377D+06	-0.4373062D+06	-0.3956823D+06
-0.3579856D+06	-0.3238886D+06	-0.2930295D+06	-0.2651264D+06	-0.2398605D+06
-0.2170163D+06	-0.1963312D+06	-0.1776300D+06	-0.1607040D+06	-0.1453883D+06
-0.1315279D+06	-0.1190014D+06	-0.1076597D+06	-0.9738420D+05	-0.8811134D+05
-0.7970832D+05	-0.7210678D+05	-0.6523102D+05	-0.5901194D+05	-0.5338056D+05
-0.4828986D+05	-0.4368352D+05	-0.3951418D+05	-0.3574389D+05	-0.3233245D+05
-0.2924612D+05	-0.2645480D+05	-0.2392687D+05	-0.2164231D+05	-0.1957530D+05
-0.1770560D+05	-0.1601255D+05	-0.1448312D+05	-0.1309745D+05	-0.1184560D+05
-0.1071254D+05	-0.9687323D+04	-0.8760586D+04	-0.7921577D+04	-0.7163309D+04
-0.6476922D+04	-0.5856481D+04	-0.5294975D+04	-0.4787018D+04	-0.4328131D+04
-0.3912438D+04	-0.3536949D+04	-0.3197243D+04	-0.2889818D+04	-0.2612095D+04
-0.2360646D+04	-0.2133477D+04	-0.1927940D+04	-0.1742124D+04	-0.1574116D+04
-0.1422159D+04	-0.1284850D+04	-0.1160597D+04	-0.1048311D+04	-0.9467980D+03
-0.8551003D+03	-0.7720770D+03	-0.6971182D+03	-0.6293647D+03	-0.5680970D+03
-0.5127310D+03	-0.4627211D+03	-0.4174971D+03	-0.3766577D+03	-0.3397496D+03
-0.3064060D+03	-0.2762843D+03	-0.2490886D+03	-0.2244936D+03	-0.2023013D+03
-0.1822776D+03	-0.1641703D+03	-0.1478280D+03	-0.1330882D+03	-0.1197753D+03
-0.1077594D+03	-0.9692006D+02	-0.8713974D+02	-0.7831546D+02	-0.7036038D+02
-0.6318420D+02	-0.5671421D+02	-0.5088400D+02	-0.4562759D+02	-0.4089560D+02
-0.3662709D+02	-0.3279065D+02	-0.2932830D+02	-0.2621981D+02	-0.2341936D+02
-0.2090151D+02	-0.1863698D+02	-0.1660324D+02	-0.1477479D+02	-0.1313476D+02
-0.1166152D+02	-0.1034075D+02	-0.9156926D+01	-0.8095507D+01	-0.7147453D+01
-0.6296962D+01	-0.5538398D+01	-0.4860129D+01	-0.4256303D+01	-0.3716834D+01
-0.3238176D+01	-0.2811871D+01	-0.2434157D+01	-0.2099285D+01	-0.1803376D+01
-0.1542356D+01	-0.1312684D+01	-0.1111096D+01	-0.9346887D+00	-0.7809419D+00
-0.6473099D+00	-0.5320852D+00	-0.4325378D+00	-0.3476248D+00	-0.2756853D+00
-0.2147974D+00	-0.1640443D+00	-0.1221456D+00	-0.8799206D-01	-0.6061072D-01
-0.3899481D-01	-0.2252701D-01	-0.1025604D-01	-0.1629768D-02	0.4014410D-02
0.7255281D-02	0.8638136D-02	0.8571026D-02	0.7658991D-02	0.6138208D-02
0.4447794D-02	0.2859530D-02	0.1475208D-02	0.4946855D-03	-0.1230237D-03
-0.3815787D-03	-0.3970005D-03	-0.2886251D-03	-0.1752851D-03	-0.1021456D-03
-0.6226481D-04	-0.3277097D-04	-0.2176121D-04	-0.1161510D-04	-0.7685411D-05
-0.7434790D-05	0.1819264D-05	-0.5069898D-05	-0.4699432D-05	-0.4658300D-06
0.4023943D-06	-0.3133102D-05	-0.6462177D-06	-0.2229629D-05	-0.6866842D-06

-0.3704777D-06	-0.1081780D-05	-0.7973494D-06	-0.9333460D-06	-0.2997568D-06
-0.6171151D-06	-0.4820059D-06	-0.1500338D-05	-0.2693005D-06	-0.3667308D-06
-0.3337061D-06	-0.6885641D-06	-0.3445065D-07	-0.3484087D-06	-0.1146422D-06
-0.4856451D-06	0.8984450D-07	-0.3667714D-06	-0.2316643D-06	-0.3680774D-06
-0.4435770D-06	-0.5129578D-06	-0.6219803D-06	-0.6383750D-06	-0.6733962D-06
-0.5488297D-06	-0.3049359D-06	-0.1603370D-06	0.5230502D-06	0.9684394D-06
0.1679114D-05	0.2308075D-05	0.2576891D-05	0.2286111D-05	0.8199431D-06
-0.2697986D-05	-0.9396480D-05	-0.2076523D-04	-0.3917068D-04	-0.6794186D-04
-0.1100449D-03	-0.1701545D-03	-0.2660969D-03	-0.3911092D-03	-0.5297531D-03
-0.8926974D-03	-0.1369328D-02	-0.8616055D-03	-0.4107406D-02	0.5469275D-02
-0.2037532D-02	-0.2465914D-01	-0.2497474D-01	-0.2527626D-01	

POTENTIALS -4

-0.3141364D-01	0.5000000D-01	0.1121395D-03	284
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-4; from a grid point #1 to a grid point # 284

-0.2385420D+09	-0.2158384D+09	-0.1953028D+09	-0.1767146D+09	-0.1598977D+09
-0.1446838D+09	-0.1309091D+09	-0.1184541D+09	-0.1071818D+09	-0.9697834D+08
-0.8775123D+08	-0.7940049D+08	-0.7184252D+08	-0.6500587D+08	-0.5881966D+08
-0.5322169D+08	-0.4815532D+08	-0.4357408D+08	-0.3942720D+08	-0.3567166D+08
-0.3228124D+08	-0.2920547D+08	-0.2642745D+08	-0.2391196D+08	-0.2163574D+08
-0.1957744D+08	-0.1771326D+08	-0.1602773D+08	-0.1450240D+08	-0.1312178D+08
-0.1187301D+08	-0.1074335D+08	-0.9719656D+07	-0.8796035D+07	-0.7957485D+07
-0.7200830D+07	-0.6515157D+07	-0.5895008D+07	-0.5334069D+07	-0.4826062D+07
-0.4366899D+07	-0.3951061D+07	-0.3574980D+07	-0.3234727D+07	-0.2926720D+07
-0.2648070D+07	-0.2396212D+07	-0.2167804D+07	-0.1961547D+07	-0.1774880D+07
-0.1605726D+07	-0.1452994D+07	-0.1314573D+07	-0.1189431D+07	-0.1076176D+07
-0.9737185D+06	-0.8809730D+06	-0.7970859D+06	-0.7211996D+06	-0.6524977D+06
-0.5903598D+06	-0.5341569D+06	-0.4832694D+06	-0.4372067D+06	-0.3956178D+06
-0.3578864D+06	-0.3238262D+06	-0.2929622D+06	-0.2650495D+06	-0.2397985D+06
-0.2169540D+06	-0.1962762D+06	-0.1775716D+06	-0.1606525D+06	-0.1453382D+06
-0.1314851D+06	-0.1189490D+06	-0.1076193D+06	-0.9734443D+05	-0.8807117D+05
-0.7966868D+05	-0.7207503D+05	-0.6519790D+05	-0.5897761D+05	-0.5335134D+05
-0.4826172D+05	-0.4365468D+05	-0.3948903D+05	-0.3571941D+05	-0.3230852D+05
-0.2922407D+05	-0.2643166D+05	-0.2390902D+05	-0.2162241D+05	-0.1955764D+05
-0.1768691D+05	-0.1599719D+05	-0.1446651D+05	-0.1308292D+05	-0.1183152D+05
-0.1069894D+05	-0.9674612D+04	-0.8748260D+04	-0.7910119D+04	-0.7152260D+04
-0.6466499D+04	-0.5846748D+04	-0.5285021D+04	-0.4778534D+04	-0.4319549D+04
-0.3904252D+04	-0.3529359D+04	-0.3189869D+04	-0.2882980D+04	-0.2605485D+04
-0.2354425D+04	-0.2127492D+04	-0.1922359D+04	-0.1736790D+04	-0.1569024D+04
-0.1417375D+04	-0.1280247D+04	-0.1156265D+04	-0.1044209D+04	-0.9429574D+03
-0.8513427D+03	-0.7686365D+03	-0.6937601D+03	-0.6262293D+03	-0.5650948D+03
-0.5099314D+03	-0.4600297D+03	-0.4149674D+03	-0.3742560D+03	-0.3374802D+03
-0.3042565D+03	-0.2742495D+03	-0.2471560D+03	-0.2226912D+03	-0.2005744D+03
-0.1806578D+03	-0.1626337D+03	-0.1463869D+03	-0.1317201D+03	-0.1184884D+03
-0.1065449D+03	-0.9577473D+02	-0.8606368D+02	-0.7730235D+02	-0.6940623D+02
-0.6228730D+02	-0.5587407D+02	-0.5009305D+02	-0.4488821D+02	-0.4020064D+02
-0.3597849D+02	-0.3218086D+02	-0.2876347D+02	-0.2568862D+02	-0.2292599D+02
-0.2044167D+02	-0.1821042D+02	-0.1620670D+02	-0.1440824D+02	-0.1279466D+02
-0.1134787D+02	-0.1005200D+02	-0.8891075D+01	-0.7852434D+01	-0.6923576D+01
-0.6093837D+01	-0.5353438D+01	-0.4692614D+01	-0.4103915D+01	-0.3581108D+01
-0.3115305D+01	-0.2702957D+01	-0.2336961D+01	-0.2013771D+01	-0.1728239D+01
-0.1476851D+01	-0.1255951D+01	-0.1062355D+01	-0.8932722D+00	-0.7460200D+00
-0.6183105D+00	-0.5079419D+00	-0.4132436D+00	-0.3322076D+00	-0.2634335D+00
-0.2054860D+00	-0.1570144D+00	-0.1169451D+00	-0.8425536D-01	-0.5792981D-01
-0.3711743D-01	-0.2109418D-01	-0.9111331D-02	-0.5926816D-03	0.5091953D-02
0.8439777D-02	0.9925394D-02	0.1005229D-01	0.9158988D-02	0.7709030D-02
0.5970080D-02	0.4222798D-02	0.2639473D-02	0.1385004D-02	0.4732186D-03
-0.5992914D-04	-0.2997248D-03	-0.3128089D-03	-0.2292276D-03	-0.1384323D-03

-0.8452999D-04	-0.4678123D-04	-0.2861005D-04	-0.1632290D-04	-0.9900929D-05
-0.9133553D-05	0.5672463D-06	-0.5784578D-05	-0.2486981D-05	-0.1756265D-05
-0.8473982D-06	-0.2437914D-05	-0.2058193D-05	0.6666014D-06	-0.2858700D-05
-0.9653699D-07	-0.8663098D-06	-0.1241396D-05	-0.5306720D-06	-0.9570929D-06
-0.7149180D-07	-0.8284890D-06	-0.5472661D-06	0.1791797D-07	-0.9128134D-06
0.1699304D-06	-0.7167075D-06	-0.2328582D-06	-0.2375209D-06	-0.2614589D-06
-0.3694613D-06	-0.3151926D-06	-0.5754833D-06	-0.2885473D-06	-0.7413515D-06
-0.5022692D-06	-0.6178373D-06	-0.6724385D-06	-0.6421691D-06	-0.5230072D-06
-0.3567385D-06	0.2244037D-07	0.2612014D-06	0.1033696D-05	0.1509366D-05
0.2284368D-05	0.2842480D-05	0.3083173D-05	0.2693087D-05	0.1069209D-05
-0.2510211D-05	-0.9115148D-05	-0.2019927D-04	-0.3747650D-04	-0.6356997D-04
-0.1013996D-03	-0.1546925D-03	-0.2278891D-03	-0.3263994D-03	-0.4584710D-03
-0.6302440D-03	-0.8206109D-03	-0.1058489D-02	-0.2557031D-02	0.3496337D-02
0.6998607D-02	-0.2465866D-01	-0.2497426D-01	-0.2527578D-01	

POTENTIALS 4

-0.2000231D-01	0.5000000D-01	0.1121395D-03	290
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=4; from a grid point #1 to a grid point # 290

-0.1859216D+09	-0.1881113D+09	-0.1908435D+09	-0.1940841D+09	-0.1986744D+09
-0.1990068D+09	-0.1829168D+09	-0.1620676D+09	-0.1466017D+09	-0.1318069D+09
-0.1187757D+09	-0.1070725D+09	-0.9655460D+08	-0.8708896D+08	-0.7854955D+08
-0.7085298D+08	-0.6390411D+08	-0.5763234D+08	-0.5197360D+08	-0.4685672D+08
-0.4224809D+08	-0.3807966D+08	-0.3431993D+08	-0.3092491D+08	-0.2786137D+08
-0.2509665D+08	-0.2260152D+08	-0.2035048D+08	-0.1831999D+08	-0.1648843D+08
-0.1483704D+08	-0.1334685D+08	-0.1200468D+08	-0.1079404D+08	-0.9704002D+07
-0.8720754D+07	-0.7835747D+07	-0.7038507D+07	-0.6320565D+07	-0.5674206D+07
-0.5092708D+07	-0.4569401D+07	-0.4098351D+07	-0.3675218D+07	-0.3294644D+07
-0.2952408D+07	-0.2645165D+07	-0.2368947D+07	-0.2121054D+07	-0.1898528D+07
-0.1698777D+07	-0.1519649D+07	-0.1359006D+07	-0.1214979D+07	-0.1085867D+07
-0.9703327D+06	-0.8667975D+06	-0.7741182D+06	-0.6912432D+06	-0.6170669D+06
-0.5507693D+06	-0.4915107D+06	-0.4385714D+06	-0.3912744D+06	-0.3490912D+06
-0.3113814D+06	-0.2777980D+06	-0.2478138D+06	-0.2210907D+06	-0.1972638D+06
-0.1760470D+06	-0.1571358D+06	-0.1402956D+06	-0.1252983D+06	-0.1119495D+06
-0.1000716D+06	-0.8949133D+05	-0.8006980D+05	-0.7169900D+05	-0.6423718D+05
-0.5759946D+05	-0.5169085D+05	-0.4642814D+05	-0.4174274D+05	-0.3756348D+05
-0.3384553D+05	-0.3052566D+05	-0.2756522D+05	-0.2492239D+05	-0.2256055D+05
-0.2045070D+05	-0.1856207D+05	-0.1687044D+05	-0.1535476D+05	-0.1399417D+05
-0.1277124D+05	-0.1167149D+05	-0.1068219D+05	-0.9788282D+04	-0.8981463D+04
-0.8251905D+04	-0.7591028D+04	-0.6991296D+04	-0.6446429D+04	-0.5950691D+04
-0.5498488D+04	-0.5086418D+04	-0.4708792D+04	-0.4363320D+04	-0.4046597D+04
-0.3755630D+04	-0.3488027D+04	-0.3241462D+04	-0.3014193D+04	-0.2804270D+04
-0.2610281D+04	-0.2430464D+04	-0.2264068D+04	-0.2109623D+04	-0.1966169D+04
-0.1832862D+04	-0.1708753D+04	-0.1593204D+04	-0.1485406D+04	-0.1384882D+04
-0.1290992D+04	-0.1203241D+04	-0.1121194D+04	-0.1044399D+04	-0.9725316D+03
-0.9052634D+03	-0.8422138D+03	-0.7831935D+03	-0.7279270D+03	-0.6761680D+03
-0.6277377D+03	-0.5824285D+03	-0.5400577D+03	-0.5004622D+03	-0.4634787D+03
-0.4289474D+03	-0.3967272D+03	-0.3666469D+03	-0.3386040D+03	-0.3124325D+03
-0.2880350D+03	-0.2652702D+03	-0.2440517D+03	-0.2242679D+03	-0.2058389D+03
-0.1886845D+03	-0.1727352D+03	-0.1579319D+03	-0.1442138D+03	-0.1315316D+03
-0.1198337D+03	-0.1090618D+03	-0.9917891D+02	-0.9011382D+02	-0.8182298D+02
-0.7424559D+02	-0.6732004D+02	-0.6099680D+02	-0.5521708D+02	-0.4992749D+02
-0.4508537D+02	-0.4064561D+02	-0.3657082D+02	-0.3283198D+02	-0.2939911D+02
-0.2625149D+02	-0.2336964D+02	-0.2073560D+02	-0.1833507D+02	-0.1615371D+02
-0.1417785D+02	-0.1239423D+02	-0.1078993D+02	-0.9352036D+01	-0.8067151D+01
-0.6924897D+01	-0.5911182D+01	-0.5016946D+01	-0.4230679D+01	-0.3543130D+01
-0.2945213D+01	-0.2428741D+01	-0.1985728D+01	-0.1608812D+01	-0.1290998D+01
-0.1025593D+01	-0.8063401D+00	-0.6270589D+00	-0.4822507D+00	-0.3666027D+00
-0.2754191D+00	-0.2043162D+00	-0.1496749D+00	-0.1081925D+00	-0.7712244D-01
-0.5418514D-01	-0.3749361D-01	-0.2557920D-01	-0.1716844D-01	-0.1136042D-01

-0.7396223D-02	-0.4737933D-02	-0.3011593D-02	-0.1848564D-02	-0.1142965D-02
-0.6853169D-03	-0.4065423D-03	-0.2403380D-03	-0.1376496D-03	-0.7823991D-04
-0.4398823D-04	-0.2691094D-04	-0.1435135D-04	-0.1239997D-04	0.5660665D-06
-0.8927524D-05	0.2209844D-05	-0.6404677D-05	0.3824306D-06	-0.2263707D-05
-0.2401954D-05	-0.7738966D-06	-0.1817380D-05	-0.1527763D-05	-0.1005038D-05
-0.1637396D-05	-0.9974447D-06	-0.1034095D-05	-0.1883596D-05	0.3022719D-06
-0.1240798D-05	-0.1076517D-05	-0.4779899D-06	-0.1019590D-05	-0.2780459D-06
-0.4243659D-06	-0.5790034D-06	-0.4133138D-06	-0.2861011D-06	-0.4806328D-06
-0.1822351D-06	-0.3969225D-06	-0.1226677D-06	-0.5274887D-06	-0.1027414D-06
-0.4799952D-06	-0.1700027D-06	-0.5162554D-06	-0.1592904D-06	-0.3347730D-06
0.4989823D-06	-0.2680573D-06	-0.1957483D-06	-0.3481925D-06	-0.4281126D-06
-0.5297925D-06	-0.4993908D-06	-0.5057044D-06	-0.3025048D-06	-0.6431597D-07
0.3730427D-06	0.9127346D-06	0.1544363D-05	0.2080791D-05	0.2426581D-05
0.2074302D-05	0.6324122D-06	-0.2738853D-05	-0.9044394D-05	-0.1960872D-04
-0.3663680D-04	-0.6149068D-04	-0.9708315D-04	-0.1521050D-03	-0.2178763D-03
-0.2876914D-03	-0.4772997D-03	-0.6617077D-03	-0.1689526D-03	-0.2156955D-02
0.7300949D-02	0.3378677D-02	-0.1505000D-01	-0.1527886D-01	-0.1549776D-01

POTENTIALS -5

-0.2000231D-01	0.5000000D-01	0.1121395D-03	290
(ε_i)	(step size)	(r_0)	(#grid points)

U^{REP} for j=-5; from a grid point #1 to a grid point # 290

-0.1942922D+08	-0.1827108D+08	-0.1706708D+08	-0.1579163D+08	-0.1441641D+08
-0.1298482D+08	-0.1175182D+08	-0.1067812D+08	-0.9665464D+07	-0.8776704D+07
-0.7968560D+07	-0.7230963D+07	-0.6566837D+07	-0.5963164D+07	-0.5414498D+07
-0.4920771D+07	-0.4470441D+07	-0.4063440D+07	-0.3692919D+07	-0.3356662D+07
-0.3054319D+07	-0.2777456D+07	-0.2526843D+07	-0.2299696D+07	-0.2092701D+07
-0.1906028D+07	-0.1735862D+07	-0.1581099D+07	-0.1440526D+07	-0.1314507D+07
-0.1197225D+07	-0.1092141D+07	-0.9971372D+06	-0.9100460D+06	-0.8306815D+06
-0.7589500D+06	-0.6933758D+06	-0.6340882D+06	-0.5794786D+06	-0.5307667D+06
-0.4853151D+06	-0.4446185D+06	-0.4071871D+06	-0.3733439D+06	-0.3421906D+06
-0.3140370D+06	-0.2881817D+06	-0.2645987D+06	-0.2433015D+06	-0.2234509D+06
-0.2055345D+06	-0.1892405D+06	-0.1741350D+06	-0.1604908D+06	-0.1478953D+06
-0.1364045D+06	-0.1259035D+06	-0.1161738D+06	-0.1073553D+06	-0.9926306D+05
-0.9177326D+05	-0.8495792D+05	-0.7863429D+05	-0.7287627D+05	-0.6755180D+05
-0.6265432D+05	-0.5813670D+05	-0.5402634D+05	-0.5015204D+05	-0.4664539D+05
-0.4338010D+05	-0.4037158D+05	-0.3759691D+05	-0.3502155D+05	-0.3264362D+05
-0.3045016D+05	-0.2840174D+05	-0.2651535D+05	-0.2476583D+05	-0.2313921D+05
-0.2163202D+05	-0.2022552D+05	-0.1892575D+05	-0.1771341D+05	-0.1658372D+05
-0.1553549D+05	-0.1455426D+05	-0.1364308D+05	-0.1279256D+05	-0.1199715D+05
-0.1125590D+05	-0.1056294D+05	-0.9914714D+04	-0.9308837D+04	-0.8741794D+04
-0.8210391D+04	-0.7713326D+04	-0.7247408D+04	-0.6810000D+04	-0.6399694D+04
-0.6015136D+04	-0.5653506D+04	-0.5314201D+04	-0.4995247D+04	-0.4695503D+04
-0.4413805D+04	-0.4147910D+04	-0.3899297D+04	-0.3663977D+04	-0.3443139D+04
-0.3235188D+04	-0.3039098D+04	-0.2854701D+04	-0.2680912D+04	-0.2517245D+04
-0.2362997D+04	-0.2217879D+04	-0.2081015D+04	-0.1952168D+04	-0.1830680D+04
-0.1716328D+04	-0.1608551D+04	-0.1507018D+04	-0.1411346D+04	-0.1321215D+04
-0.1236285D+04	-0.1156239D+04	-0.1080899D+04	-0.1009799D+04	-0.9429322D+03
-0.8798662D+03	-0.8205474D+03	-0.7646774D+03	-0.7121249D+03	-0.6627212D+03
-0.6162754D+03	-0.5726818D+03	-0.5317631D+03	-0.4934050D+03	-0.4574560D+03
-0.4238193D+03	-0.3923247D+03	-0.3628917D+03	-0.3353534D+03	-0.3096537D+03
-0.2856289D+03	-0.2631995D+03	-0.2422710D+03	-0.2227406D+03	-0.2045344D+03
-0.1875773D+03	-0.1718014D+03	-0.1571509D+03	-0.1435653D+03	-0.1309933D+03
-0.1193897D+03	-0.1086973D+03	-0.9887201D+02	-0.8985510D+02	-0.8159946D+02
-0.7404756D+02	-0.6714586D+02	-0.6083798D+02	-0.5507169D+02	-0.4979828D+02
-0.4497111D+02	-0.4054696D+02	-0.3649067D+02	-0.3276951D+02	-0.2935521D+02
-0.2622612D+02	-0.2336016D+02	-0.2074137D+02	-0.1835311D+02	-0.1618179D+02
-0.1421350D+02	-0.1243547D+02	-0.1083488D+02	-0.9399315D+01	-0.8116416D+01
-0.6974692D+01	-0.5962397D+01	-0.5068376D+01	-0.4283097D+01	-0.3595767D+01
-0.2997984D+01	-0.2481018D+01	-0.2036799D+01	-0.1658101D+01	-0.1337698D+01
-0.1069036D+01	-0.8459490D+00	-0.6625167D+00	-0.5132979D+00	-0.3933403D+00

-0.2978054D+00	-0.2228452D+00	-0.1646982D+00	-0.1200589D+00	-0.8634545D-01
-0.6121639D-01	-0.4276141D-01	-0.2943513D-01	-0.1994483D-01	-0.1331988D-01
-0.8757095D-02	-0.5654404D-02	-0.3634671D-02	-0.2236295D-02	-0.1412898D-02
-0.8384945D-03	-0.5102314D-03	-0.3005584D-03	-0.1703699D-03	-0.9842615D-04
-0.5816041D-04	-0.2993528D-04	-0.1791820D-04	-0.8982034D-05	-0.5358755D-05
-0.6331018D-05	0.4846541D-06	-0.2104586D-05	-0.2313177D-05	-0.1199872D-05
-0.5380383D-06	-0.1136259D-05	-0.1355599D-05	-0.1219538D-05	-0.7761547D-06
-0.1446197D-05	-0.1090622D-05	-0.1193163D-05	-0.5889706D-06	-0.1295216D-05
-0.1146733D-05	-0.1068152D-05	-0.4668499D-06	-0.1006950D-05	-0.2017040D-06
-0.1203547D-05	-0.1673618D-06	-0.3981510D-06	-0.5151634D-06	-0.4480033D-06
-0.1718330D-06	-0.3913818D-06	-0.1420848D-06	-0.2478590D-06	-0.1524272D-06
-0.2425397D-06	-0.2290945D-06	-0.1745931D-06	-0.3411003D-06	-0.7564074D-07
-0.1376773D-06	-0.4162062D-06	-0.3535429D-06	-0.4508263D-06	-0.5212541D-06
-0.4562657D-06	-0.4408578D-06	-0.2693407D-06	-0.2300045D-07	0.3384525D-06
0.7571383D-06	0.1399060D-05	0.1942141D-05	0.2359916D-05	0.2424539D-05
0.1743819D-05	-0.2377123D-06	-0.4267658D-05	-0.1141513D-04	-0.2312172D-04
-0.4108676D-04	-0.6768031D-04	-0.1055885D-03	-0.1580538D-03	-0.2288870D-03
-0.3233840D-03	-0.4453333D-03	-0.5839708D-03	-0.7593961D-03	-0.1696922D-02
0.2604002D-02	0.5477496D-02	-0.1505000D-01	-0.1527886D-01	-0.1549776D-01

APPENDIX D

TABLE XXIX

POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MH

R (Bohr)	Energy (a.u.)		
	ScH	LuH	LrH
2.75	-2.016	-	-
3.00	-2.031	-1.892	-1.871
3.25	-2.039	-1.907	-1.889
3.50	-2.041	-1.916	-1.899
3.75	-2.036	-1.918	-1.903
4.00	-2.027	-1.914	-1.903
5.00	-1.973	-1.872	-1.871
7.00	-1.886	-1.796	-1.807
10.00	-1.831	-1.736	-1.748

TABLE XXX

POTENTIAL ENERGIES FROM THE RCI CALCULATIONS FOR MH

R (Bohr)	Energy (a.u.)		
	ScH	LuH	LrH
2.75	-2.070	-	-
3.00	-2.087	-1.945	-1.919
3.25	-2.096	-1.960	-1.936
3.50	-2.100	-1.968	-1.946
3.75	-2.098	-1.970	-1.950
4.00	-2.093	-1.997	-1.949
5.00	-2.062	-1.933	-1.920
7.00	-2.039	-1.888	-1.869
10.00	-2.038	-1.880	-1.849

TABLE XXXI

POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MO

R (Bohr)	Energy (a.u.)		
	ScO	LuO	LrO
2.50	-17.074	-16.796	-16.533
2.75	-17.161	-16.921	-16.777
3.00	-17.197	-17.001	-16.933
3.25	-17.195	-17.043	-17.006
3.50	-17.169	-17.053	-17.029
3.75	-17.129	-17.038	-17.022
4.00	-17.098	-17.008	*
5.00	-17.054	-16.992	-17.004
7.00	-17.027	-16.903	-16.921
10.00	-17.022	-16.852	-16.856

* The correct root is skipped.

TABLE XXXII

POTENTIAL ENERGIES FROM THE RCI CALCULATIONS OF MO

R (Bohr)	Energy (a.u.)		
	ScO	LuO	LrO
2.50	-17.207	-	-
2.75	-17.298	-	-
3.00	-17.339	-17.1170	-17.041
3.25	-17.345	-17.164	-17.120
3.50	-17.329	-17.181	-17.151
3.75	-17.303	-17.175	-17.155
4.00	-17.275	-17.157	-17.144
5.00	-17.167	-17.073	-17.078
7.00	-17.140	-16.983	-16.987
10.00	-17.140	-16.976	-16.949

TABLE XXXIII

POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MF

R (Bohr)	Energy (a.u.)		
	ScF	LuF	LrF
2.50	-25.200	-25.034	-
2.75	-25.348	-25.191	-25.076
3.00	-25.425	-25.289	-25.234
3.25	-25.453	-25.340	-25.311
3.50	-25.452	-25.357	-25.341
3.75	-25.434	-25.351	-25.345
4.00	-25.410	-25.334	-25.334
5.00	-25.315	-25.243	-25.253
7.00	-25.211	-25.139	-25.157
10.00	-25.157	-25.081	-25.096

TABLE XXXIV

POTENTIAL ENERGIES FROM THE RCI CALCULATIONS OF MF

R (Bohr)	Energy (a.u.)		
	ScF	LuF	LrF
2.50	-25.318	-25.138	-
2.75	-25.462	-25.294	-25.174
3.00	-25.537	-25.392	-25.332
3.25	-25.563	-25.443	-25.409
3.50	-25.561	-25.459	-25.439
3.75	-25.544	-25.454	-25.443
4.00	-25.520	-25.436	-25.432
5.00	-25.434	-25.344	-25.349
7.00	-25.381	-25.238	-25.246
10.00	-25.380	-25.199	-25.182

TABLE XXXV

POTENTIAL ENERGIES FROM THE REP-SCF CALCULATIONS FOR MCl

R (Bohr)	Energy (a.u.)		
	ScCl	LuCl	LrCl
3.50	-16.049	-15.854	-15.875
3.75	-16.126	-15.968	-15.979
4.00	-16.167	-16.038	-16.023
4.25	-16.182	-16.074	-16.094
4.50	-16.183	-16.088	-16.114
4.75	-16.175	-16.087	-16.119
5.00	-16.163	-16.079	-16.114
7.00	-16.063	-15.988	-16.026
10.00	-16.002	-15.927	-15.962

TABLE XXXVI

POTENTIAL ENERGIES FROM THE RCI CALCULATIONS OF MCl

R (Bohr)	Energy (a.u.)		
	ScCl	LuCl	LrCl
3.50	-16.092	-15.892	-15.824
3.75	-16.169	-16.005	-15.947
4.00	-16.210	-16.074	-16.021
4.25	-16.226	-16.110	-16.063
4.50	-16.228	-16.123	-16.083
4.75	-16.221	-16.122	-16.089
5.00	-16.211	-16.113	-16.085
7.00	-16.123	-16.017	-16.003
10.00	-16.098	-15.950	-15.944

APPENDIX E

(Only *p* orbital of ligands are treated, except H atom)

TABLE XXXVII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScH

R (bohr)	Configuration contribution
3.00	0.937 $1\sigma^2 2\sigma^2$, 0.018 $1\sigma^2 \delta^2$, 0.004 $1\sigma^2 1\sigma^{*2}$,
3.50	0.914 $1\sigma^2 2\sigma^2$, 0.018 $1\sigma^2 \delta^2$, 0.006 $1\sigma^2 1\sigma^{*2}$, 0.011 $2\sigma^2 2\sigma^{*2}$
4.00	0.878 $1\sigma^2 2\sigma^2$, 0.025 $1\sigma^2 \delta^2$, 0.014 $1\sigma^2 1\sigma^{*2}$, 0.008 $2\sigma^2 2\sigma^{*2}$, 0.003 $2\sigma^2 1\sigma^{*2}$, 0.008 $2\sigma^2 1\sigma^* 2\sigma^*$, 0.016 $1\sigma 2\sigma 1\sigma^* 2\sigma^*$, 0.011 $1\sigma^2 1\sigma^* 2\sigma^*$, 0.006 $1\sigma 2\sigma 2\sigma^{*2}$, 0.004 $1\sigma 2\sigma 1\sigma^{*2}$
5.00	0.735 $1\sigma^2 2\sigma^2$, 0.033 $1\sigma^2 \delta^2$, 0.085 $1\sigma^2 1\sigma^{*2}$, 0.003 $2\sigma^2 1\sigma^{*2}$, 0.022 $1\sigma 2\sigma 1\sigma^* 2\sigma^*$, 0.029 $1\sigma^2 1\sigma^* 2\sigma^*$, 0.035 $1\sigma 2\sigma 1\sigma^{*2}$, 0.030 $1\sigma 2\sigma^2 1\sigma^*$
7.00	0.380 $1\sigma^2 2\sigma^2$, 0.276 $1\sigma^2 1\sigma^{*2}$, 0.011 $1\sigma 2\sigma 1\sigma^* 2\sigma^*$, 0.115 $1\sigma 2\sigma 1\sigma^{*2}$, 0.062 $1\sigma 2\sigma^2 1\sigma^*$, 0.005 $1\sigma 2\sigma \delta^2$, 0.006 $2\sigma^2 \delta^2$, 0.100 $1\sigma^2 2\sigma 1\sigma^*$, 0.025 $1\sigma^2 2\sigma 2\sigma^*$
10.00	0.289 $1\sigma^2 2\sigma^2$, 0.295 $1\sigma^2 1\sigma^{*2}$, 0.046 $1\sigma 2\sigma^2 1\sigma^*$, 0.141 $1\sigma 2\sigma 1\sigma^{*2}$, 0.007 $1\sigma 2\sigma 1\sigma^* 2\sigma^*$, 0.003 $1\sigma^* \delta^2$, 0.006 $2\sigma^2 \delta^2$, 0.151 $1\sigma^2 2\sigma 1\sigma^*$, 0.025 $1\sigma^2 2\sigma 2\sigma^*$

TABLE XXXVIII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScO

R (bohr)	Configuration contribution
3.00	0.90 $1\sigma^2 2\sigma\,\pi^4$, 0.03 $1\sigma^2 2\sigma\,\pi^3\pi^*$
3.50	0.86 $1\sigma^2 2\sigma\,\pi^4$, 0.06 $1\sigma^2 2\sigma\,\pi^3\pi^*$
4.00	0.40 $1\sigma^2 2\sigma\,\pi^4$, 0.16 $1\sigma\,2\sigma^2\,\pi^4$, 0.15 $1\sigma^2 2\sigma\,\pi^3\pi^*$, 0.06 $1\sigma\,2\sigma\,1\sigma^*\pi^3\pi^*$, 0.04 $1\sigma 2\sigma\,1\sigma^*\pi^4$, 0.10 $1\sigma^2 1\sigma^*\pi^3\pi^*$, 0.03 $1\sigma^2 1\sigma^*\pi^4$, 0.15 $1\sigma 2\sigma\,1\sigma^*\pi^4$
5.00	0.15 $1\sigma^2 2\sigma\,\pi^4$, 0.01 $1\sigma\,2\sigma^2\,\pi^4$, 0.13 $1\sigma^2 2\sigma\,\pi^3\pi^*$, 0.04 $1\sigma\,2\sigma\,1\sigma^*\pi^3\pi^*$, 0.02 $1\sigma 2\sigma\,1\sigma^*\pi^4$, 0.46 $1\sigma^2 1\sigma^*\pi^3\pi^*$, 0.03 $1\sigma^2 1\sigma^*\pi^4$, 0.15 $1\sigma 2\sigma\,1\sigma^*\pi^4$
7.00	0.90 $1\sigma^2 1\sigma^*\,\pi^3\pi^*$, 0.04 $1\sigma^2 2\sigma^*\,\pi^3\pi^*$
10.00	0.86 $1\sigma^2 1\sigma^*\,\pi^3\pi^*$, 0.10 $1\sigma^2 2\sigma^*\,\pi^3\pi^*$

TABLE XXXIX

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScF

R (bohr)	Configuration contribution
3.00	0.943 $1\sigma^2 2\sigma^2 \pi^4$, 0.006 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.011 $1\sigma^2 \delta^2 \pi^4$, 0.007 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.006 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
3.50	0.924 $1\sigma^2 2\sigma^2 \pi^4$, 0.009 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.018 $1\sigma^2 \delta^2 \pi^4$, 0.004 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.008 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
4.00	0.902 $1\sigma^2 2\sigma^2 \pi^4$, 0.016 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.026 $1\sigma^2 \delta^2 \pi^4$, 0.009 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.002 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.006 $1\sigma^2 1\sigma^* 2\sigma^* \pi^4$
5.00	0.820 $1\sigma^2 2\sigma^2 \pi^4$, 0.045 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.034 | $1\sigma^2 \delta^2 \pi^4$, 0.003 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.022 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.007 $1\sigma^2 1\sigma^* 2\sigma^* \pi^4$, 0.021 $1\sigma\, 2\sigma^2\, 1\sigma^* \pi^4$, 0.007 $1\sigma\, 2\sigma^2\, 2\sigma^* \pi^4$, 0.004 $2\sigma^2 1\sigma^* 2\sigma^* \pi^4$, 0.003 $2\sigma^2\, 1\sigma^{*2} \pi^4$
7.00	0.221 $1\sigma^2 2\sigma^2 \pi^4$, 0.109 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.244 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.035 $1\sigma\, 2\sigma^2\, 1\sigma^* \pi^4$, 0.002 $1\sigma\, 2\sigma^2\, 2\sigma^* \pi^4$, 0.004 $2\sigma^2 \delta^2 \pi^4$, 0.331 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.013 $1\sigma^2 2\sigma\, 2\sigma^* \pi^4$, 0.013 $1\sigma\, 2\sigma\, 1\sigma^* 2\sigma^* \pi^4$
10.00	0.083 $1\sigma^2 2\sigma^2 \pi^4$, 0.078 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.302 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.019 $1\sigma\, 2\sigma^2\, 1\sigma^* \pi^4$, 0.003 $1\sigma\, 2\sigma^2\, 2\sigma^* \pi^4$, 0.455 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.009 $1\sigma^2 2\sigma\, 2\sigma^* \pi^4$, 0.021 $1\sigma\, 2\sigma\, 1\sigma^* 2\sigma^* \pi^4$

TABLE XL

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR ScCl

R (bohr)	Configuration contribution
3.00	0.960 $1\sigma^2 2\sigma^2 \pi^4$
4.00	0.930 $1\sigma^2 2\sigma^2 \pi^4$, 0.020 $1\sigma^2 \delta^2 \pi^4$, 0.010 $1\sigma^2 1\sigma^{*2} \pi^4$
5.00	0.870 $1\sigma^2 2\sigma^2 \pi^4$, 0.050 $1\sigma^2 \delta^2 \pi^4$, 0.040 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.100 $1\sigma^2 1\sigma^* 2\sigma^* \pi^4$
7.00	0.660 $1\sigma^2 2\sigma^2 \pi^4$, 0.080 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.110 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.070 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.020 $12\sigma^2 1\sigma^{*2} \pi^4$
10.00	0.089 $1\sigma^2 2\sigma^2 \pi^4$, 0.472 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.323 $1\sigma\, 2\sigma\, 1\sigma^{*2} \pi^4$, 0.049 $1\sigma^2 1\sigma^{*2} \pi^4$,

TABLE XLI

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuH

R (bohr)	Configuration contribution
3.00	0.921 $1\sigma^2 2\sigma^2$, 0.045 $1\sigma^2 \delta^2$, 0.002 $1\sigma^2 1\sigma^{*2}$, 0.002 $2\sigma^2 1\sigma^{*2}$, 0.003 $2\sigma^2 1\sigma^* 2\sigma^*$
3.50	0.914 $1\sigma^2 2\sigma^2$, 0.050 $1\sigma^2 \delta^2$, 0.002 $1\sigma^2 1\sigma^{*2}$, 0.004 $2\sigma^2 1\sigma^{*2}$, 0.002 $2\sigma^2 1\sigma^* 2\sigma^*$, 0.001 $1\sigma^2 2\sigma\, 1\sigma^*$
4.00	0.904 $1\sigma^2 2\sigma^2$, 0.051 $1\sigma^2 \delta^2$, 0.004 $1\sigma^2 1\sigma^{*2}$, 0.005 $2\sigma^2 1\sigma^{*2}$, 0.002 $1\sigma^2 2\sigma\, 1\sigma^*$, 0.002 $2\sigma^2 \pi^2$, 0.001 $1\sigma^2 2\sigma\, \pi$, 0.002 $1\sigma\, 2\sigma\, 1\sigma^{*2}$
5.00	0.855 $1\sigma^2 2\sigma^2$, 0.038 $1\sigma^2 \delta^2$, 0.022 $1\sigma^2 1\sigma^{*2}$, 0.005 $2\sigma^2 1\sigma^{*2}$, 0.011 $1\sigma^2 2\sigma\, 1\sigma^*$, 0.004 $2\sigma^2 \pi^2$, 0.002 $1\sigma^2 2\sigma\, \pi$, 0.014 $1\sigma\, 2\sigma\, 1\sigma^{*2}$, 0.021 $1\sigma\, 2\sigma\, \delta^2$, 0.003 $1\sigma\, 2\sigma^2\, 1\sigma^*$
7.00	0.572 $1\sigma^2 2\sigma^2$, 0.159 $1\sigma^2 1\sigma^{*2}$, 0.145 $1\sigma^2 2\sigma\, 1\sigma^*$, 0.004 $2\sigma^2 \pi^2$, 0.018 $1\sigma^2 2\sigma\, \pi$, 0.028 $1\sigma\, 2\sigma\, \delta^2$, 0.013 $2\sigma^2\, \delta^2$, 0.004 $1\sigma^2\, 1\sigma^*\, \pi$
10.00	0.267 $1\sigma^2 2\sigma^2$, 0.226 $1\sigma^2 1\sigma^{*2}$, 0.339 $1\sigma^2 2\sigma\, 1\sigma^*$, 0.059 $1\sigma^2 2\sigma\, \pi$, 0.022 $1\sigma\, 2\sigma\, \delta^2$, 0.006 $2\sigma^2\, \delta^2$, 0.012 $1\sigma^2\, 1\sigma^*\, \pi$

TABLE XLII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuO

R (bohr)	Configuration contribution
3.00	0.94 $1\sigma^2 2\sigma\,\pi^4$, 0.02 $1\sigma^2 2\sigma\,\pi^2\pi^{*2}$, 0.01 $1\sigma 2\sigma^2\,\pi^4$
3.50	0.91 $1\sigma^2 2\sigma\,\pi^4$, 0.04 $1\sigma^2 2\sigma\,\pi^2\pi^{*2}$, 0.02 $1\sigma^2 2\sigma\,\pi^3\pi^*$
4.00	0.86 $1\sigma^2 2\sigma\,\pi^4$, 0.03 $1\sigma^2 2\sigma\,\pi^2\pi^{*2}$, 0.02 $1\sigma^2 2\sigma\,\pi^3\pi^*$
5.00	0.69 $1\sigma^2 2\sigma\,\pi^4$, 0.10 $1\sigma\,2\sigma^2\,\pi^4$, 0.11 $1\sigma\,2\sigma^2\pi^3\pi^*$, 0.03 $1\sigma^2 2\sigma\,\pi^3\pi^*$, 0.03 $1\sigma\,2\sigma 1\sigma^*\,\pi^3\pi^*$
7.00	0.20 $1\sigma^2 2\sigma\,\pi^4$, 0.62 $1\sigma^2 2\sigma\pi^3\pi^*$, 0.03 $1\sigma^2 2\sigma\,\pi^2\pi^{*2}$
10.00	0.92 $1\sigma^2 1\sigma^*\,\pi^3\pi^*$

TABLE XLIII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuF

R (bohr)	Configuration contribution
3.00	0.953 $1\sigma^2 2\sigma^2 \pi^4$, 0.002 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.022 $1\sigma^2 \delta^2 \pi^4$
3.50	0.943 $1\sigma^2 2\sigma^2 \pi^4$, 0.002 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.027 $1\sigma^2 \delta^2 \pi^4$, 0.004 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.004 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
4.00	0.934 $1\sigma^2 2\sigma^2 \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.032 $1\sigma^2 \delta^2 \pi^4$, 0.003 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.006 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
7.00	0.810 $1\sigma^2 2\sigma^2 \pi^4$, 0.016 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.008 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.101 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.011 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.020 $2\sigma^2 \delta^2 \pi^4$, 0.006 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$
10.00	0.119 $1\sigma^2 2\sigma^2 \pi^4$, 0.030 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.754 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.012 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.003 $2\sigma^2 \delta^2 \pi^4$, 0.038 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$, 0.006 $1\sigma^2 2\sigma \pi^4 \pi^*$
15.00	0.109 $1\sigma^2 2\sigma^2 \pi^4$, 0.067 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.734 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.011 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.028 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$, 0.017 $1\sigma^2 2\sigma \pi^4 \pi^*$, 0.004 $1\sigma 2\sigma 1\sigma^{*2} \pi^4$
20.00	0.139 $1\sigma^2 2\sigma^2 \pi^4$, 0.094 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.687 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.009 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.021 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$, 0.018 $1\sigma^2 2\sigma \pi^4 \pi^*$, 0.004 $1\sigma 2\sigma 1\sigma^{*2} \pi^4$

TABLE XLIV

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LuCl

R (bohr)	Configuration contribution
3.00	0.956 $1\sigma^2 2\sigma^2 \pi^4$, 0.029 $1\sigma^2 \delta^2 \pi^4$, 0.003 $1\sigma^2 1\sigma^{*2} \pi^4$,
4.00	0.940 $1\sigma^2 2\sigma^2 \pi^4$, 0.041 $1\sigma^2 \delta^2 \pi^4$, 0.002 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.003 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
4.25	0.937 $1\sigma^2 2\sigma^2 \pi^4$, 0.044 $1\sigma^2 \delta^2 \pi^4$, 0.00 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.003 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
5.00	0.927 $1\sigma^2 2\sigma^2 \pi^4$, 0.049 $1\sigma^2 \delta^2 \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.002 $1\sigma\, 2\sigma^2 1\sigma^* \pi^3 \pi^*$, 0.002 $1\sigma^2\, 2\sigma\, 1\sigma^* \pi^4$, 0.001 $1\sigma\, 2\sigma^2 1\sigma^* \pi^4$
7.00	0.914 $1\sigma^2 2\sigma^2 \pi^4$, 0.006 $1\sigma^2 \delta^2 \pi^4$, 0.004 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.003 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.014 $1\sigma^2\, 2\sigma\, 1\sigma^* \pi^4$, 0.024 $1\sigma\, 2\sigma\, \delta^2 \pi^4$, 0.020 $2\sigma^2 \delta^2 \pi^4$, 0.002 $1\sigma\, 2\sigma 1\sigma^*\, 2\sigma^* \pi^4$, 0.001 $2\sigma^2 1\sigma^{*2} \pi^4$
10.00	0.910 $1\sigma^2 2\sigma^2 \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.001 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.032 $1\sigma^2\, 2\sigma\, 1\sigma^* \pi^4$, 0.004 $1\sigma 2\sigma\, \delta^2 \pi^4$, 0.034 $2\sigma^2 \delta^2 \pi^4$, 0.004 $1\sigma\, 2\sigma 1\sigma^*\, 2\sigma^* \pi^4$, 0.006 $2\sigma^2 1\sigma^{*2} \pi^4$
15.00	0.003 $1\sigma^2 2\sigma^2 \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.887 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.018 $1\sigma\, 2\sigma\, \delta^2 \pi^4$, 0.060 $1\sigma\, 2\sigma 1\sigma^*\, 2\sigma^* \pi^4$, 0.009 $1\sigma\, 2\sigma 1\sigma^{*2} \pi^4$, 0.013 $1\sigma^2 2\sigma \pi^4 \pi^*$

TABLE XLV

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrH

R (bohr)	Configuration contribution
3.00	0.933 $1\sigma^2 2\sigma^2$, 0.034 $1\sigma^2 \delta^2$, 0.003 $1\sigma^2 \delta \delta^*$
3.50	0.931 $1\sigma^2 2\sigma^2$, 0.034 $1\sigma^2 \delta^2$, 0.003 $1\sigma^2 \delta \delta^*$, 0.002 $2\sigma^2 \pi^2$, 0.003 $1\sigma 2\sigma \delta^2$, 0.001 $2\sigma^2 1\sigma^{*2}$
4.00	0.930 $1\sigma^2 2\sigma^2$, 0.029 $1\sigma^2 \delta^2$, 0.002 $1\sigma^2 \delta \delta^*$, 0.002 $2\sigma^2 \pi^2$, 0.005 $1\sigma 2\sigma \delta^2$, 0.002 $2\sigma^2 1\sigma^{*2}$, 0.001 $1\sigma^2 1\sigma^{*2}$
5.00	0.913 $1\sigma^2 2\sigma^2$, 0.014 $1\sigma^2 \delta^2$, 0.005 $2\sigma^2 \pi^2$, 0.016 $1\sigma 2\sigma \delta^2$, 0.002 $2\sigma^2 1\sigma^{*2}$, 0.010 $1\sigma^2 1\sigma^{*2}$, 0.004 $1\sigma^2 2\sigma 1\sigma^*$, 0.003 $2\sigma^2 \delta^2$
7.00	0.770 $1\sigma^2 2\sigma^2$, 0.006 $2\sigma^2 \pi^2$, 0.016 $1\sigma 2\sigma \delta^2$, 0.074 $1\sigma^2 1\sigma^{*2}$, 0.072 $1\sigma^2 2\sigma 1\sigma+$, 0.011 $2\sigma^2 \delta^2$, 0.002 $1\sigma^2 2\sigma \pi$, 0.003 $1\sigma 2\sigma 1\sigma^{*2}$
10.00	0.368 $1\sigma^2 2\sigma^2$, 0.017 $1\sigma 2\sigma \delta^2$, 0.206 $1\sigma^2 1\sigma^{*2}$, 0.309 $1\sigma^2 2\sigma 1\sigma^*$, 0.006 $2\sigma^2 \delta^2$ 0.017 $1\sigma^2 2\sigma \pi$, 0.003 $1\sigma^2 1\sigma^* \pi$
15.00	0.279 $1\sigma^2 2\sigma^2$, 0.017 $1\sigma 2\sigma \delta^2$, 0.273 $1\sigma^2 1\sigma^{*2}$, 0.335 $1\sigma^2 2\sigma 1\sigma^*$, 0.004 $2\sigma^2 \delta^2$, 0.019 $1\sigma^2 2\sigma \pi$, 0.006 $1\sigma^2 2\sigma \pi$, 0.004 $1\sigma^2 1\sigma^* \pi$

TABLE XLVI

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrO

R (bohr)	Configuration contribution
3.00	0.95 $1\sigma^2 2\sigma\,\pi^4$
3.50	0.90 $1\sigma^2 2\sigma\,\pi^4$, 0.02 $1\sigma\,2\sigma^2\,\pi^4$, 0.02 $1\sigma^2 2\sigma\,\pi^2\pi^{*2}$, 0.02 $1\sigma^2 2\sigma\,\pi^3\pi^*$
4.00	0.71 $1\sigma^2 2\sigma\,\pi^4$, 0.14 $1\sigma\,2\sigma^2\,\pi^4$, 0.08 $1\sigma 2\sigma^2\,\pi^3\pi^*$
5.00	0.88 $1\sigma^2 2\sigma\,\pi^4$, 0.02 $1\sigma\,2\sigma^2\,\pi^4$, 0.02 $1\sigma\,2\sigma^2\pi^3\pi^*$, 0.02 $1\sigma^2 2\sigma\,\pi^3\pi$
7.00	0.86 $1\sigma^2 2\sigma\,\pi^4$, 0.08 $1\sigma^2 2\sigma\pi^3\pi^*$
10.00	0.11 $1\sigma^2 1\sigma^*\,\pi^3\pi^*$, 0.80 $1\sigma^2 2\sigma\pi^3\pi^*$, 0.02 $1\sigma^2 2\sigma\pi^2\pi^{*2}$

TABLE XLVII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrF

R (bohr)	Configuration contribution
3.00	0.958 $1\sigma^2 2\sigma^2 \pi^4$, 0.017 $1\sigma^2 \delta^2 \pi^4$
3.50	0.954 $1\sigma^2 2\sigma^2 \pi^4$, 0.019 $1\sigma^2 \delta^2 \pi^4$
4.00	0.951 $1\sigma^2 2\sigma^2 \pi^4$, 0.019 $1\sigma^2 \delta^2 \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.004 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
5.00	0.941 $1\sigma^2 2\sigma^2 \pi^4$, 0.019 $1\sigma^2 \delta^2 \pi^4$, 0.007 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$ 0.003 $1\sigma 2\sigma^2 1\sigma^* \pi^4$
7.00	0.922 $1\sigma^2 2\sigma^2 \pi^4$, 0.003 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.010 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.002 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.004 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.022 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.011 $2\sigma^2\ \delta^2 \pi^4$
10.00	0.707 $1\sigma^2 2\sigma^2 \pi^4$, 0.004 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.002 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.005 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.231 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.009 $2\sigma^2\ \delta^2 \pi^4$, 0.001 $1\sigma^2 2\sigma \pi^4 \pi^*$, 0.007 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$
15.00	0.037 $1\sigma^2 2\sigma^2 \pi^4$, 0.015 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$ 0.015 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.865 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.016 $1\sigma^2 2\sigma \pi^4 \pi^*$, 0.024 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$
20.00	0.062 $1\sigma^2 2\sigma^2 \pi^4$, 0.033 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$ 0.012 $1\sigma 2\sigma\ \delta^2 \pi^4$, 0.822 $1\sigma^2 2\sigma 1\sigma^* \pi^4$, 0.022 $1\sigma^2 2\sigma \pi^4 \pi^*$, 0.020 $1\sigma 2\sigma 1\sigma^* 2\sigma^* \pi^4$

TABLE XLVIII

CONFIGURATION CONTRIBUTION AT VARIOUS DISTANCES FOR LrCl

R (bohr)	Configuration contribution
3.00	0.956 $1\sigma^2 2\sigma^2 \pi^4$, 0.027 $1\sigma^2 \delta^2 \pi^4$, 0.003 $1\sigma^2 \delta \delta^* \pi^4$,
4.00	0.954 $1\sigma^2 2\sigma^2 \pi^4$, 0.029 $1\sigma^2 \delta^2 \pi^4$, 0.002 $1\sigma^2 \delta \delta^* \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$
4.50	0.955 $1\sigma^2 2\sigma^2 \pi^4$, 0.028 $1\sigma^2 \delta^2 \pi^4$, 0.002 $1\sigma^2 \delta \delta^* \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.001 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$
5.00	0.955 $1\sigma^2 2\sigma^2 \pi^4$, 0.026 $1\sigma^2 \delta^2 \pi^4$, 0.002 $1\sigma^2 \delta \delta^* \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^2 \pi^{*2}$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.001 $1\sigma\, 2\sigma\, \delta^2 \pi^4$ 0.002 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.001 $2\sigma^2 1\sigma^{*2} \pi^4$
7.00	0.960 $1\sigma^2 2\sigma^2 \pi^4$, 0.002 $1\sigma^2 \delta^2 \pi^4$, 0.001 $1\sigma^2 1\sigma^{*2} \pi^4$, 0.002 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.009 $1\sigma\, 2\sigma\, \delta^2 \pi^4$, 0.003 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.002 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.009 $2\sigma^2 \delta^2 \pi^4$
10.00	0.9711$\sigma^2 2\sigma^2 \pi^4$, 0.001 $1\sigma^2 2\sigma^2 \pi^3 \pi^*$, 0.001 $1\sigma\, 2\sigma\, \delta^2 \pi^4$, 0.003 $1\sigma^2 2\sigma\, 1\sigma^* \pi^4$, 0.005 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.014 $2\sigma^2 \delta^2 \pi^4$, 0.001 $2\sigma^2 \delta \delta^* \pi^4$
15.00	0.977 $1\sigma^2 2\sigma^2 \pi^4$, 0.006 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.013 $2\sigma^2 \delta^2 \pi^4$, 0.001 $2\sigma^2 \delta \delta^* \pi^4$
20.00	0.978 $1\sigma^2 2\sigma^2 \pi^4$, 0.006 $2\sigma^2 1\sigma^{*2} \pi^4$, 0.012 $2\sigma^2 \delta^2 \pi^4$

APPENDIX F

TABLE XLIX

ACRONYMS AND CORRESPONDING NAMES

Acronym	Name
WF	Wavefunction
HF	Hartree-Fock
DF	Dirac-Fock
DHF	Dirac-Hartree-Fock
EP	Effective Potential
REP	Relativistic Effective Potential
AREP	Averaged Relativistic Effective Potential
LCAO	Linear Combination of Atomic Orbital
AE	All Electron
SCF	Self Consistent Field
MCSCF	Multiconfiguration Self Consistent Field
CI	Configuration Interaction
RCI	Relativistic Configuration Interaction
SO	Spin-Orbit
MO	Molecular Orbital
MO molecules	Metal Oxide molecules
MP	Model Potential
STF	Slater Type Function
GTF	Gaussian Type Function

TABLE XLIX (continued)

Acronym	Name
RC	Reference Configuration
SDCI	Singly and Doubly excited Configuration Interaction
AHF	Atomic Hartree-Fock
DF-OCE	Dirac-Fock One Center Expansion
FV-MCSCF	Full Valence-Multiconfiguration Self Consistent Field
FO-CI	First Order-Configuration Interaction
MRD-CI	Multireference Doubly excited Configuration Interaction
CPF	Coupled Pair Function
MCPF	Modified Coupled Pair Function
SEFIT	Single-Electron Fit
MEFIT	Multielectron Fit
GVB	Generalized Valence Bond
CASSCF	Complete Active Space Self Consistent Field

VITA

Noppawan Tanpipat was born in Pang-nga, Thailand, on April 26, 1961. Her family moved to Phuket, a resort island in the south of Thailand, when she was nine years old. She graduated from Phuket Wittayalai High School in 1978. Then, she attended the Faculty of Science, Prince of Songkla University, Thailand, in 1978. In April of 1981, her junior year in college, a tragedy happened to her family; her father was assassinated. In 1982 she received a B.Sc. degree with the second honors in Chemistry from Prince of Songkla University.

The author came to the University of Tennessee in 1983 where she held a DOE graduate research assistantship throughout her graduate study. In December 1987, she received the Ph.D. degree in Chemistry from the University of Tennessee.

The author is a member of the American Chemical Society.