AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVISTIC EFFECTS AND THEIR APPLICATION TO THE ELECTRONIC STRUCTURE CALCULATIONS OF HEAVY ATOMS AND MOLECULES

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Abstract

The effects of the 4f shell of electrons and the relativity on valence electrons are compared. The effect of 4f shell (lanthanide contraction) is estimated from the numerical Hartree-Fock (HF) calculations of pseudo-atoms corresponding to Hf, Re, Au, Hg, Tl, Pb and Bi without 4f electrons and with atomic numbers reduced by 14. The relativistic effect estimated from the numerical Dirac-Hartree-Fock (DHF) calculations of those atoms is comparable in the magnitude with that of the 4f shell of electrons. Both are larger for 6s than for 5d or 6p electrons. The various relativistic effects on valence electrons are discussed in detail to determine the proper level of the approximation for the valence electron calculations of systems with heavy elements.

An effective core potential system has been developed for heavy atoms in which relativistic effects are included in the effective potentials (EP). The EP's are based on numerical Dirac-Hartree-Fock calculations for atoms and on the Phillips-Kleinman transformation with other aspects similar to the treatments of Goddard and Melius and Kahn, Baybutt, and Truhlar. The EP's may be written

$$U^{EP} = \sum_{\ell} \sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}} \sum_{m=-j}^{m=j} U_{\ell}^{EP}(r)\,|\ell j m\rangle\langle \ell j m|$$

where $|\ell j m\rangle$ is a two-component angular basis function that is a product of a two-component Pauli spinor and spherical harmonics. The numerical functions $U_{\ell j}^{EP}(r)$ are approximated as expansions in terms of Gaussian or exponential functions. The use of these EP's enables one to use the jj-coupling scheme for subsequent applications in all-valence-electron calculations on heavy atoms and their molecules.

A standard atomic SCF program has been modified to accommodate these EP's and Gaussian and exponential basis sets having the proper j-angular dependence. Energy levels for many atomic states of Xe and Au were calculated. The study of Xe excited states indicates that the spin-orbit splittings are reasonably approximated and that the numerical DHF calculations are adequately reproduced. Au has been treated as an atom with 1, 11, 17, 19, or 33 valence electrons to investigate the effects of re-definition of the core.

Application of EP to the molecular calculations is also discussed.

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TABLE OF CONTENTS

Page

I INTRODUCTION. 1

II THE LANTHANIDE CONTRACTION AND THE RELATIVISTIC EFFECTS ON VALENCE ELECTRONS. . . . 3

A. *Calculation of the Lanthanide* Contraction. 3

B. Relativistic Atomic Calculations. . . 4

C. *Relativistic and f-shell Effects on* Valence Electrons. 9

III EFFECTIVE CORE POTENTIALS (EP) FROM ATOMIC DHF CALCULATIONS. 31

A. Theory. 31

B. Calculations of EP. 39

1. Pseudo-orbitals. 39

2. Effective Potentials 48

IV ATOMIC HF CALCULATIONS WITH EP FOR j-j BASIS SETS. 55

A. Theory. 55

B. Results of Calculations 58

1. Xenon. 59

2. Gold 66

V PROSPECT OF APPLICATIONS OF EP TO MOLECULAR CALCULATIONS. 73

REFERENCES. 82

APPENDIX A OPEN-SHELL VECTOR COUPLING COEFFICIENTS FOR jj-COUPLED ATOMIC CONFIGURATIONS. 85

APPENDIX B TABLES OF THE ANALYTIC EXPANSIONS OF EP; Ne, Xe, and Au. 92

I. INTRODUCTION

The elements following the lanthanide series exhibit a number of unusual properties in relation to trends from lighter elements in the corresponding groups of the periodic table. The main causes for these anomalies are probably the introduction of a filled f-shell with 14 electrons and the substantial increase of relativistic effects due to the larger nuclear charges. Since results of electronic structure calculations of atoms are available in various levels of approximation with and without relativistic effects, it is possible to compare these effects on atoms. These effects on valence electrons are studied in the following chapter from non-relativistic Hartree-Fock[1,2] (HF) and relativistic Dirac-Hartree-Fock (DHF)[3] calculations.

The results of the above study indicate that many properties of molecules with heavy atoms may not be properly calculated unless relativistic effects are included. All electron self-consistent-field (SCF) calculations of those molecules, however, have not made even without relativistic effects due to the large number of two-electron integrals that arise. With the exception of the H_2^+ molecular ion,[4] relativistic effects on molecules have not been calculated in the full SCF level although the formalism has been developed by Malli and Oreg.[5] Actual calculations including relativistic effects have been performed using various levels of approximations, such as single-center expansions,[6,7] perturbation theory,[8] semi-empirical models,[9] and a discrete-basis-set method using a local exchange approximation.[10] One of the promising ways to handle this problem is to treat only the valence electrons explicitly using a frozen core approximation. This usually involves the substitution of the effect of the core electrons with some form of pseudopotential. Many methods have been developed and we modify one of *ab initio* approaches[11,12] to include the relativistic effects in the effective core potentials (EP). Our methods are based upon *ab initio* DHF calculation for atoms and the Phillips-Kleinman[13] transformation to effective potentials.

Since the EP's developed in this thesis emphasize the non-relativistic characteristics of valence electrons, the applications to the atomic and the molecular calculations can be done with either LS- or JJ-coupling scheme. Practical applications are studied in later sections.

II. THE LANTHANIDE CONTRACTION AND THE RELATIVISTIC EFFECTS ON VALENCE ELECTRONS

A. Calculation of the Lanthanide Contraction

The elements following the rare earth series have 14 more electrons in the filled 4f shell in addition to electrons in s, p and d shells compared with the previous members in the group. The effect of these additional electrons is commonly called the "lanthanide contraction"; it arises from the incompleteness of shielding by 4f electrons of the additional nuclear charge and yields a contraction of the radii of outer electrons as well as other effects. In order to estimate these effects, we made HF calculations for pseudo-atoms[14] without a 4f shell and with atomic numbers less by 14. The pseudo-atom calculations were performed using the numerical HF program of Fischer[15] slightly modified by Bagus.[14]

The Hamiltonian for n electrons[15] is

$$H^{NR} = \sum_{i=1}^{n} \left(\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{i>j} \frac{1}{r_{ij}} \qquad (1)$$

where Z is the nuclear charge, r_i is the distance between the electron i and the nucleus and r_{ij} is the distance between electrons i and j. The energies and wave functions can be calculated if the total wave function of the system is given by the antisymmetrized product of one-electron wave functions. Calculations were made for the LS configuration average for pseudo-atoms of Hf, Re, Au, Hg, Tl, Pb, and Bi. Comparing these results with those of HF calculations on the corresponding real atoms, a reasonable estimate of f-shell effect can be obtained. Some of the results are summarized in Tables I, II, and III and Figures 1 and 2. Discussions of the results in relation to the relativistic effects are given in a later section.

B. Relativistic Atomic Calculations (DHF)

Relativistic effects on atoms may be observed by comparing DHF with HF calculations. The relativistic Hamiltonian, which is used for DHF calculations, is given for n electrons by[16,17]

$$H^R = \sum_{i=1}^{n} h_D(i) + \sum_{i>j} \frac{1}{r_{ij}} \tag{2}$$

when many-electron relativistic terms, usually approximated by Breit interaction terms,[17] are not included. In Equation (2) h_D is the Dirac one-electron Hamiltonian which may be written as

$$h_D = c\,\boldsymbol{\alpha} \cdot \boldsymbol{p} + \boldsymbol{\beta}\, c^2 - \frac{Z}{r} \tag{3}$$

where r is the distance from the nucleus of charge Z, $\boldsymbol{p}$ is the momentum operator ($-i\nabla$). Also Dirac operators $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are given by

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}^P \\ \boldsymbol{\sigma}^P & 0 \end{pmatrix} \tag{4}$$

with $\underset{\approx}{\sigma}^{P}$ being a Pauli matrix and

$$\underset{\approx}{\beta} = \begin{pmatrix} \underset{\approx}{I} & 0 \\ 0 & -\underset{\approx}{I} \end{pmatrix} \tag{5}$$

with $\underset{\approx}{I}$ the 2 x 2 unit matrix. In atomic units, which are used for all equations throughout this thesis, the velocity of the light c is equal to $1/\alpha$ where α is the hyperfine structure constant. This α should not be confused with Dirac operator $\underset{\approx}{\alpha}$ of Equation (4).

The total wave function for a system with n electrons may be approximated by the antisymmetrized product of one electron wave function,[17]

$$\Psi^{R} = \mathcal{A}(\psi_1^{R}\ \psi_2^{R}\ldots\ldots\psi_n^{R}) \tag{6}$$

where $\mathcal{A}$ is an antisymmetrizer. In Equation (6) ψ_i^{R}'s are four-component Dirac spinors which may be expressed as

$$\psi_{nkm}^{R} = \frac{1}{r}\begin{pmatrix} P_{nk}(r)\Omega_{km}(\theta,\phi) \\ iQ_{nk}(r)\Omega_{-km}(\theta,\phi) \end{pmatrix} \tag{7}$$

where

$$\Omega_{km}(\theta,\phi) = \sum_{\sigma=\pm\frac{1}{2}} C(\ell\tfrac{1}{2}j;m-\sigma,\sigma)\ Y_{\lambda}^{m-\sigma}(\theta,\phi)\ \phi_{1/2}^{\sigma} \tag{8}$$

$Y_{\lambda}^{m-\sigma}$ is a spherical harmonic,

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

Pauli spinors, $C(1\frac{1}{2}j;m-\sigma,\sigma)$ is a Clebsch-Gordon coefficients, and $\lambda = k = (j + \frac{1}{2})$ if $j = \ell - \frac{1}{2}$ and $\lambda = -(k + 1) = (j + \frac{1}{2})$ if $j = \ell + \frac{1}{2}$. k is called the relativistic quantum number. The radial components P_{nk} and Q_{nk} are called the large and the small components respectively. P_{nk} and Q_{nk} satisfy the relativistic Hartree-Fock equations which have the form of two coupled linear equations.[17] The essential features of these equations can be understood from the simple case of a single electron in the central field of the nucleus.* In this case the radial equations are[17,18]

$$\frac{dP_{nk}}{dr} + \frac{kP_{nk}}{r} - (\frac{2}{\alpha} + \alpha[V-\varepsilon_{nk}])\ Q_{nk} = 0, \tag{9a}$$

$$\frac{dQ_{nk}}{dr} - \frac{kQ_{nk}}{r} + \alpha[V - \varepsilon_{nk}]\ P_{nk} = 0, \tag{9b}$$

where V is the potential. In the non-relativistic limit, $\frac{2}{\alpha} >> \alpha|V - \varepsilon_{nk}|$, these two equations are reduced into the familiar Schrödinger equation after eliminating the small component, Q_{nk}.[17,18] Therefore, by comparing the large component, P_{nk}, with the corresponding HF radial wave functions, a reasonable qualitative picture of relativistic effects may be obtained. For this reason radial wave functions for several atoms have been calculated with the numerical DHF program of Desclaux.[16] The calculations have

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*The radial equations for many electron cases may be found in the literature e.g., Equation (9.8) of Reference 17. All the additional terms not present in Equation (9) come from the coulomb and the exchange interactions among Dirac spinors.

been performed with the assumption of point nuclei to facilitate comparison with the published HF calculations of Mann.[1] The effect of this approximation is small for the valence electrons although it may be substantial for 1s electrons. Table I shows that these effects for DHF calculations on Pb are less than 0.1% for orbital energies. The details of calculations are omitted since they are available in the literature.[3,16]

Table I. Orbital Energies of Pb. (Average Energy of LS Configurations)

Negative of Orbital Energies in a.u.

	Point Nucleus	Finite Nucleus[a]
1s	3258.3	3255.9
2s	588.25	587.88
$2p_{1/2}$	563.50	563.49
$2p_{3/2}$	482.89	482.90
3s	143.84	143.75
$3p_{1/2}$	132.81	132.80
$3p_{3/2}$	114.59	114.59
$3d_{3/2}$	96.807	96.811
$3d_{5/2}$	92.967	92.970
4s	34.007	33.986
$4p_{1/2}$	29.212	29.212
$4p_{3/2}$	24.695	24.697
$4d_{3/2}$	16.918	16.919
$4d_{5/2}$	16.065	16.066
$4f_{5/2}$	5.9324	5.9332
$4f_{7/2}$	5.7406	5.7414
5s	6.1493	6.1450
$5p_{1/2}$	4.4404	4.4405
$5p_{3/2}$	3.5933	3.5937
$5d_{3/2}$	1.1385	1.1388
$5d_{5/2}$	1.0357	1.0360
6s	.56701	.56651
$6p_{1/2}$	.27504	.27511
$6p_{3/2}$	.21982	.21992

[a] From Reference 3.

C. Relativistic and f-shell Effects on Valence Electrons

Orbital energies for 5d, 6s, and 6p levels are given in Table II for Hf, Re, Au, Hg, Tl, Pb and Bi. Three calculations, HF[1] and DHF[3] calculations of atoms and HF calculations of pseudo-atoms, are comparable in accuracies and levels of approximations. Thus, the differences among the results are consequences of the different physical models used.

Of the trends in orbital energies shown in Table II and Figures 1 and 2, the simplest and most important is that for s electrons. These orbitals penetrate deeply into the atom and are subject to the largest relativistic effects. The effect of f-shell is in the same direction with that of relativity but the magnitude of the former is less than half as large as that of the latter.

There is no unique trend in the f-shell effects for the 5d electrons and these effects are very small. The incomplete shielding of f electrons is probably compensated for by the more effective shielding of the penetrating 5s and 5p electrons, since 5d orbitals are relatively diffuse. In the relativistic cases, 5s and 5p electrons are even more tightly bound and both $5d_{3/2}$ and $5d_{5/2}$ orbitals become less bound than in the HF atoms.

The f-shell effects on the 6p electrons (Fig. 2) are smaller but otherwise similar to those for 6s electrons. The relativistic effect for the weighted average ($\frac{1}{3}\, p_{1/2}$ + $\frac{2}{3}\, p_{3/2}$) is very small, although the $p_{1/2}$ - $p_{3/2}$ splitting is

Table II. Orbital Binding Energies (Atomic Units)

		5d		6s		6p	
	$(5d_{3/2})$		$(5d_{5/2})$	$(6s_{1/2})$	$(6p_{1/2})$		$(6p_{3/2})$
pseudo Hf		.3192		.1805			
Hf(HF)[a]		.2992		.2104			
Hf(DHF)[b]	.2473		.2355	.2397			
pseudo Re		.4660		.2031			
Re(HF)		.4538		.2347			
Re(DHF)	.3972		.3661	.2783			
pseudo Au		.5372		.1905			
Au(HF)		.5210		.2208			
Au(DHF)	.4935		.4287	.2917			
pseudo Hg		.7191		.2288			
Hg(HF)		.7142		.2610			
Hg(DHF)	.6501		.5746	.3280			
pseudo Tℓ		.9472		.3162		.1836	
Tℓ(HF)		.9683		.3611		.1924	
Tℓ(DHF)	.8945		.8062	.4492	.2114		.1765
pseudo Pb		1.1772		.4025		.2268	
Pb(HF)		1.2245		.4589		.2398	
Pb(DHF)	1.1388		1.0360	.5665	.2751		.2199
pseudo Bi		1.4131		.4906		.2693	
Bi(HF)		1.4874		.5582		.2862	
Bi(DHF)	1.3894		1.2710	.6862	.3385		.2612

[a] Reference 1

[b] Reference 3

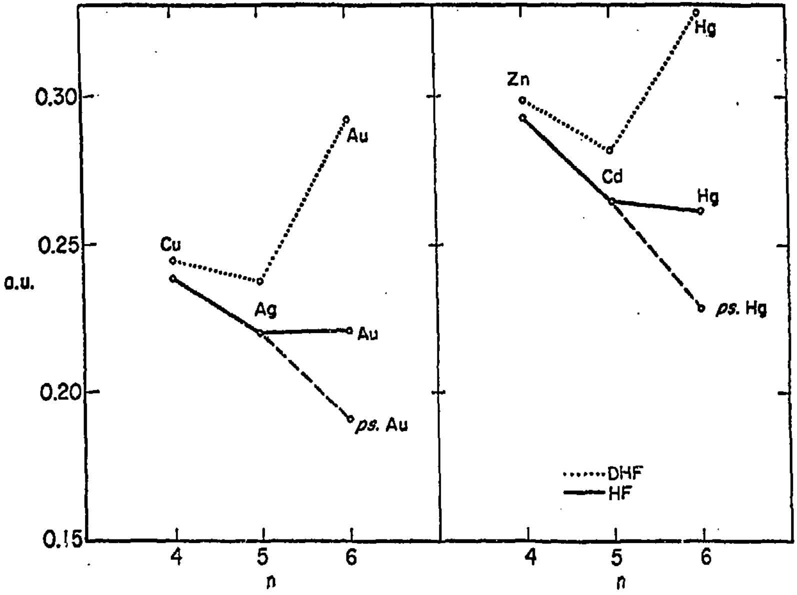

Figure 1. Orbital energies for valence-shell s-electrons. Dotted lines connect relativistic (DHF) values: solid lines connect non-relativistic (HF) values; pseudo-atoms are indicated as ps. Au and ps. Hg.

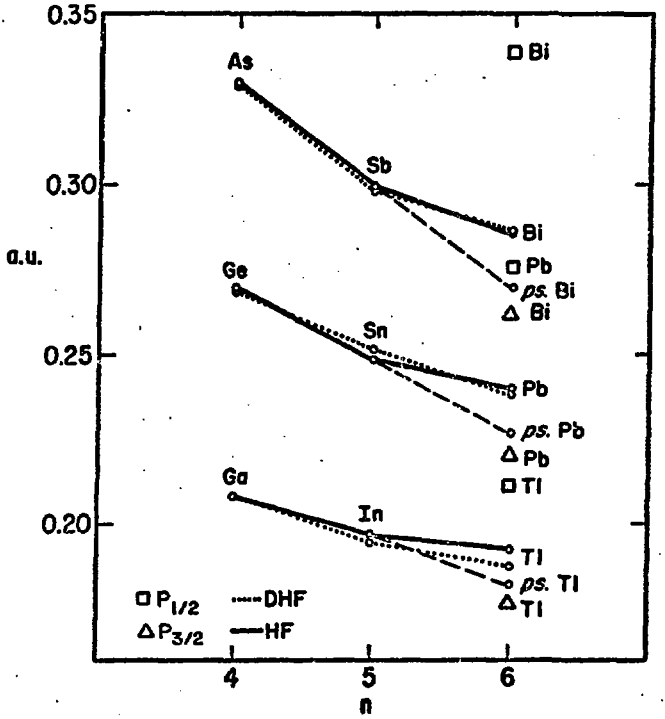

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Figure 2. Orbital energies for valence-shell p-electrons. Separate $6p_{1/2}$ and $6p_{3/2}$ values are shown as well as the weighted average $(1/3\ p_{1/2} + 2/3\ p_{3/2})$ connected with the dotted line.

becoming substantial. This splitting, which is significantly larger than the effect of f-shell, may play an important role in bonding.

Table III and Figure 3 show the expectation values for the radius of the valence electrons in these same atoms. The lanthanide contraction (4f-shell) effects are now more nearly comparable to the relativistic effects in magnitude. The various differences can be understood on the same basis as that given for the energies. Here we note that $<r>$ for pseudo-atoms is always larger than the HF value for the real atom indicating that the 4f screening is incomplete.

In summary, the relativistic effect is as important as the 4f-shell effect for atoms considered. The proper account of the relativistic effect is desirable for most calculation of the systems including these atoms. Since the relativistic effects are expected to increase several fold for the atoms from 104 to 115 as compared to Hf to Bi, the predictions of the chemical behavior should be based upon the DHF calculations for those atoms. These predictions, in some cases, may deviate significantly from those based on the simple extrapolation from the group trends.[19]

In order to determine what level of the relativistic formation is required for the valence electron calculations, a closer examination of the relativistic effect on valence electrons is given. Although this topic has been already discussed,[20,21] a slightly different approach is taken here.

Table III. Comparison of Radial Expectation Values <R>

	$d_{3/2}$	5d	$d_{5/2}$	6s	$p_{1/2}$	6p	$p_{3/2}$
pseudo Hf		2.5048		4.6934			
Hf(HF)		2.2277		4.0684			
Hf(DHF)	2.3376		2.4198	3.6939			
pseudo Re		2.0326		4.2162			
Re(HF)		1.7999		3.6942			
Re(DHF)	1.8301		1.9047	3.2770			
pseudo Au		1.7228		4.2230			
Au(HF)		1.5433		3.7006			
Au(DHF)	1.5359		1.6185	3.0609			
pseudo Hg		1.6040		3.7500			
Hg(HF)		1.4327		3.3284			
Hg(DHF)	1.4312		1.4987	2.8434			
pseudo Tℓ		1.5042		3.3294		4.2434	
Tℓ(HF)		1.3412		2.9669		3.9262	
Tℓ(DHF)	1.3387		1.3940	2.5792	3.5166		4.0123
pseudo Pb		1.4214		3.0475		3.7532	
Pb(HF)		1.2671		2.7242		3.4569	
Pb(DHF)	1.2641		1.3119	2.3916	3.0739		3.5162
pseudo Bi		1.3506		2.8336		3.4116	
Bi(HF)		1.2046		2.5939		3.1366	
Bi(DHF)	1.2012		1.2439	2.2429	2.7802		3.1862

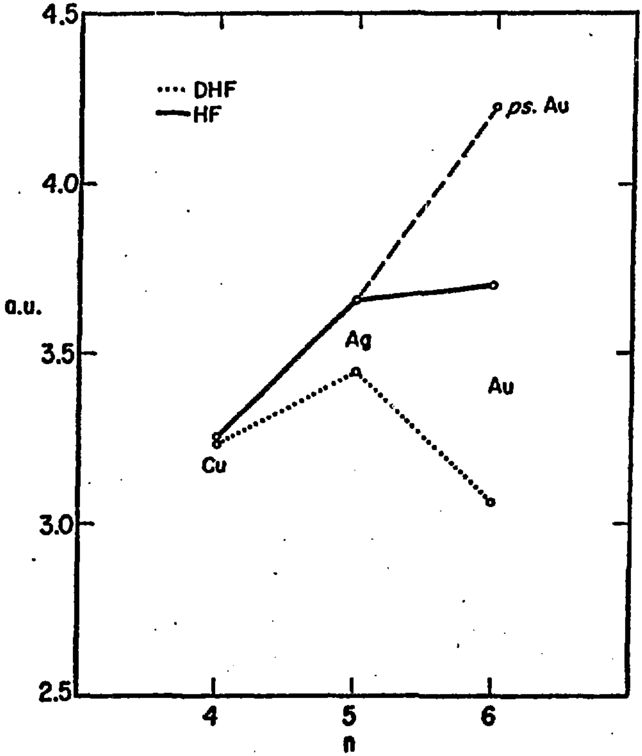

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Figure 3. Expectation values for the radius <r> for the valence-shell s-electron.

Radial wave functions of the valence orbitals of Pb and U are shown in Figures 4 through 8. There are relatively large contractions in 6s orbitals of Pb (Fig. 4) and 7s orbitals of U (Fig. 6). These are due to the penetrating nature of those electrons and less effective screening of inner electrons with high angular quantum numbers (e.g., 5d) as was discussed previously. The $6p_{1/2}$ orbital of Pb (Fig. 5) is noticeably different from the non-relativistic 6p whereas the $6p_{3/2}$ is almost the same as the non-relativistic 6p. The 6d (Fig. 7) and 5f (Fig. 8) wave functions of U are more diffuse in the relativistic case due to the more effective shielding of the nuclear charge by electrons with smaller angular quantum numbers. For this reason, the roles of 5f and 6d electrons in bonding are probably more important than would be estimated from non-relativistic calculations.

Small components are relatively large near the nucleus and decrease rapidly as the radial distance increases. In Table IV the electron densities represented by small components are negligible compared with those by large components for valence electrons of U (less than 0.03%) although 15% of the electron density is due to the small component for the 1s electrons. Since small components become even less important in the outer region (Table IV), it may be reasonable to assume that small components can be neglected in calculations that emphasize the description of valence electrons.[21]

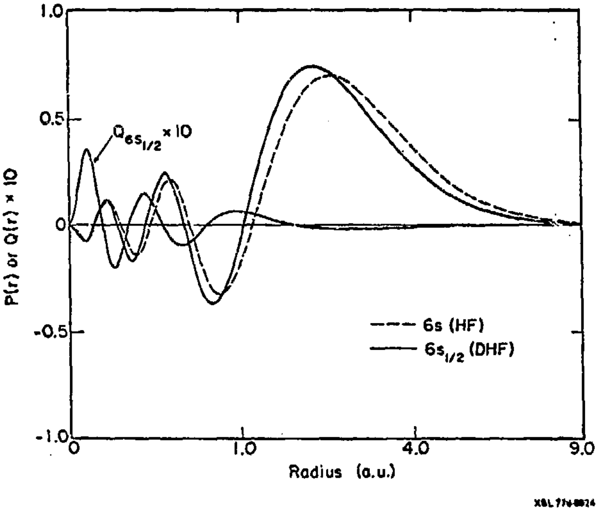

Figure 4. Relativistic (DHF) and non-relativistic (HF) radial components of 6s wave functions of Pb. Only the small component of DHF is labeled.

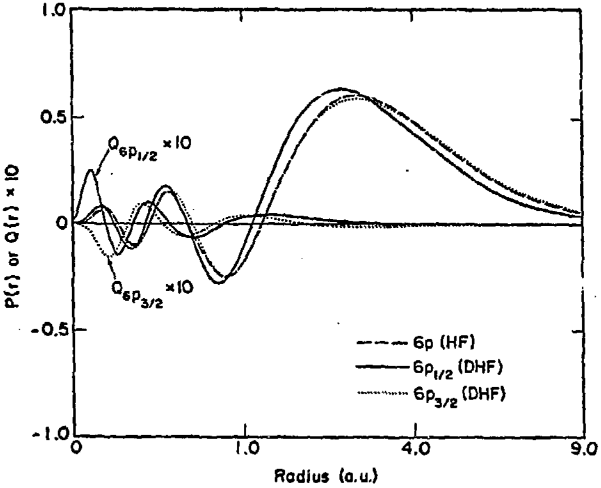

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Figure 5. Relativistic (DHF) and non-relativistic (HF) radial components of 6p wave functions of Pb.

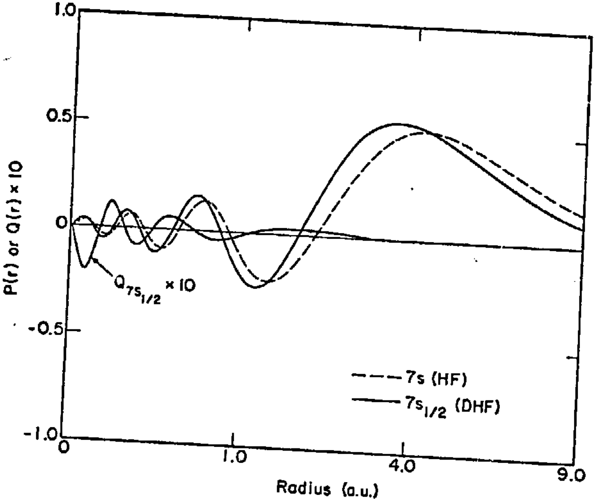

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Figure 6. Relativistic (DHF) and non-relativistic (HF) radial components of 7s wave functions of U.

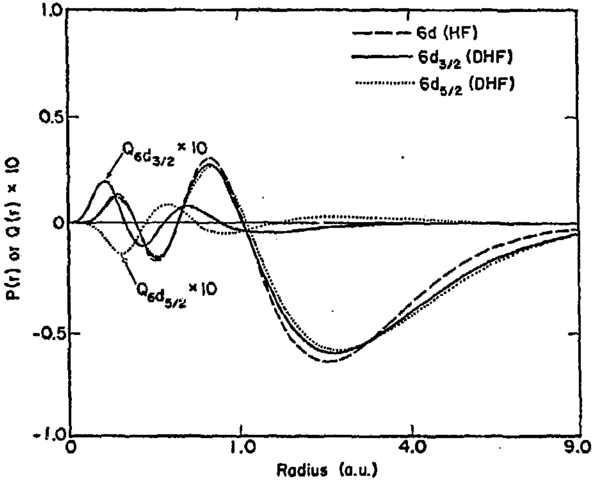

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Figure 7. Relativistic (DHF) and non-relativistic (HF) radial components of 6d wave functions of U.

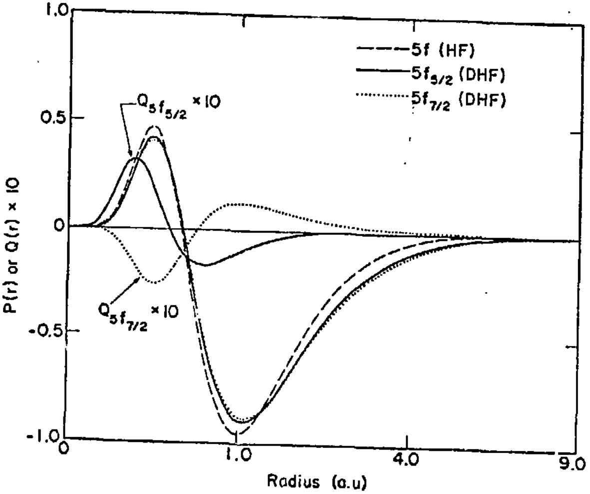

Figure 8. Relativistic and non-relativistic (HF) radial components of 5f wave functions of U.

Table IV. Normalized Electron Densities Represented by the Large and the Small Components of U Radial Wave Function

Orbital	Portion Inside R_{max}	$\frac{\text{Small}}{\text{Large}}$	Portion Outside R_{max}	$\frac{\text{Small}}{\text{Large}}$	R_{max}	$\frac{\text{Small}}{\text{Large}}$ (total)
1s	.292	1.48×10^{-1}	.708	1.46×10^{-1}	.00801	1.46×10^{-1}
2s	.395	6.11×10^{-2}	.605	1.23×10^{-2}	.0485	3.10×10^{-2}
$2p_{1/2}$	.386	8.04×10^{-2}	.614	2.26×10^{-3}	.0359	3.11×10^{-2}
$2p_{3/2}$	.366	2.72×10^{-2}	.634	2.56×10^{-2}	.0439	2.62×10^{-2}
3s	.438	2.09×10^{-2}	.562	2.48×10^{-3}	.138	1.04×10^{-2}
$3p_{1/2}$	.406	2.53×10^{-2}	.594	3.86×10^{-4}	.125	1.04×10^{-2}
$3p_{3/2}$	.430	1.57×10^{-2}	.570	4.02×10^{-3}	.146	9.00×10^{-3}
$3d_{3/2}$	.395	2.11×10^{-2}	.605	1.02×10^{-3}	.113	8.85×10^{-3}
$3d_{5/2}$	.357	9.41×10^{-3}	.643	8.00×10^{-4}	.113	8.50×10^{-3}
4s	.447	7.63×10^{-3}	.553	6.18×10^{-4}	.308	3.74×10^{-3}
$4p_{1/2}$	.458	7.85×10^{-3}	.542	9.65×10^{-5}	.308	3.63×10^{-3}
$4p_{3/2}$	.452	9.14×10^{-3}	.548	5.87×10^{-3}	.341	3.14×10^{-3}
$4d_{3/2}$	.421	6.81×10^{-3}	.579	1.19×10^{-4}	.324	2.93×10^{-3}
$4d_{5/2}$	.444	4.64×10^{-3}	.556	1.34×10^{-3}	.341	2.80×10^{-3}
$4f_{5/2}$	.348	6.11×10^{-3}	.652	4.85×10^{-4}	.279	2.43×10^{-3}

Table IV (continued)

Orbital	Portion Inside R_{max}	$\frac{\text{Small}}{\text{Large}}$	Portion Outside R_{max}	$\frac{\text{Small}}{\text{Large}}$	R_{max}	$\frac{\text{Small}}{\text{Large}}$ (total)
$4f_{7/2}$	.378	3.02×10^{-3}	.622	1.99×10^{-3}	.293	2.38×10^{-3}
$5s$	.390	2.76×10^{-3}	.610	1.39×10^{-4}	.621	1.16×10^{-3}
$5p_{1/2}$	.412	2.56×10^{-3}	.588	2.28×10^{-5}	.652	1.08×10^{-3}
$5p_{3/2}$	.411	1.92×10^{-3}	.589	1.96×10^{-4}	.721	9.05×10^{-4}
$5d_{3/2}$	.418	1.69×10^{-3}	.582	1.74×10^{-5}	.797	7.16×10^{-4}
$5d_{5/2}$	.380	1.41×10^{-4}	.620	2.26×10^{-4}	.797	6.76×10^{-4}
$5f_{5/2}$	.337	8.30×10^{-4}	.663	2.93×10^{-5}	1.08	2.99×10^{-4}
$5f_{7/2}$	.318	6.22×10^{-4}	.682	1.29×10^{-4}	1.08	2.86×10^{-4}
$6s$	.416	6.25×10^{-4}	.584	2.78×10^{-5}	1.38	2.76×10^{-4}
$6p_{1/2}$	.360	6.19×10^{-4}	.640	3.24×10^{-6}	1.45	2.25×10^{-4}
$6p_{3/2}$	.392	3.90×10^{-4}	.608	3.10×10^{-5}	1.69	1.72×10^{-4}
$6d_{3/2}$	.319	1.87×10^{-4}	.681	2.17×10^{-6}	2.39	6.13×10^{-5}
$6d_{5/2}$	.324	1.37×10^{-4}	.676	1.58×10^{-5}	2.52	5.50×10^{-5}
$7s$	.336	8.35×10^{-5}	.664	2.57×10^{-6}	3.57	2.97×10^{-5}

The total relativistic effects or the difference between results of DHF and HF calculations which we have discussed so far, may be divided into two kinds, one due to the use of different Hamiltonians (direct effects) and the other to rearrangement (indirect effects).[20] The relativistic character of valence electrons apparently depends more on the magnitude of the former than the latter. Although the exact separation of the two may not be possible, the former can often be reasonably estimated from the perturbation theory.[22,23]

From the Pauli approximation of the Dirac theory,[22,23,24] the effective relativistic Hamiltonian, which is correct to the order of $1/c^2$, may be expressed as

$$H^R_{eff}(r \qquad H_0(r) + H_m(r) + H_d(r) + H_{so}(r) \tag{10}$$

where $H_0(r)$ is the non-relativistic Hamiltonian, H_m the mass-velocity correction term given by

$$H_m(r) = -(\alpha^2/2)[E^o - V(r)]^2, \tag{11}$$

H_d the Darwin term

$$H_d(r) = -(\alpha^2/4)[dV(r)/dr](d/dr), \tag{12}$$

and H_{so} the spin-orbital coupling term

$$H_{so}(r) = -(\alpha^2/4)(k+1)(1/r)[dV(r)/dr], \tag{13}$$

where k is the relativistic quantum number. The corresponding matrix elements, or energy expectation values, may be expressed as, $E_o \equiv E^o_{nl}$ (non-relativistic energy eigenvalues of nl shell),

$$E_m = -(\frac{\alpha^2}{2}) \int_0^\infty dr\ r^2 [R^o_{nl}(r)]^2\ [E^o_{nl} - V(r)]^2, \qquad (14)$$

$$E_d = -(\frac{\alpha 2}{4}) \int_0^\infty dr\ r^2\ R^o_{nl}(r)\ [\frac{dV(r)}{dr}]\ (\frac{1}{r}), \qquad (15)$$

and

$$E_{so} = -(\frac{\alpha^2}{4})(k+1) \int_0^\infty dr\ r^2 [R^o_{nl}(r)]^2\ [\frac{dV(r)}{dr}](\frac{1}{r}) \qquad (16)$$

where R_{nl} is the radial wave function. Orbital energies of Pb corrected by applying these perturbations to the Hartree-Fock-Slater (HFS) calculations[22] are shown in Table V. The results of DHF, HF, and Dirac-Hartree-Fock-Slater (DHFS)[25] are also given in the Table V. Within the Slater approximation[22,25] direct relativistic effects appear larger than the total in the magnitude although some of the differences are probably due to the different configuration (closed $6p_{1/2}$ orbital) assumed in DHFS calculations. If we assume that relativistic corrections from the perturbational method are same for HF and HFS, the same is true with the HF and DHF calculations since $\Delta\varepsilon$[HFS(II)-HFS(I)] is larger than the energy difference between DHF and HF results.

Therefore, s and p valence electrons for the atoms following lanthanide series are substantially relativistic although most relativistic effects are probably in the core region. In order to clarify this point, the Equations (14),

Table V. Orbital Energies of Pb Valence Electrons.
(All are negative and in a.u.)

	DHF	HF[a]	DHFS[b]	HFS(I)[c]	HFS(II)[c,d]	$\Delta\epsilon$[HFS(II)-HFS(I)]
6s	.5670	.4586	.5259	.4444	.5883	.1438
$6p_{1/2}$	.2750	.2398	.2376	.2123	.2847	.0724
$6p_{3/2}$	.2198				.2380	.0257

[a] from Reference 1.

[b] from Reference 25 (The electrons were considered to occupy only the $6p_{1/2}$ orbital).

[c] from Reference 22.

[d] relativistic energy calculated from the perturbation theory.

(15), and (16) can be more carefully studied.

For valence electrons R^o_{nl} may be reasonably approximated by r^{-1} P_{nk} for the qualitative studies. Then the relativistic correction terms become

$$E_m \cong -(\frac{\alpha^2}{2}) \int_0^\infty dr[P_{nk}]^2 \ [E_{nl}-V(r)]^2, \qquad (17)$$

$$E_d + E_{so} \cong -(\frac{\alpha}{2}) \int_0^\infty dr \ P_{nk} \ Q_{nk}[\frac{dV(r)}{dr}]. \qquad (18)$$

Equation (9a) has been used to derive Equation (18) and the second term within the parenthesis [Eq. (9a)] is neglected in comparison to $2/\alpha$. From the above expressions it is easier to obtain the picture of the direct relativistic effects since the derivative of the wave function is eliminated inside the integral. We do not intend to calculate above quantities exactly; instead we merely present trends of all terms involved. Pb is used as an example with similar trends expected for other heavy elements.

P_{nk} and Q_{nk} appear in Figure 4 and Figure 5. Although V(r) can be obtained from HF or DHF calculations, the HFS potential of Herman and Skillman[22] is presented in Figure 9. The choice of this potential is a matter of convenience and should not introduce any serious error in this discussion. A plot of dV(r)/dr is given in Figure 10.

Since V(r) is quite large near nucleus and rapidly decreases as radius increase, most contributions to the E_m

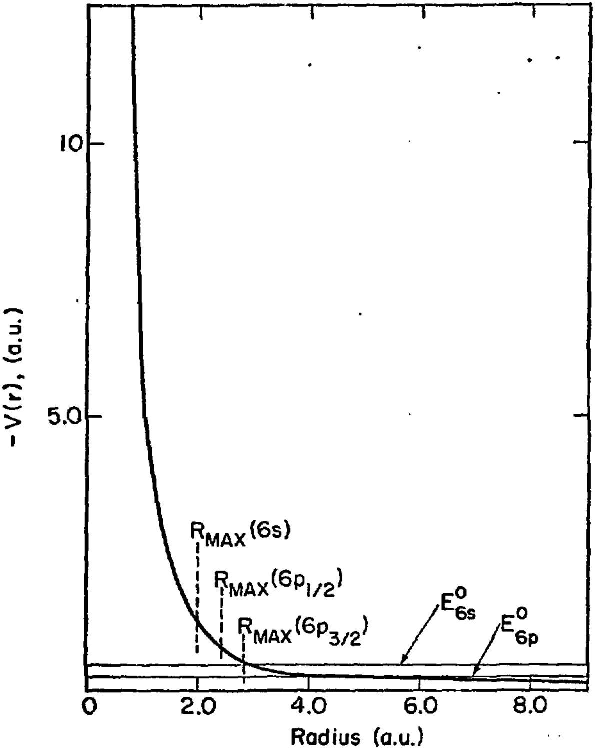

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Figure 9. V(r) of Pb from Ref. 22.

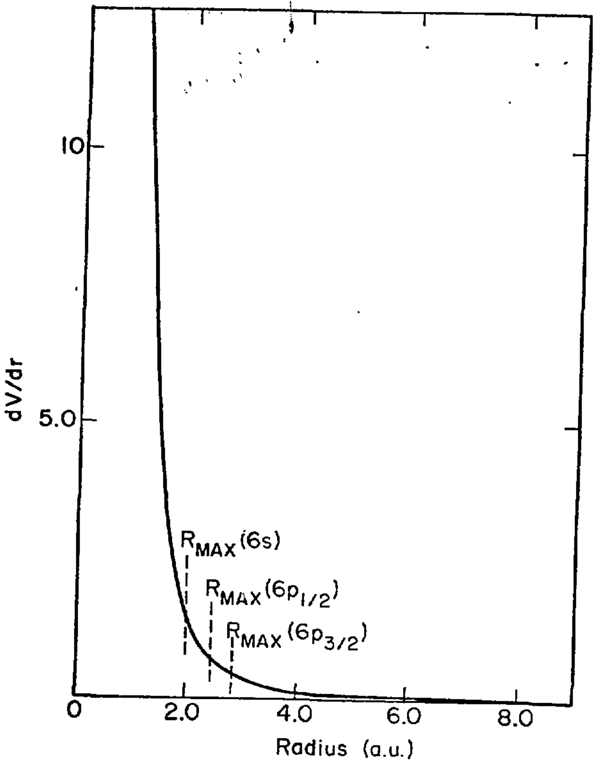

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Figure 10. dV(r)/dr calculated from the V(r) of Fig. 9.

terms are from the core region, as expected on physical grounds. dV(r)/dr behaves similarly and terms inside the integral of E_d + E_{so} [Eq. (18)] decrease even more rapidly due to the presence of Q_{nk}. Therefore, valence electrons appear to be essentially non-relativistic in the valence region in spite of the substantial magnitude of relativistic effects already mentioned. This evidence as well as the non-importance of the small components suggest that treating the valence electrons non-relativistically, but in the field of EP derived from a relativistic DHF calculation for the atom, may be a reasonable approximation.

III. EFFECTIVE CORE POTENTIALS FROM ATOMIC DHF CALCULATIONS

A. Theory

If we divide the antisymmetrized product of one-electron Dirac spinors [Eq. (6)] into two classes, core orbitals and valence orbitals, the wave function for many-electron atom may be expressed as

$$\Psi^R = \mathcal{A}[(\psi_1^R\ \psi_2^R\cdots\psi_{m_c}^R)^{\text{core}}\ (\psi_1^R\ \psi_2^R\cdots\psi_{m_v}^R)^{\text{val}}] \qquad (19)$$

for a single configuration. In Equation (19), m_c is the number of core electrons, and m_v is the number of valence electrons with separate indexing for core and valence wave functions. Then the total energy may be expressed as the sum of core, valence, and core-valence interaction energies

$$E_t^R = E_c^R + E_v^R + E_{cv}^R. \qquad (20)$$

Since, in many respects, the relativistic formalism for the many-electron atom is essentially the same as the non-relativistic, when the Breit interaction and quantum electrodynamic effects are not included, many methods used in the non-relativistic theory are also valid here. For example, the last two terms may be combined to obtain an energy expression

$$E_v + E_{cv} = \langle\Psi_v^R|H_v^R|\Psi_v^R\rangle/\langle\Psi_v^R|\Psi^R{}_v\rangle, \qquad (21)$$

where

$$\Psi_v^R = \mathcal{A}(\psi_1^R\psi_2^R\cdots\psi_{m_v}^R) \tag{22}$$

and

$$H_v^R = \sum_i^{m_v} [h_D(i) + \sum_j^{m_c} (J_j^D(i) - K_j^D(i))] + \sum_{i>i'}^{m_v} \frac{1}{r_{ii'}}. \tag{23}$$

In Equation (23), $J_j^D(i)$ and $K_j^D(i)$ are Coulomb and exchange operators defined for the four-component Dirac spinors.[17] In general, H_v^R is a sum of 4 x 4 matrices unlike the non-relativistic case. Based upon Equation (23), the straightforward frozen-core calculations may be performed. The difficulty for this procedure is the large number of two-electron integrals to be calculated as was discussed in the non-relativistic case.[12] The use of EP may be a solution to this problem.

Our effective potentials are obtained from atomic DHF calculations using a method that is essentially parallel to that developed by Melius[11] and Kahn[12] and their co-workers for the non-relativistic case, although it was necessary to introduce some modifications and approximations to accommodate the relativistic characteristics.

Effective potentials (EP's) have been most successfully applied to one-valence-electron systems, and in these cases the physical meaning of EP's can be rather well understood. In this section EP's are derived first for the one-valence electron atoms and later they are generalized to include many-valence-electron atoms.

When an orthonormal set is used for valence and core orbitals, the DHF equation for a single valence electron v outside the closed-shell becomes

$$[h_D + \sum_c (J_c^R - K_c^R)]\, \psi_v^R = \varepsilon_v \psi_v^R + \sum \psi_c^R\, \varepsilon_{cv} \qquad (24)$$

where c is the number and index for the core electrons [Note the change of indices from Equation (23)], and the ε_{cv} is an off-diagonal Lagrange multiplier which may be written as

$$\varepsilon_{cv} = \langle \psi_v | h_D + \sum_c (J_c^R - K_c^R) | \psi_c \rangle . \qquad (25)$$

Again, Equation (24) is essentially the same as that of HF formalism[12] except that operators are 4 x 4 matrices operating on four-component wave functions.

A core projection operator may be defined as

$$\mathcal{P} = \sum_c |\psi_c^R\rangle\langle\psi_c^R| , \qquad (26)$$

where the bra $\langle\psi_c^R|$ is a row-vector with four components and the ket $|\psi_c^R\rangle$ is a column-vector with four components. With Equations (24) and (26) it is possible to follow the non-relativistic formalism to obtain the relativistic version of the generalized Phillips-Kleinman pseudopotential.[13,26] The complete derivation is omitted here since it may be found in the non-relativistic work.[12] Several essential parts, however, will be reproduced in the following to clarify the development. Using Equation (26), Equation (24) may be rewritten as

$$(1-\mathcal{P})\ H_v^R\ \psi_v^R = \varepsilon_v\ \psi_v^R, \tag{27}$$

where

$$H_v^R = h_D + \sum_c (J_c^R - K_c^R). \tag{28}$$

If we define the relativistic pseudo-orbital, χ_v^R, as

$$\chi_v^R \equiv \psi_v^R + \sum_c a_c \psi_c^R \tag{29}$$

such that

$$\psi_v^R = (1-\mathcal{P})\ \chi_v^R, \tag{30}$$

then Equation (27) becomes

$$(1-\mathcal{P})\ H_v^R (1-\mathcal{P})\ \chi_v^R = \varepsilon_v (1-\mathcal{P})\ \chi_v. \tag{31}$$

From Equation (31), one can define the relativistic analog of the generalized Phillips-Kleinman pseudopotential,

$$V^{RGPK} = -\mathcal{P} H_v^R - H_v^R \mathcal{P} + \mathcal{P} H_v^R \mathcal{P} + \varepsilon_v \mathcal{P}, \tag{32}$$

where

$$(H_v^R + V^{RGPK})\ \chi_v^R = \varepsilon_v \chi_v, \tag{33}$$

or

$$(h_D + U^{core})\ \chi_v^R = \varepsilon_v \chi_v, \tag{34}$$

if

$$U^{core} = \sum_{c} (J_c - K_c) + V^{RGPK}. \tag{35}$$

It may be noted that U^{core} in Equation (34) is again a 4 x 4 matrix operating on four-component spinors, χ_v^R's.

To investigate the characteristics of the EP desired, we assume that U^{core} is expanded in terms of an angular basis set of Dirac spinors. The following equations are then obtained for the radial pseudo-wave-function

$$\frac{d}{dr}\begin{pmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{pmatrix} = \begin{pmatrix} -\frac{k_v}{r} & (\frac{2}{\alpha}) + \alpha[\epsilon_v - U_v^Q(r)] \\ -\alpha[\epsilon_v - U_v^P(r)] & \frac{k_v}{r} \end{pmatrix}\begin{pmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{pmatrix}, \tag{36}$$

where $U_v^Q(r)$ and $U_v^P(r)$ are radial components of U^{core}.

In theory, one may derive $U_v^P(r)$ and $U_v^Q(r)$ in Equation (36) from any $P_v^{ps}(r)$ and $Q_v^{ps}(r)$ satisfying Equation (31). Relativistic effective core potentials obtained from these pseudo-orbitals would not be continuous at points where nodes of $P_v^{ps}(r)$ or $Q_v^{ps}(r)$ occur. This difficulty may be avoided if the transformation of Equation (29) can be carried out in a manner to yield nodeless $P_v^{ps}(r)$ and $Q_v^{ps}(r)$ functions. However, nodes may not, in general, be removed simultaneously for the large and small components.

Since the role of small components and direct relativistic effects are assumed to be negligible in the valence region, as discussed in the previous section, we develop a method which does not include manipulations with small components. The Dirac Hamiltonian can be expanded after substitution with the wave functions containing only large components. The radial equation obtained this way may be given as[24]

$$\{H_o(r) + H_m(r) + H_d(r) + H_{so}(r) + H[\mathcal{O}(\alpha^4)]\}\, P_v(r) = \varepsilon_v P_v(r), \quad (37)$$

where all terms have the same meaning as in Equation (11), Equation (12), and Equation (13) and $H[\mathcal{O}(\alpha^4)]$ denotes the higher order terms which are not included in the Pauli approximation.

If higher order terms are neglected in Equation (37), a $U_v^{core}(r)$, which is correct within the Pauli approximation, can be obtained from a nodeless $P_v^{ps}(r)$. This involves solving a differential equation [Eq. (37)] for $U_v^{core}(r)$. Furthermore, it is correct only to order α^2 and all terms of the Hamiltonian have to be included when the EP obtained is applied in molecular calculations. It may be noted that the EP from Equation (37) still contains higher-order relativistic corrections, since ε_v is the solution of the DHF equation.

However, for our purposes, it is of little importance to have an accurate explicit representation of relativistic effects arising from the core region, where most of these effects exist as shown in the previous section, since we are mainly concerned with a reasonable representation of valence orbitals in the valence region. Thus, all relativistic effects may be incorporated into the EP.

With these approximations, the radial equation becomes

$$[H_o'(r) + U_v^{EP}(r)]\ P_v(r) = \varepsilon_v P_v(r) \tag{38}$$

where $H_o'(r)$ denotes the absence of core potential terms from the non-relativistic Hamiltonian. The EP in Equation (38) contains all one-electron relativistic effects of the atom being considered. When this EP is used for calculations on molecules or excited states of atoms, the validity of the results will depend on the difference between relativistic effects of the molecule and its constituent atoms or between that in ground and excited electronic states. This approximation appears to be reasonable since the most pronounced relativistic effects are present near the nucleus, as was discussed above.

The original form of Equation (38), before the reduction to the radial equation, is

$$[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U_v^{EP}]\ \chi_v^T = \varepsilon_v \chi_v^T, \tag{39}$$

where χ_v^T is a two-component pseudo-wave function containing only the large radial component of Equation (7).

When there is more than one valence electron, the wave equation may be given as[12]

$$[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U_v^{EP'} + W']\ \chi_v^T = \varepsilon_v \chi_v^T, \tag{40}$$

where W' includes all interactions between pseudo-orbitals and between pseudo-orbitals and core orbitals. Since the ultimate goal of this procedure is the reasonable and simple representation of the behavior of valence electrons in the valence region, interactions between the pseudo-orbital and the core orbitals may also be included in EP. Then Equation (40) becomes

$$[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U_v^{EP} + W(\chi^T, \chi_{v'}^T)]\,\chi_v^T = \epsilon_v \chi_v^T, \qquad (41)$$

where $W(\chi_v^T, \chi_{v'}^T)$ is the sum of Coulomb and exchange interactions of a given pseudo-orbital, χ_v^T, with all other pseudo-orbitals, $\chi_{v'}^T$'s.

From Equation (41) it is seen that U_v^{EP} will not be the same for different pseudo-orbitals. Therefore, the EP may be conveniently expressed as products of angular projection operators and radial functions, as are the EP's derived from HF calculations.[12] Since orbitals with different total angular moments, j, but with the same orbital angular momentum, ℓ, are nondegenerate in DHF results, the EP is expressed as*

$$U^{EP} = \sum_{\ell=0}^{\infty} \sum_{j=\ell-1/2}^{\ell+1/2} \sum_{m=-j}^{j} U_{\ell j}^{EP}(r)\,|\ell jm\rangle\langle\ell jm|, \qquad (42)$$

with the understanding that $|\ell jm\rangle$ and $\langle\ell jm|$ are two-component angular bases that are eigenfunctions in the Pauli approximation of the Dirac Hamiltonian.[24] It may be noted that the direct application of the EP of Equation (42) in atomic and molecular calculations requires the use of jj-coupling,

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*Two indices ℓj of Equation (42) can also be expressed as one index, k, the relativistic quantum number in Equation (7).

instead of conventional LS-coupling schemes.

B. Calculations of EP

1. Pseudo-orbitals

In the previous section, it has been shown that EP's can be obtained if suitable pseudo-orbitals in the form of Equation (29) are found. Because of orthogonalities of angular basis sets with distinct angular quantum numbers, the radial part of the pseudo-orbitals may be separated and expressed as

$$P_{nk}^{ps}(r) = \sum_{q=1}^{n} a_{qk} P_{qk}(r), \tag{43}$$

where n is a principal quantum number, k is the relativistic quantum number previously defined, and the P_{qk}'s are the large components of DHF radial wave functions.

For our purposes, the following properties are desired for $P_{nk}^{ps}(r)$; (i) the $P_{nk}^{ps}(r)$ should be nodeless and (ii) the form of $P_{nk}^{ps}(r)$ should be similar to that of the original valence wave function $P_{nk}(r)$ in the valence region. Property (i) is essential to prevent the occurrence of singularities, since the derivation of $U_j^{EP}(r)$ from the radial part of Equation (41) [Eq (46) of the following section] involves division by $P_{nk}^{ps}(r)$, whereas (ii) will hopefully prevent the generation of physically unreasonable pseudo-wave-functions.

Although many methods developed for the non-relativistic case[11,12] may be applicable, we pursue the following procedure for finding the appropriate coefficients, a_{qk}. Initially, the a_{qk}'s are obtained from a least square fit of a pseudo-orbital of Equation (43) to a given Slater-type function $C_\zeta r^t e^{-\zeta r}$. C_ζ and ζ are selected so that the maximum of the function, $C_\zeta\, r^t\, e^{-\zeta r}$, coincides with that of the original valence orbital $P_{nk}(r)$. This choice of ζ and C_ζ probably satisfies our condition (ii) better than the procedure based on the orbital energy adopted by Goddard and Melius.[11] For this choice of the standard function, the least square fit is accomplished by minimizing the following function F

$$F = \sum_{i=1}^{N_p} w(r_i)\ [\sum_{q=1}^{n} a_{qk}\, P_{qk}(r_i) - C_\zeta r_i{}^t\, e^{-\zeta r_i}]^2 , \quad (44)$$

where N_p is the number of grid points for the numerical radial valence orbital $P_{nk}(r)$[16] and $w(r_i)$ is a weight of a point r_i.

The starting values of $w(r_i)$'s are unities. When nodes are not eliminated with these weights, the $w(r_i)$'s are changed to $[1/P_{nk}^{ps}(r_i)]^2$ of the previous run and the minimization of F in Equation (44) is repeated until all nodes are eliminated.

In DHF calculations $P_{nk}(r)$ near the origin may be expanded in terms of a polynomial

$$P_{nk}(r) = r^{\gamma_k}(p_0 + p_1 r + p_2 r^2 + \ldots), \quad (45)$$

where $\gamma_k = \sqrt{k^2 - (\alpha Z)^2}$. Although γ_k may be used as t in Equation (35), several integer and half-integer values are tried and the one that appears to be most satisfactory in terms of condition (ii) is selected. In the case of the 6s orbital of Au (Table VI), t = 2.0 was chosen since this value of t yields the largest a_{6s}. The other criterion used in the selection of t is the smoothness of the orbital, as judged by the presence or absence of oscillations, a_{qk}'s obtained this way are summarized in Tables VII(Ne), VIII(Xe) and IX(Au). Typically, values of t range from 1.5 to 3.0 with larger values for orbitals with higher angular momenta.

Large and small radial components of the 6s valence orbital and pseudo-orbital of Au are shown in Figures 11 and 12. It is interesting that the small component of the pseudo-orbital becomes quite small compared with that of the original valence orbital in the core region. This seems to be the case for s and p orbitals for other heavy atoms; we found it true also for Bi. Based upon this observation, one may expect that the role of the small components is even less important than that anticipated from the analysis of Section II, which makes our approximation of eliminating small components even more attractive.

Finally, it should be noted that the above procedure of determining pseudo-orbitals is not unique since the selection of t and ζ is not.

Table VI. a_{qk}'s of 6s (Au) for Different Choices of t

t	n_i[a]	a_{1s}	a_{2s}	a_{3s}	a_{4s}	a_{5s}	a_{6s}
1.0	1	0.0031	0.0192	0.0634	0.1730	0.4650	0.8658
1.5	1	0.00060	0.0066	0.0331	0.1246	0.4303	0.8935
2.0	1	0.0001	0.0024	0.0176	0.0901	0.3976	0.9131
2.5							
.							
.		Nodes remain after 8 iterations.					
.							
5.0							

[a] n_i is the number of iterations required to eliminate all nodes from $P_{nk}(r)$.

Table VII. a_{qk}'s for Ne

n	k	t	n_i[a]	a_{1k}	a_{2k}
2	-1(s)	2.0	2	.2516	.9679

[a] n_i is the number of iterations required to eliminate all nodes from $P_{nk}(r)$.

Table VIII. a_{qk}'s for Xe

n	k	t	n_i[a]	a_{1k}	a_{2k}	a_{3k}	a_{4k}	a_{5k}
5	$-1(s)$	2.0	1	.0010	.0193	.1275	.5030	.8546
5	$1(p_{1/2})$	3.0	2	-	.0032	.0550	.3952	.9170
5	$-2(p_{3/2})$	3.0	2	-	.0031	.0528	.3852	.9213
5	$2(d_{3/2})$	3.0	2	-	-	.0060	.1162	.9930

[a] n_i is the number of iterations required to eliminate all nodes from $P_{nk}(r)$.

Table IX. a_{qk}'s of Au[a]

n	k	t	n_i	a_{1k}	a_{2k}	a_{3k}	a_{4k}	a_{5k}	a_{6k}
5	-1(s)	2.0	1	.0018	.0318	.1809	.5872	.7884	
6	-1(s)	2.0	1	.0001	.0024	.0176	.0901	.3976	.9131
5	$1(p_{1/2})$	2.0	1	-	.0230	.1598	.5762	.8013	
6	$1(p_{1/2})$	2.0	2	-	.0007	.0062	.0381	.2168	.9921
5	$-2(p_{3/2})$	2.0	1	-	.0222	.1493	.5436	.8257	
6	$-2(p_{3/2})$	2.0	2	-	.0007	.0057	.0355	.2064	.9756
5	$2(d_{3/2})$	3.0	1	-	-	.0406	.3536	.9346	
6	$2(d_{3/2})$	3.0	2	-	-	-.0001	-.0012	-.0596	.9977
5	$-3(d_{5/2})$	3.0	1	-	-	.0375	.3388	.9401	
6	$-3(d_{5/2})$	3.0	2	-	-	.0001	.0012	.0657	.9970
4	$3(f_{5/2})$	3.0	1	-	-	-	-.0007	1.0000	
5	$3(f_{7/2})$	3.0	1	-	-	-	.0005	1.0000	

[a] Pseudo-orbitals are obtained for more than one value of n for each symmetry since the definition of the valence space varies for different core sizes.

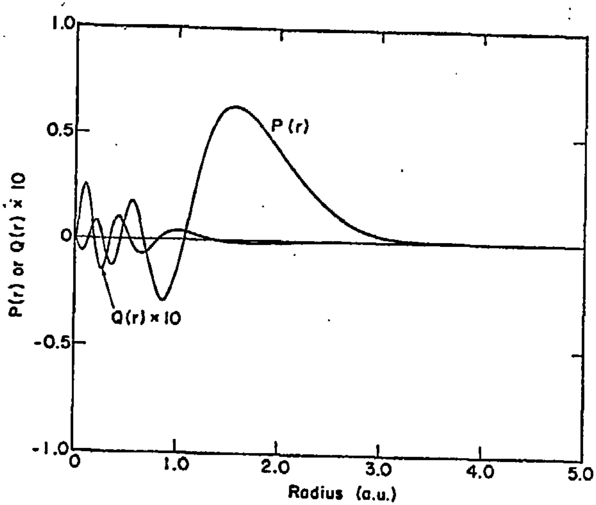

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Figure 11. Radial components of 6s orbitals of Au (DHF calculation).

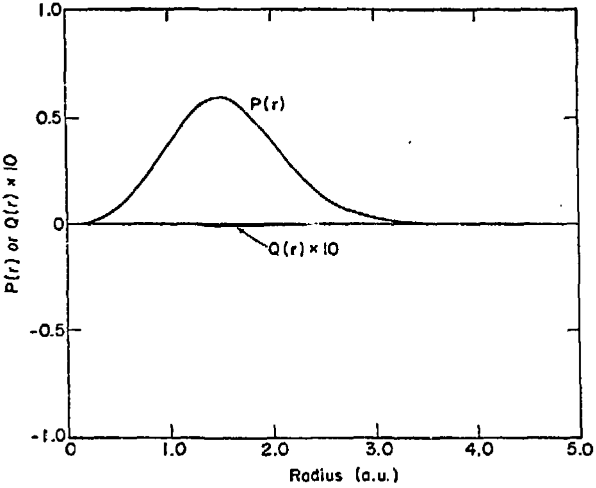

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Figure 12. Radial components of 6p pseudo-orbitals of Au obtained with t = 2.0 (Table VI).

2. Effective potentials

The following radial equation for a closed-shell or the average energy of an open shell configuration may be algebraically solved for each term $U^{EP}_{j}(r)$ of the EP of Equation (42):

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{\ell_A(\ell_A+1)}{2r_1{}^2}+U^{EP}_{\ell_A j_A}(r_1)-\frac{Z}{r_1}\right]P_A(r_1)$$

$$+\left[(N_A-1)\int_0^\infty P_A(r_2)^2\,\frac{1}{r_>}\,dr_2-\frac{1}{2}\,\frac{N_A-1}{2j_A}\sum_{\nu>0}(2j_A+1)\,\Gamma_{j_A\nu j_A}\right.$$

$$\left.\times\int_0^\infty P_A(r_2)^2\,\frac{r_<{}^{\nu}}{r_>{}^{\nu+1}}\,dr_2+\sum_{A'\neq A}N_{A'}\int_0^\infty P_{A'}(r_2)^2\,\frac{1}{r_>}\,dr_2\right]P_A(r_1)$$

$$-\frac{1}{2}\sum_{A'\neq A}N_{A'}\sum_{\nu}\Gamma_{j_A\nu j_{A'}}\int_0^\infty P_A(r_2)\,P_{A'}(r_2)\,\frac{r_<{}^{\nu}}{r_<{}^{\nu+1}}\,dr_2\,P_{A'}(r_1)$$

$$=\varepsilon_A P_A(r_1)+\sum_{A'\neq A}N_{A'}\,\delta(k_A,k_{A'})\,P_{A'}(r\ )\,\varepsilon_{AA'}, \qquad (46)$$

where ℓ_A, j_A, k_A and N_A denote the orbital angular momentum, the total angular momentum, the relativistic quantum number, and the number of electrons, respectively, of the shells A and A' with the understanding that $P_A(r)$ and $P_{A'}(r)$ refer to pseudo-orbitals and ε_A and $\varepsilon_{AA'}$ are diagonal and off-diagonal Lagrange multipliers. The $r_<$ and $r_>$ are the smaller and the larger of r_1 and r_2 respectively and ν satisfies the triangular condition,

$$|j_A - j_{A'}| \le \nu \le j_A + j_{A'}, \qquad (47)$$

with the additional requirement of

$$j_A + j_{A'} + \nu = \text{even} \quad \text{if} \quad a \neq a'$$
$$\text{odd} \quad \text{if} \quad a = a', \tag{48}$$

where a and a' are signs of relativistic quantum numbers k_A and $k_{A'}$. $\Gamma_{j_A \nu j_{A'}}$ is defined in terms of 3j-symbols by

$$\Gamma_{j_A \nu j_{A'}} = 2\begin{pmatrix} j_A & \nu & j_{A'} \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}^2 . \tag{49}$$

Equation (46) can be obtained from the similar equation of DHF theory.[17]

In theory, an infinite number of calculations for highly excited states is required to complete the expansion of the EP given by Equation (42), since there are only a few occupied valence orbitals in neutral atoms. This difficulty also exists in the non-relativistic case and is resolved by using the closure property of the projection operator with the assumption that radial parts of EP are same for all orbitals having higher angular quantum numbers than are present in the core. The same approximation is applicable in our approach if relativistic effects are not too different for electrons in the highly excited orbitals. We expect that this is the case since those electrons spend less time near the nucleus. If this assumption is valid, the EP may be given by

$$U^{EP} \approx U^{EP}_{LJ}(r) + \sum_{\ell=0}^{L-1} \sum_{j=\ell-1/2}^{\ell+1/2} \sum_{m=-j}^{j} [U^{EP}_{\ell j}(r) - U^{EP}_{LJ}(r)] \, |\ell j m\rangle\langle \ell j m| \tag{50}$$

where L could be found by series of actual calculations. The EP's of Ne (Fig. 13) indicate that the $U_{\ell j}(r)$ for p, d and f are almost identical. EP's of Xe (Fig. 14) and Au (Fig. 15) are nearly indistinguishable for $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ for f orbitals and those with higher angular momenta. EP's of Au shown in Figure 15 are the results of 11 valence electron calculations. Based upon the above observations, the reasonable choice of L appears to be that of one plus, or the same as, the largest ℓ present in the core, as was concluded for non-relativistic EP's.[11,12]

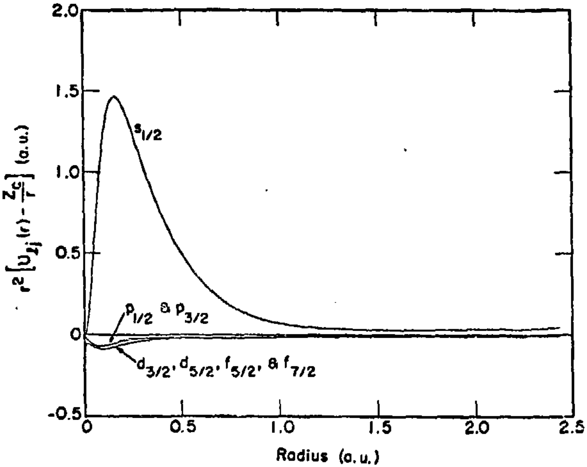
Although numerical forms of the EP's can be used in applications, it may be more convenient to have them expanded in terms of M exponential (x=1) or Gaussian (x=2) functions

$$[U_{\lambda}^{EP}(r)-Z_c/r] = \sum_{i=1}^{M} b_{\lambda i}\, r^{n_{\lambda i}}\, e^{-\zeta_{\lambda i} r^{x}}, \qquad (51)$$

where λ represents the quantum numbers j and ℓ of Equation (50) and Z_c is the number of core electrons. By using the polynomial expansion of $P_{nk}(r)$ [Eq. (45)], the smallest $n_{\lambda i}$ necessary to satisfy Equation (46) can be obtained. If this done, one finds $\min(n_{\lambda i}) = -2$ with

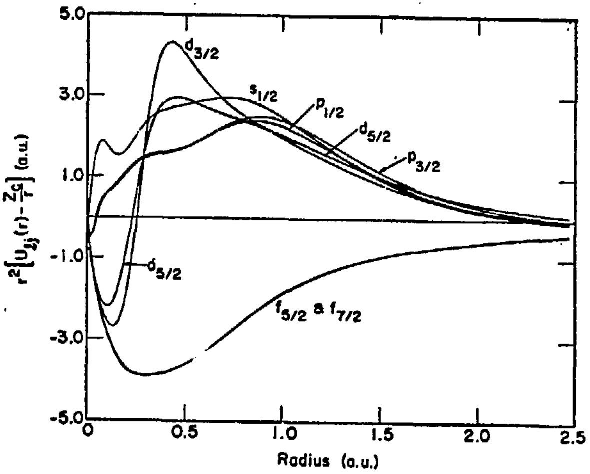
$$\sum_{i=1}^{M_{-2}} b_{\lambda i} = \frac{1}{2}\,[\gamma_k(\gamma_k-1)-k(k+1)], \qquad (52)$$

where M_{-2} is the number of terms with $n_{\lambda i} = -2$ and γ_k and k are previously defined. In practice, we use only one term with $n_{\lambda i} = -2$ and find the corresponding value of $b_{\lambda i}$ by



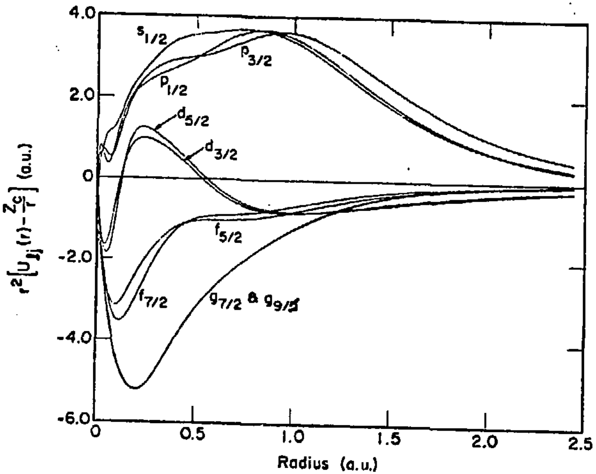
XBL 776-8921

Figure 13. Effective core potentials of Ne.



XBL 778-9922

Figure 14. Effective core potentials of Xe.



XBL 778-9923

Figure 15. Effective core potentials of Au.

fitting Equation (51) for the region near the nucleus. There is no guarantee that Equation (45) is strictly valid after the transformation defined by Equation (43), but for Xe and Au the $b_{\lambda i}$ as obtained from the numerical EP agree reasonably well with those given by Equation (52). After the $n_{\lambda i} = -2$ term is determined, the numerical EP's are fitted with a number of $n_{\lambda i} = -1$ and $n_{\lambda i} = 0$ terms with the asymptotic condition $U_{\lambda}^{EP}(r) \rightarrow Z_c/r$ as $r \rightarrow \infty$. This asymptotic behavior is ensured by fitting $[U_{\lambda}^{EP}(r) - Z_c/r]$ instead of $U_{\lambda}^{EP}(r)$.

IV. ATOMIC HARTREE-FOCK EQUATIONS FOR j-j BASIS SETS

A. Theory

We solve the Hartree-Fock self-consistent-field equations for the valence electrons of an atom assuming that the core electrons are represented by an effective potential (EP) derived from numerical Dirac-Hartree-Fock (DHF) calculations for selected states of the atom (Sec. III). It is further assumed that the valence electrons may be described non-relativistically in terms of only the large component of the atomic orbitals as expressed in terms of expansions in Slater- or Gaussian-type functions.

The Hamiltonian for the N valence electrons is

$$H = \sum_{\mu=1}^{N} h_\mu + \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}}, \qquad (53)$$

where

$$h_\mu = -\frac{1}{2}\nabla_\mu{}^2 - \frac{Z_v}{r_\mu} + U^{EP}(\underline{r}) - \frac{Z_c}{r_\mu}, \qquad (54)$$

in which Z_v is the "shielded" nuclear charge (viz. the atomic number minus the number of core electrons) and $U^{EP}(r)$ is the "relativistic" EP operator of Equation (50).

The eigenfunctions of H are chosen to be in the form of antisymmetrized products of the large components, $\frac{1}{r} P_{n\lambda}(r)\, \chi_{\lambda m}(\theta,\phi)$, of the atomic orbitals $\psi_{n\lambda m}$ of Equation (7). The radial functions are represented as expansions in B basis functions

$$\frac{1}{r} P_{n\lambda}(r) = \sum_{p=1}^{B} C_{n\lambda p} R_{\lambda p}(r). \qquad (55)$$

The $R_{\lambda p}(r)$ are either Slater-type functions (STO's) or Gaussian-type functions (GTO's).

Atomic self-consistent field equations may be derived by analogy with those of Bagus and Roothaan[27] for the non-relativistic case and of Kagawa[28] for the Dirac Hamiltonian. In addition to the overlap ($S_{\lambda pq}$), nuclear attraction ($U_{\lambda pq}$) and kinetic energy ($T_{\lambda pq}$) matrix elements, those due to the EP are also required,

$$U^{EP}_{\lambda pq} = \sum_{i=1}^{M} b_{\lambda i} \int_0^\infty du\, u^{n_{\lambda i}} e^{-\zeta_{\lambda i} u^x} R_{\lambda p}(u) R_{\lambda q}(u). \qquad (56)$$

In Equation (56) x=1 for STO's and 2 for GTO's and we have assumed that the EP of Equation (50) has been fitted by a least squares procedure to an expansion of M terms as in Equation (51). The one-electron matrices enter the SCF iterative procedure as

$$h = T - Z'U + U^{EP}. \qquad (57)$$

The required Coulomb ($\mathcal{J}^{\nu}_{\lambda pq,\mu rs}$) and exchange ($\mathcal{K}^{\nu}_{\lambda pq,\mu rs}$) matrix elements are collected into supermatrices

$$P_{\lambda pq,\mu rs} = J^{0}_{\lambda pq,\mu rs} - \frac{1}{2} \sum_{\nu} A_{\lambda\mu\nu} \mathcal{K}^{\nu}_{\lambda pq,\mu rs} \qquad (58)$$

and

$$\mathcal{Q}_{\lambda pq,\mu rs} = \sum_{\nu} J_{\lambda\mu\nu} \mathcal{J}^{\nu}_{\lambda pq,\mu rs} - \frac{1}{2} \sum_{\nu} K_{\lambda\mu\nu} \mathcal{K}^{\nu}_{\lambda pq,\mu rs}. \qquad (59)$$

(Closed-form formulas for the matrix elements are given by Roothaan and Bagus[27] for STO's and by Huzinaga[29] for GTO's. The EP integrals of Equation (56) are simple modifications of the $U_{\lambda pq}$ formulas.) The allowed values of ν are given by Equations (47) and (48).

The vector coupling coefficients $A_{\lambda\mu\nu}$, $J_{\lambda\mu\nu}$, and $K_{\lambda\mu\nu}$ are chosen to give the proper total symmetry of the atomic electronic state. The closed shell coefficients are given in terms of Clebsch-Gordon coefficients[28]

$$A_{\lambda\mu\nu} = C(j_\lambda j_\mu \nu;\ \tfrac{1}{2},\ -\tfrac{1}{2})^2/(2\nu+1), \tag{60}$$

whereas the open-shell coefficients are given by[30]

$$J_{\lambda\mu o} = 0 \tag{61}$$

$$J_{\lambda\mu\nu} = -f_\nu(\lambda,\mu)/N_\lambda N_\mu \qquad (\nu\neq 0) \tag{62}$$

$$K_{\lambda\lambda o} = A_{\lambda\lambda o} - 2/N_\lambda \tag{63}$$

$$K_{\lambda\lambda\nu} = A_{\lambda\lambda\nu} + 4f_\nu(\lambda,\lambda)/N_\lambda^{\ 2} \qquad (\nu\neq 0) \tag{64}$$

$$K_{\lambda\mu\nu} = A_{\lambda\mu\nu} + 2g_\nu(\lambda,\mu)/N_\lambda N_\mu \qquad (\lambda\neq\mu) \tag{65}$$

for N_λ and N_μ open-shell electrons. The coefficients of Slater integrals needed in Equations (62) and (63) are derived[31] from the energy expression for the general open shell interaction. Vector coupling coefficients for the cases through $f_{7/2}$ and values of $f_\nu(\lambda,\mu)$ and $g_\nu(\lambda,\mu)$ are given in Appendix A for many electronic configurations. The one-electron matrix elements of Equation (57) and the supermatrices of Equation (58) are collected into closed and open shell Fock matrices, which are used to construct the SCF equations using the coupling operator method exactly as given in Reference 27.

It should be noted here that the two differences from the non-relativistic atomic SCF equations as developed in Reference 27 are that the vector coupling coefficients $A_{\lambda\mu\nu}$ of Equation (60) and the coefficients of Slater integrals $f_\nu(\lambda,\mu)$ and $g_\nu(\lambda,\mu)$ of Equations (61) ~ (65) are chosen to properly account for the jj-coupling scheme as required by the form of our EP's. Thus, the basis functions $R_{\lambda p}(r)$ of Equation (55) represent the (n,ℓ,j) set of quantum numbers and are designated $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, $3d_{5/2}$, etc. for (n,ℓ,j) values of $(1,0,1/2)$, $(2,0,1/2)$, $(2,1,1/2)$, $(2,1,3/2)$, $(3,1,1/2)$, $(3,1,3/2)$, $(3,2,3/2)$, $(3,2,5/2)$, etc. (The notation $s_{1/2} \equiv s$, $p_{1/2} \equiv \bar{p}$, $p_{3/2} \equiv p$, $d_{3/2} \equiv \bar{d}$, $d_{5/2} \equiv d$ etc. is often used.)

B. Results of Calculations

We have chosen the Xe and Au atoms to serve as test cases for the application of the EP and atomic SCF formalisms presented in the previous sections. Pseudo-orbitals and EP's were generated for Xe through $f_{7/2}$ and for Au through $g_{9/2}$ and fits to exponential and Gaussian expansions were computed. Tables of these fitting parameters are collected in Appendix B. These fits were used in atomic SCF calculations for the eight valence electrons of Xe and for choices of 1, 11, 17, 19, and 33 valence electrons for Au. In each instance ground, positive ion, and several excited electronic states were investigated. Both average energies of configurations and individual multiplet energies were computed.

1. Xenon

Table B2 contains the parameters necessary to describe the Xe EP's in terms of Gaussian functions according to Equation (51) for all symmetries through $f_{7/2}$ (see also Fig. 14). The EP's for $s_{1/2}$, $p_{1/2}$, and $p_{3/2}$ are given with respect to a set of 13 functions and the EP's for $d_{5/2}$, $d_{7/2}$, $f_{7/2}$ and $f_{9/2}$ with respect to a different set of 11 functions.

Basis sets of GTO's for use in describing the eight valence electrons of Xe are given in Table X. These were determined by taking three term least squares fits of the $5s_{1/2}$, $5p_{1/2}$ and $5p_{3/2}$ pseudo-orbital as initial guesses and optimizing the ground state valence energy. To provide adequate flexibility in the basis set to describe the excited (Rydberg) states of Xe two $s_{1/2}$, $p_{1/2}$, and $p_{3/2}$ and three $d_{3/2}$, $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$ GTO's were added to the basis and the exponents were optimized to give the lowest average energies of respective excited electronic configurations. Also shown in Table X are the atomic orbital expansion coefficients for the ground state as determined by the SCF procedure and those derived by a least squares fit of the same basis set to the numerical pseudo-orbitals.

Table X. Xenon GTO Valence Basis Set

Type	ζ	Ground State AO Coef's	Fit of Pseudo-orbital
$s_{1/2}$	33.091	-.00956	-.00978
	2.221	-.11806	-.11680
	.272	.96220	.95847
	.055	.15334	.16190
	.021	-.03893	-.00797
$2p_{1/2}$	3.191	.04373	.04505
	.517	.44008	.43131
	.186	.58198	.58852
	.036	.10023	.10543
	.013	-.03031	-.03703
$2p_{3/2}$	3.080	.04097	.04230
	.481	.42319	.41569
	.174	.58843	.59424
	.036	.11816	.12197
	.013	-.03315	-.03940
$3d_{3/2}, 3d_{5/2}$	.310		
	.058		
	.014		
$4f_{5/2}, 4f_{7/2}$	.100		
	.010		
	.003		

The valence basis set, as obtained from three-term fits to the respective pseudo-orbitals, showed significant differences from the set optimized by means of the SCF procedure for the eight valence electrons with the EP. For example, the fitted ζ's for the $p_{1/2}$ pseudo-orbital were 1.296, 0.417, and 0.134 as compared with the optimized values of 3.191, 0.517, and 0.186 (Table X). The ground state valence energy resulting from the fitted basis set was 0.034 a.u. higher than that of the optimized set. This implies that merely obtaining the best fit to the pseudo-orbital does not, in general, yield a valence basis set that is optimum with respect to the valence energy. In particular it appears that additional functions having larger ζ's are required for describing residual core-like characteristics that may not have been totally removed by the EP. However, the use of the energy optimized basis to fit the pseudo-orbital does yield coefficients that are nearly the same as the SCF atomic orbital coefficients (Table I).

Results of atomic SCF calculations using the basis set of Table X and the EP parameters of Table B2 are given for the average energies of configurations in Table XI. The excitation energies are compared with weighted averages of the experimentally observed[32] multiplet energies in Table X'I. Results of selected numerical DHF calculations are given in Tables XI and XII for comparison. In Table XII the excitation energies have been adjusted to give the experimental values for the lowest states arising from the promotion of a $5p_{1/2}$ or a $5p_{3/2}$ electron. This adjustment was

Table XI. Xe and Xe$^+$ - Average Energies of Configurations (a.u.)

Config.	Valence Energy (+16) EP	$-\varepsilon_{5s}$ EP	DHF	$-\varepsilon_{5\bar{p}}$ EP	DHF	$-\varepsilon_{5p}$ EP	DHF	$-\varepsilon_{Ry}$ EP	DHF
$5s^2 5\bar{p}^2 5p^4$	-.4953	.997	1.010	.481	.493	.430	.440		
$5p^3 6s$	-.2363	1.149		.643		.596		.133	
$5\bar{p}6s$	-.1914	1.155		.673		.593		.134	
$5p^3 6\bar{p}$	-.1905	1.195	1.198	.691	.688	.643	.637	.087	.084
$5\bar{p}6p$	-.1434	1.204		.724		.645		.085	
$5p^3 5\bar{d}$	-.1643	1.201	1.179	.697	.670	.649	.619	.061	.065
$5p^3 5d$	-.1649	1.198	1.187	.694	.675	.648	.628	.061	.063
$5\bar{p}5\bar{d}$	-.1175	1.212		.733		.652		.059	
$5\bar{p}5d$	-.1209	1.198		.718		.639		.063	
$5p^3 4\bar{f}$	-.1344	1.279		.773		.727		.031	
$5p^3 4f$	-.1344	1.279	1.271	.773	.759	.727	.709	.031	.031
$5\bar{p}4\bar{f}$	-.0889	1.285		.805		.725		.031	
$5\bar{p}4f$	-.0889	1.285		.805		.725		.031	
$5p^3$	-.1036	1.339	1.330	.833	.820	.787	.772		
$5\bar{p}$	-.0582	1.345		.865		.785			

Table VII. Xe and Xe^+ Excitation Energies for Averages of Configurations (cm^{-1})

Config.	ΔE_{SCF}	ΔE_{DHF}^{a}	ΔE_{exp}^{b}	$\Delta E_{SCF}(adj)$	% Error	$\Delta E_{DHF}(adj)$	% Error
$5p^3 6s$	56853		67435	(67435)[c]			
$5\bar{p}6s$	66705		76938	(76938)[d]			
$5p^3 6\bar{p}$	66902	72253	78484	77484	1.3	(77484)[e]	
$5\bar{p}6p$	77251		88869	87484	1.6		
$5p^3 5\bar{d}$	72653	76474	81206	83235	-2.5	81705	-0.6
$5p^3 5d$	72523	76864	81206	83105	-2.3	82095	-1.1
$5\bar{p}5\bar{d}$	82922		92078	93155	-1.5		
$5\bar{p}5d$	82169		91622	92751	-1.2		
$5p^3 4\bar{f}$	79213	83675	90893	89795	1.2	88906	2.2
$5p^3 4f$	79213		90893	89795	1.2		
$5\bar{p}4\bar{f}$	89199			99432			
$5\bar{p}4f$	89197			99430			
$5p^3$	85966	94741	97834	95618	-2.3	99972	-2.2
$5\bar{p}$	95950		108371	106183	-2.0		

[a] DHF calculations correspond to freezing the core orbitals in their ground state form and allowing the valence orbitals to re-adjust self-consistently.

[b] Reference 32.

[c] Configurations with a $\bar{p}^2 p^3$ core are adjusted to give ΔE_{exp} of $5p^3 6s$.

[d] Configurations with a $\bar{p}p^4$ core are adjusted to give ΔE_{exp} of $5\bar{p}6s$.

[e] DHF results adjusted to give ΔE_{exp} of $5p^3 6\bar{p}$.

done to provide some estimate of the ability of the SCF calculations to predict term values, since the absolute excitation energies are expected to contain large errors due to the neglect of electron correlation.

The SCF multiplet energies for all of the possible states of Xe involving the excitation of one electron from the $5p_{1/2}$ or $5p_{3/2}$ shell to all higher shells through $3d_{5/2}$ are tabulated in Table XIII (with the exception of those arising from the $5p_{1/2}$ $6p_{1/2}$ and $5p_{3/2}$ $6p_{3/2}$ configurations, which cannot be treated because of the presence of two open shells of the same symmetry[27]). The excitation and ionization energies have been adjusted as in Table XII.

The results in Tables XI-XIII indicate that the EP's of Table B1 and valence basis set of Table X are capable of reproducing the DHF calculations to reasonable accuracy and yield excitation energies that are of comparable quality to all election SCF calculations. When adjusted to approximately account for the neglect of electron correlation the excitation energies are generally within 1-2% of the observed values. Since the excited states of Xe are all Rydberg states, an alternative procedure of using EP's derived from Xe^+ DHF calculations may be desirable. However, since the EP's are ultimately intended for use in molecular calculations, those due to neutral atom DHF results are generally more appropriate.

Table XIII. SCF Results for Xe Multiplets[a]

Config.	J	$-E_{val}-16$	$-\epsilon_{5s}$	$-\epsilon_{5\bar{p}}$	$-\epsilon_{5p}$	$-\epsilon_{Ry}$	ΔE_{SCF}	ΔE_{adj}	ΔE_{exp}
$5\bar{p}^2 5p^4$	0	.49533	.9970	.4806	.4295				
$5p^3 6s$	1	.23237	1.1529	.6461	.5990	.1291	57713	(68046)[b]	68046
	2	.23889	1.1469	.6402	.5944	.1362	56282	66615	67068
$5\bar{p}6s$	0	.19373	1.1524	.6729	.5912	.1366	66194	(76197)[c]	76197
	1	.19066	1.1554	.6736	.5941	.1332	66867	76870	77186
$5p^3 6\bar{p}$	1	.19100	1.1940	.6904	.6422	.0874	66793	77126	77270
	2	.19021	1.1955	.6919	.6434	.0866	66966	77299	79213
$5\bar{p}6p$	1	.14384	1.2031	.7236	.6439	.0858	77143	87146	88380
	2	.14307	1.2046	.7242	.6453	.0849	77312	87315	89163
$5p^3 5\bar{d}$	0	.16077	1.2099	.7053	.6571	.0572	73427	83760	79772
	1	.16292	1.2054	.7011	.6532	.0593	72956	83289	79987
	2	.16867	1.1860	.6829	.6359	.0653	71694	82027	80323
	3	.16297	1.2052	.7009	.6531	.0594	72945	83278	82431
$5p^3 5d$	1	.15741	1.2242	.7187	.6714	.0538	74164	84497	83890
	2	.16788	1.1867	.6815	.6373	.0645	71867	82200	81926
	3	.16985	1.1820	.6768	.6335	.0665	71435	81768	80971
	4	.16549	1.1944	.6891	.6438	.0620	72392	82725	80197
$5\bar{p}5\bar{d}$	1	.11532	1.2212	.7407	.6611	.0572	83403	93406	93619
	2	.11971	1.2026	.7263	.6427	.0617	82439	92442	91448
$5\bar{p}5d$	2	.12176	1.1944	.7154	.6358	.0638	81989	91992	91153
	3	.12041	1.2005	.7204	.6416	.0624	82285	92288	91747

[a] E_{val} and ϵ's are in a.u. and ΔE's are in cm^{-1}.

[b] States with a Xe^+ (p^3) core adjusted to give ΔE_{exp} of $5p^3 6s$ (J=1).

[c] States with a Xe^+ ($\bar{p}$) core adjusted to give ΔE_{exp} of $5\bar{p}6s$ (J=0).

2. Gold

As the nuclear charge increases, it becomes more difficult to intuitively specify the size of the core. In order to gain some insight into this problem, Au has been studied as an atom comprised of 1, 11, 17, 19, and 33 valence electrons having cores of [Xe]$4f^{14}5d^{10}$, [Xe]$4f^{14}$, [Kr]$4d^{10}4f^{14}5s^2$, [Kr]$4d^{10}4f^{14}$, and [Kr]$4d^{10}$, respectively. Numerical EP's obtained for each case have been fitted with exponential and Gaussian functions. The EP's for the 11-electron case are plotted in Figure 15. The expansions in terms of exponential and Gaussian functions are given in Appendix B.

Several atomic states have been calculated using the modified atomic SCF program described in Section A and a valence basis set of five STO's for each symmetry (Table XIV). Results of the ground state calculations are summarized in Table XV. The original DHF results are reasonably reproduced for most orbital energies except for 6s of 19- and 33-valence electron cases. Since the 6s orbital for those cases is calculated as the excited orbital from the EP of 5s orbitals, the magnitudes of valence interactions are expected to be slightly different between those contained in Equation (46) and those recovered from the atomic SCF calculations. The differences between 17- and 19-valence electron cases are likely to be the result of these valence-interaction differences. Several excitation energies of Au and Au^+ with ionization potentials of Au are shown in Table XVI. Since there

Table XIV. Au STO Valence Basis Set

Symmetry	ζ
$2s_{1/2}$	9.2
	4.7
	2.96
	.898
	.25
$2p_{1/2}$	5.5478
	2.78
	1.0048
	.552
	.2675
$2p_{3/2}$	5.2857
	2.43
	1.0
	.491
	.245
$3d_{3/2}$	3.4873
	2.5973
	1.1575
	.3196
	.0639
$3d_{5/2}$	3.2186
	2.493
	1.1207
	.3164
	.0633
$4f_{5/2}$	18.6706
	10.3406
	5.7646
	1.2524
	.2505
$4f_{7/2}$	18.0529
	10.1093
	5.6835
	1.2524
	.2505

Table XV. Ground State Calculations for Au([Xe] $5d_{5/2}{}^4$ $5d_{7/2}{}^6$ $6s_{1/2}$)[a]

	-T.E.	Orbital Energies (-ε)							
		$4f_{7/2}$	$4f_{9/2}$	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$5d_{5/2}$	$5d_{7/2}$	$6s_{1/2}$
DHF	19018.1992	3.8675	3.7202	4.6873	3.1893	2.5588	0.4934	0.4286	0.2919
1-elec	.2912								.2912
11-elec	35.3827						.4932	.4254	.2936
17-elec	109.4704				3.2294	2.5473	.5106	.4368	.2985
19-elec	145.2199			4.6462	3.2661	2.5843	.4856	.4176	.3395
33-elec	610.9816	3.9555	3.8123	4.6494	3.2376	2.5760	.4972	.4254	.3438

[a] Due to the EP's expanded in STF's and the valence basis set of Table XIV. All energies are in atomic units.

Table XVI. Au Excitation Energies[a]

		1-e	11-e	17-e	19-e	33-e	Exp.
[Xe] $5d_{3/2}^{4}$ $5d_{5/2}^{6}$	6s	0.0	0.0	0.0	0.0	0.0	0.0
[Xe] $5d_{3/2}^{4}$ $5d_{5/2}^{6}$	$6p_{1/2}$	.1500	.1442	.1309	.1799	.1854	.1702
	$6p_{3/2}$	.1646	.1553	.1499	.1986	.2026	.1876
	$6d_{3/2}$	.2367	.2227	.2268	.2755	.2799	.2823
	$6d_{5/2}$	.2370	.2230	.2273	.2757	.2801	.2826
	$5f_{5/2}$	.2599	.2463				.3075
	$5f_{7/2}$	.2599	.2463				.3075
[Xe] $5d_{3/2}^{4}$ $5d_{5/2}^{6}$	-	.2919	.2776	.2820	.3301	.3346	.3390

Au^{+} Excitation Energies

		0-e	10-e	16-e	18-e	32-e	Exp.
$5d_{3/2}^{4}$ $5d_{5/2}^{6}$		0.0	0.0	0.0	0.0	0.0	0.0
$5d_{3/2}^{4}$ $5d_{5/2}^{5}$ 6s	(Av)		.0689	.0767	.0126	.0171	.0735
	(J=3)		.0519	.0596	.0053	.0097	.0685
	(J=2)		.0920	.1000	.0228	.0273	.0804
$5d_{3/2}^{3}$ $5d_{5/2}^{6}$ 6s	(Av)		.1254	.1397	.0694	.0776	.1318
	(J=1)		.1087	.1229	.0628	.0710	.1265
	(J=2)		.1352	.1496	.0734	.0815	.1350

---

[a] See footnote a of Table XIII.

is rather close agreement between 19- and 33-electron calculations, it appears reasonable that the $4f_{5/2}$ and $4f_{7/2}$ electrons may be included in the core without introducing serious errors in Au valence electron calculations. The discrepancy between 19- and 17-valence cases is caused by the lowering of the ground state of the 19-valence electron case (and the 33-valence electron case) due to the irreproducibility of the valence interactions as mentioned above.

If these effects (about 0.05 a.u.) are taken into account, 17- and 19-electron results are almost identical as expected. Although there are some differences between 11- and 17-electron cases (especially for $6p_{1/2}$ states), an 11-valence-electron model appears to be the most reasonable one for Au. A 1-electron representation of Au is the most simple and may be useful in some applications, but meaningful descriptions of chemical bonds involving Au are not expected when the participation of 5d electrons is completely neglected.

Table XVII gives the orbital energies and mean values for the radius from a numerical DHF calculation for Au. It is apparent that the orbital energies for the 5d levels are not enough greater than that for 6s to justify the omission of the 5d orbitals from the valence shell. With a 2 a.u. difference for 5p from 5d, however, it seems clear that the 5p electrons, and those more tightly bound, will be little affected by valence shell changes. Arguments based on radii are less clear cut but support the same conclusion. Since

Table XVII. Au Orbital Energies and Radial Expectation Values from a DHF Calculation (a.u.)

	$4d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$	5s	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$	6s
O.E.	13.17	3.87	3.72	4.69	3.19	2.56	.493	.429	.292
$<r>$	.462	.492	.499	.943	1.02	1.11	1.54	1.62	3.06
$<r^4>^{1/4}$	.557	.646	.655	1.100	1.21	1.32	1.99	2.12	3.77

the radius of the outer part of the distribution is of primary interest, values of $<r^4>^{1/4}$ are more meaningful than those of $<r>$. From Figure 11 one notes that the radius of the outermost node in the 6s orbital is at about 1.1 a.u. Hence one should include in the valence shell other orbitals with effective radii substantially greater than this value. Clearly the 5d orbitals should be included. While the case for the 5p orbitals may be marginal, it seems reasonable to omit them from the valence shell on this basis as well as on the basis of orbital energies. Thus we believe that the 11-electron valence shell will be appropriate for gold, but more definite conclusions will be possible after molecular calculations have been carried out.

V. PROSPECT OF APPLICATIONS OF EP TO MOLECULAR CALCULATIONS

The EP's developed here are for use in calculations on molecules containing one or more heavy atoms. The interest in these molecules is increasing due to their possible roles in chemical lasers and the recent developments in various spectroscopic techniques. For these molecules, the effective potential approach appears to be most promising at the present stage.

The direct use of the EP's of Equation (50) in a molecular calculation requires that the basis set be in terms of functions appropriate for the jj-coupling scheme. The molecular orbitals for valence electrons would be approximated by linear combinations of two-component atomic orbitals which are eigenfunctions of the EP calculation described in the previous section. The molecular integrals necessary for wave functions of this form are the special cases of those which appear in molecular DHF theory as discussed by Malli and Oreg.[5] They have shown that the required two-electron integrals can be written in terms of non-relativistic integrals. Molecular integrals requiring projection operators can also be written in terms of non-relativistic integrals.

The use of jj-coupling in the atomic basis sets has the advantage of yielding the self-consistent molecular orbitals which obey Hunds coupling case (c). Two-component molecular orbitals based on our EP formalism will have the same structure as the four-component relativistic molecular orbitals.[33] They are quite different from the non-relativistic orbitals as indicated by the correlation diagrams of diatomic molecules (Figures 16 and 17). The spin-orbit coupling of atoms is automatically transferred to molecules in this procedure.

In many applications it may be reasonable to assume that LS-coupling is dominant in the valence shell of the molecule. In such cases the most important relativistic effects may be due to the mass velocity and Darwin terms. Approaches based on this premise are being investigated by Kahn, Kay, and Cowan,[34] and by Das and Wahl.[35] Our EP can be applied at this level of approximation by taking the weighted average of the two EP's having the same value of the quantum number $\ell (\ell > 0)$,

$$\sum_{\ell} |\ell m\rangle \, U_{\ell}^{AEP}(r) \langle \ell m| = \sum_{\ell} |\ell m\rangle \, \frac{\ell U^{EP}_{\ell \ell - \frac{1}{2}} + (\ell+1) U^{EP}_{\ell \ell + \frac{1}{2}}}{(2\ell+1)} \langle \ell m| \qquad (66)$$

where $U_{\ell}^{AEP}(r)$ denotes the averaged effective potential of Equation (42) and $|\ell m\rangle\langle \ell m|$ is the angular projection operator defined in the non-relativistic work.[12] EP of Equation (66) can be applied in the same way as the non-relativistic EP's[12] in conjunction with standard non-relativistic molecular programs.

For the light atoms such as Ne, the relativistic effect is almost negligible and the averaged effective core potentials (AEP's) of Equation (66) are expected to be almost the same as the EP's obtained from the non-relativistic atomic

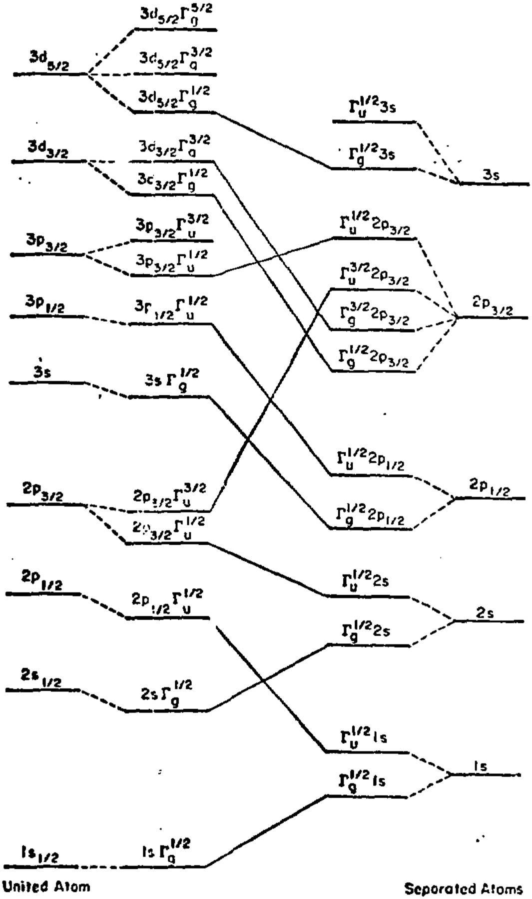


Figure 16. Correlation of relativistic molecular spinors in a two-center system for equal nuclear charges.

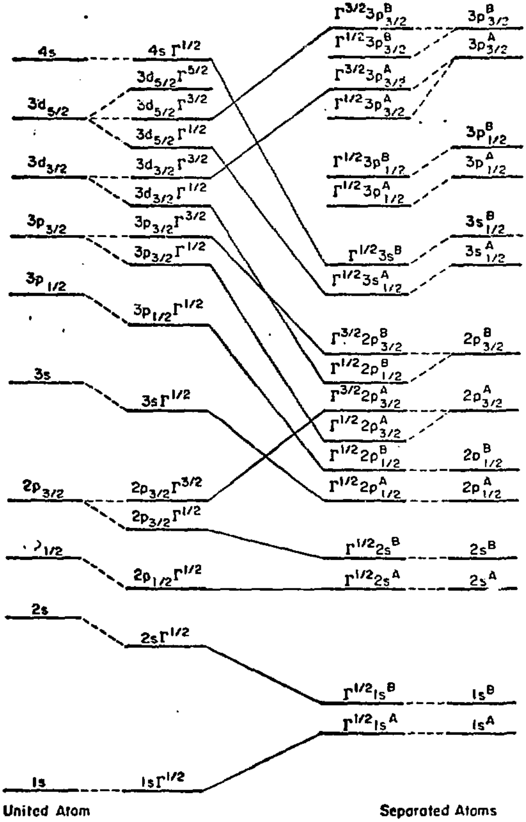


Figure 17. Correlation of relativistic molecular spinors in a two-center system for unequal nuclear charges.

calculation with the analogous method. Therefore, for light elements molecular calculations with AEP's may be directly compared with the non-relativistic all-electron calculations to estimate the accuracy of the AEP result. This method of the checking is most attractive at present, since the relativistic (DHF) all-electron calculations are not available for the molecules with many electrons. Diatomic Ne (Ne_2) with R = 2.0 a.u. is chosen as an example and the orbital energies are shown in Table XVIII. In order to eliminate the possible basis set effect, an all-electron basis set of Ne[36] is also used for the AEP calculation, although the smaller basis set may be good enough for the AEP of Table B1. In Table XVIII, the agreement between the AEP and the all-electron calculation is excellent. Therefore, our method of obtaining EP appears to be quite reasonable.

Several preliminary calculations for molecules with Xe have also been performed with the average of the EP of Table B3. Although the EP of Table B2 and that of Table B3 differ in their expansions, they yield essentially the same results in the atomic calculations. The differences are less than 0.2% in the orbital energies. The use of EP of Table B3 in obtaining the AEP is merely a matter of convenience in the actual calculations. The basis set used in the calculations is the average of that given in Table X. XeF_2 and XeF have been calculated for several internuclear distances with the AEP. Among these calculations, the result for XeF_2 at R - 2.0 Å is given in Table XIX.

Table XVIII. Orbital Energies of Ne_2 at R = 2.0 a.u. (Energies are in a.u.)

	AEP[a,b]	AE[b]
$3\sigma_g$	2.314	2.330
$3\sigma_u$	1.754	1.729
$2\sigma_g$	1.118	1.112
$2\sigma_u$	1.024	1.023
$1\pi_u$	.7087	.7072
$1\pi_g$	.2945	.2806

[a] Valence electron calculation with the averaged EP of Table B1.

[b] Basis set used is the (9s5p) GTO of Huzinaga.[36]

Orbital energies of XeF_2 from other calculations[10,37] and the experiment[38] are also summarized in Table XIX. The results of the AEP calculation agree reasonably with those of the all-electron (HF).[37] All orbitals involving a substantial amount of Xe atomic character ($5\pi_u$, $10\sigma_g$ and $9\sigma_g$) are somewhat more tightly bound for the AEP calculation than for the HF. One of the reasons may be due to the basis set, since our basis set is probably more complete than that used for the HF calculation as far as the valence space is concerned. Most of the discrepancies in the $5\pi_u$ and $10\sigma_g$ orbitals may be due to this effect. The larger difference for the $9\sigma_g$ orbital is due to the relativistic effect on the 5s orbital of Xe. This may also be seen from the Xα calculations.[10] Although an accurate estimate is not possible, our calculation seems to predict larger relativistic effects than the Xα method. Orbital energies from SCF calculations (e.g., AEP and HF of Table XIX) are usually poor approximations to the vertical ionization potentials (Koopmans' theorem). However, reasonable agreement with the experimental values can be obtained, except for the reversal of the order of the $5\pi_u$ and $10\sigma_g$ orbitals, if the calculated values are multiplied by the empirically obtained factor of 0.92.[39] It may be noted that a similar but much better improvement can be made for the Xα method by using the transition-state approximation.[10]

Table XIX. Comparison of Calculated and Experimental Orbital Energies (in eV) of XeF_2, R(Xe-F) = 2.0 Å

			Xα(DVS)[c]		
Orbital	AEP[a]	HF[b]	NR	R	Exp.[d]
$5\pi_u(3/2)$[e]	14.6	13.6	7.1	6.7	12.42
$(1/2)$[e]				7.5	12.89
$10\sigma_g$	13.5	12.8	10.1	10.3	13.65
$3\pi_g$	16.3	16.0	11.1	11.1	14.35
$4\pi_u(3/2)$[e]	17.6	17.3	11.5	11.3	15.60
$(1/2)$[e]				11.4	16.00
$6\sigma_u$	18.4	18.4	13.5	13.3	17.35
$9\sigma_g$	30.4	27.4	17.9	19.2	≈22.5

[a] EP and basis set of F from Reference (12).

[b] From Reference 37.

[c] Discrete Basis Set[10]

[d] From the photoelectron spectra.[38]

[e] Value of the total angular momentum Ω.

Procedures for introducing the atomic-spin-orbit splitting into the molecular results[9] may be used after the molecular wave functions based on the AEP have been computed. Calculations on the ground and excited states of Xe_2 and Xe_2^+ using this approach are in progress and appear to be yielding reasonable results.

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APPENDIX A. OPEN-SHELL VECTOR COUPLING COEFFICIENTS FOR jj-COUPLED ATOMIC CONFIGURATIONS

Table A1. Open-Shell Vector Coupling Coefficients Required for Cases through f

#	Configuration	Required Coefficients
1	s	K_{ss0}
2	$\bar{p}$	$K_{\bar{p}\bar{p}0}$
3	p^n	K_{pp0}, K_{pp2}
4	$\bar{d}^n$	$K_{\bar{d}\bar{d}0}, K_{\bar{d}\bar{d}2}$
5	d^n	$K_{dd0}, D_{dd2}, K_{dd4}$
6	$\bar{f}^n$	$K_{\bar{f}\bar{f}0}, K_{\bar{f}\bar{f}2}, K_{\bar{f}\bar{f}4}$
7	f^n	$K_{ff0}, K_{ff2}, K_{ff4}, K_{ff6}$
8	$s\bar{p}$	$K_{s\bar{p}1}$ + 1,2
9	sp^n	K_{sp1} + 1,3
10	$s\bar{d}^n$	$K_{s\bar{d}2}$ + 1,4
11	sd^n	K_{sd2} + 1,5
12	$s\bar{f}^n$	$K_{s\bar{f}3}$ + 1,6
13	sf^n	K_{sf3} + 1,7
14	$\bar{p}p^n$	$K_{\bar{p}p2}$ + 2,3
15	$\bar{p}\bar{d}^n$	$K_{\bar{p}\bar{d}1}$ + 2,4
16	$\bar{p}d^n$	$K_{\bar{p}d3}$ + 2,5
17	$\bar{p}\bar{f}^n$	$K_{\bar{p}\bar{f}2}$ + 2,6
18	$\bar{p}f^n$	$K_{\bar{p}f4}$ + 2,7
19	$p^m\bar{d}^n$	$J_{p\bar{d}2}, K_{p\bar{d}1}, K_{p\bar{d}3}$ + 3,4
20	$p^m d^n$	$J_{pd2}, K_{pd1}, K_{pd3}$ + 3,5
21	$p^m\bar{f}^n$	$J_{p\bar{f}2}, K_{p\bar{f}2}, K_{p\bar{f}4}$ + 3,6
22	$p^m f^n$	$J_{pf2}, K_{pf2}, K_{pf4}$ + 3,7
23	$\bar{d}^m d^n$	$J_{\bar{d}f2}, K_{\bar{d}d2}, K_{\bar{d}d4}$ + 4,5
24	$\bar{d}^m\bar{f}^n$	$J_{\bar{d}\bar{f}2}, K_{\bar{d}\bar{f}1}, K_{\bar{d}\bar{f}3}$ + 4,6
25	$\bar{d}^m f^n$	$J_{\bar{d}f2}, K_{\bar{d}f3}, K_{\bar{d}f5}$ + 4,7
26	$d^m\bar{f}^n$	$J_{d\bar{f}2}, J_{d\bar{f}4}, K_{d\bar{f}1}, K_{df3}, K_{df5}$ + 5,6
27	$d^m f^n$	$J_{df2}, J_{df4}, K_{df1}, K_{df3}, K_{df5}$ + 5,7
28	$\bar{f}^m f^n$	$J_{\bar{f}f2}, J_{\bar{f}f4}, K_{\bar{f}f2}, K_{\bar{f}f4}, K_{\bar{f}f6}$ + 6,7

Table A2. Coefficients of Slater Integrals for jj-Coupling

	Configuration	J	Coefficients ($\nu>0$)
1	$s\bar{p}$	0	$g_{ps1} = -1/3$
2		1	$-1/9$
3	sp	1	$g_{ps1} = 1/9$
4		2	$-1/3$
5	p^2	0	$g_{pp2} = 1/5$
6		2	$-3/25$
7	$\bar{p}p$	1	$g_{p\bar{p}2} = -1/5$
8		2	$-1/25$
9	p^3	3/2	$g_{pp2} = -1/5$
10	sp^2	1/2	$g_{ps1} = -1/3 + p^2(J=0)$
11		3/2	$0 + p^2(J=2)$
12		5/2	$-5/9 + p^2(J=2)$
13	$\bar{p}p^2$	1/2	$g_{pp2} = -1/5 + p^2(J=0)$
14		3/2	$8/25 + p^2(J=2)$
15		5/2	$-3/25 + p^2(J=2)$
16	sp^3	1	$g_{ps1} = -2/9 + p^3$

Table A2 (continued)

	Configuration	J	Coefficients ($\nu>0$)
17		2	$-2/3 + p^3$
18	$\bar{p}p^3$	1	$g_{p\bar{p}2} = -2/5 + p^3$
19		2	$-6/25 + p^3$
20	$s\bar{d}$	1	$g_{ds2} = -1/5$
21		2	$-1/25$
22	sd	1	$g_{ds2} = 1/25$
23		2	$-1/5$
24	$\bar{p}\bar{d}$	1	$g_{\bar{d}\bar{p}1} = 1/9$
25		2	$g_{\bar{d}\bar{p}1} = -1/3$
26	$\bar{p}d$	2	$g_{d\bar{p}3} = -1/7$
27		3	$-1/49$
28	$p\bar{d}$	0	$g_{\bar{d}p1} = -.06666667$, $g_{\bar{d}p3} = -.25714286$, $f_{\bar{d}p2} = .20000000$
29		1	$.04888889$, $-.15428571$, $.04000000$
30		2	$-.01333333$, $-.05142857$, $-.12000000$
31		3	$-.04000000$, $-.00734694$, $.04000000$
32	pd	1	$g_{dp1} = .04000000$, $g_{dp3} = .06857143$, $f_{dp2} = .16000000$

Table A2 (continued)

	Configuration	J	Coefficients (ν>0)		
33		2	-.12000000,	-.07510204,	-.02285714
34		3	.24000000,	-.05795918,	-.12571429
35		4	-.40000000,	-.01224490,	.05714286
36	$\bar{d}^2$	0	$g_{\bar{d}\bar{d}2}$ = .04000000		
37		1	.20000000		
38		2	-.12000000		
39		3	.04000000		
40	d^2	0	g_{dd2} = .22857143,	g_{dd4} = .09523810	
41		1	.15020408,	-.01360544	
42		2	.02285714,	-.04761905	
43		3	-.09469388,	.04308390	
44		4	-.11428571	-.01587302	
45		5	.08163265	.00226757	
46	$\bar{d}d$	1	$g_{d\bar{d}2}$ = -.01714286,	$g_{d\bar{d}4}$ = -.19047619,	$f_{d\bar{d}2}$ = .16000000
47		2	.03836735	-.08163265	-.02285714
48		3	-.03755102	-.02040816	-.12571429

Table A2 (continued)

	Configuration	J	Coefficients ($\nu>0$)					
49		4		-.02448980		-.00226757		.05714286
50	$p^3\bar{d}$	0	$g_{\bar{d}p1} =$	-.06666667.	$g_{\bar{d}p3} =$	-.257143	$f_{\bar{d}p2} =$	.200000 + p^3
51		1		.022222		-.257143		.040000 + p^3
52		2		-.066667		-.257143		-.120000 + p^3
53		3		-.066667		-.110204		.040000 + p^3
54	p^3d	1	$g_{dp1} =$	400000	$g_{dp3} =$	-.114286	$f_{dp2} =$	.160000 + p^3
55		2		-.400000		-.114286		-.022857 + p^3
56		3		-.400000		-.016327		-.125714 + p^3
57		4		-.400000		-.114286		.057143 + p^3
58	$\bar{d}^3$	3/2	$g_{\bar{d}\bar{d}2} =$	-1/5				
59	d^3	3/2	$g_{dd2} =$	-.048980,	$g_{dd4} =$	-.115656		
60		5/2		.000000		.000000		
61		9/2		-.254694		-.068027		
62	d^4	0	$g_{dd2} =$	.000000	$g_{dd4} =$	.000000		
63		2		-.205714		-.142857		
64		4		-.342857		-.1[illegible]1		

Table A2 (continued)

	Configuration	J	Coefficients (ν>0)		
65	d^5	5/2	$g_{dd2} = -.457143$,	$g_{dd4} = -.190476$	
66	$p^3\bar{f}$	1	$g_{\bar{f}p2} = -.057743$,	$g_{\bar{f}p4} = -.190476$,	$f_{\bar{f}p2} = -.160000 + p^3$
67		2	.011429	-.190476	$.022857 + p^3$
68		3	-.057143	-.190476	$.125714 + p^3$
69		4	-.057143	-.063492	$-.057143 + p^3$
70	p^3f	2	$g_{fp2} = .154286$,	$g_{fp4} = -.079365$,	$f_{fp2} = -.142857 + p^3$
71		3	-.257143	-.079365	$.047619 + p^3$
72		4	-.257143	-.008818	$.123810 + p^3$
73		5	-.257143	-.079365	$-.066667 + p^3$
74	$\bar{p}\bar{f}$	2	$g_{\bar{f}\bar{p}2} = 1/25$		
75		3	-1/5		
76	$\bar{p}f$	3	$g_{f\bar{p}4} = -1/9$		
77		4	-1/81		
78	$\bar{d}^3s$	1	$g_{\bar{d}s2} = -2/5 + \bar{d}^3$		
79		2	$-6/25 + \bar{d}^3$		
80	d^5s	2	$g_{ds2} = -9/25 + d^5$		
81		3	$-3/5 + d^5$		

APPENDIX B. TABLES OF THE ANALYTIC EXPANSIONS OF EP; Ne, Xe, and Au.

All tables are relative to Equation (51) and in atomic units. ETF and GTF denote for the exponential [$x = 1$ in Equation (51)] and the Gaussian [$n = 2$ in Equation (51)] type functions respectively. The weight for the fitting is r^2.

Table B1. Gaussian Representations of Ne Averaged Effective Core Potentials

n	ζ	b(s)	b(p)	b(d)
0	29226.600	57.18520	-4263.92290	4321.10810
0	3733.356	39.35410	-62.04250	101.36990
0	356.363	33.56650	6.18930	27.37720
0	119.600	227.21210	-11.15530	238.36740
0	92.770	-74.63730	20.27640	-94.91370
0	42.195	121.39190	3.84020	117.55170
0	10.640	21.85690	-.56125	22.41815
0	2.440	.86783	-.05179	.91962
0	.600	.02330	-.02030	.04360
1	27069.340	-.26080	22.71940	-22.98020
1	41.299	-2.40947	-2.28060	-.12887
2	50000.000	0.00	-.10133	.10133

Table B2. EP of Xe (8 Valence electrons) - GTF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$
0	3101.0580	3300.6124	-3614.3979	1815.4878
0	1656.9400	1803.2145	1415.6830	582.3106
0	400.1800	116.3312	201.2012	-638.3250
0	213.5110	-952.3547	1186.5252	532.7408
0	172.2200	815.8060	-360.3208	-340.7842
0	8.7230	11.6117	19.4800	28.1350
0	5.3170	5.1503	-18.6829	-31.6556
0	1.4510	7.3448	1.5500	-4.2792
-1	1377.9700	-77.5880	6.1604	-70.8533
-1	185.4100	42.3396	-50.3378	4.5462
-1	12.9100	3.8923	.1701	-3.2248
-1	1.0300	2.1115	5.6172	10.0200
-2	50000.0000	0.0000	-.9650	0.0000

n	ζ	$b(d_{3/2})$	$b(d_{5/2})$	$b(f_{5/2})$	$b(f_{7/2})$
0	60.1000	-389.2453	-415.5537	-256.2135	-247.5275
0	18.0000	-23.1888	-100.3266	-71.5177	-72.6316
0	5.4000	29.5468	56.3986	-36.6237	-36.1695
0	1.3300	6.2846	5.0261	-5.4657	-5.5721
0	.3000	.2034	.1704	-.3319	-.3215
0	.0446	-.0084	-.0128	-.0032	-.0040
-1	7257.5000	-312.5458	-93.3057	-380.5876	-7.6836
-1	5425.0000	209.5445	84.5263	234.8154	-9.7199
-1	1000.0000	-34.9143	-34.0789	-26.0590	-5.5409
-1	217.0000	-24.3855	-17.5347	-32.7976	-33.1078
-2	165000.0000	-1.9000	-.0800	-2.7700	-.0800

Table B3. EP of XE with the Uniform Basis (8 valence electrons)
- GTF

n	ζ	b($s_{1/2}$)	b($p_{1/2}$)	b($p_{3/2}$)	b($d_{3/2}$)	b($d_{5/2}$)
0	3101.058	3304.0724	14906.0247	2141.9114	22080.8808	1112.7298
0	1656.440	4714.1007	16625.0151	2454.3004	25695.5051	207.2405
0	400.180	407.4007	-618.0113	201.1421	-1001.7600	-608.6796
0	211.511	-1247.2065	-300.9066	244.5041	-2260.7752	-3704.4077
0	172.220	1101.7540	42.7500	114.5729	1130.4540	2048.1700
0	60.100	357.2927	44.1161	4.9765	664.7441	2630.1600
0	18.000	279.7260	66.6792	15.0882	604.6652	1926.7457
0	8.721	24.0250	17.6702	25.3004	112.3650	281.9984
0	5.311	1.0060	-22.3630	-19.4972	-30.7520	-70.0174
0	1.451	4.1116	-2.7651	-0.6012	-12.3785	.0828
0	.300	-.0118	-.0938	-.0421	-.0154	-.0281
0	.045	.0006	.0007	.0036	.0001	.0007
-1	7251.500	-6.3065	152.4417	24.0409	219.5400	26.1910
-1	5425.000	61.9419	151.0712	19.0360	260.7747	-.7539
-1	1177.970	-122.0570	-567.8075	-89.2742	-819.5568	-8.7130
-1	185.410	71.5508	43.2070	-29.0474	170.6561	287.8027
-1	12.910	-57.3044	-14.2506	-11.0447	-176.4254	-479.7499
-1	1.010	4.2016	8.9405	12.4632	14.2197	9.5196
-2	165000.000	0.0000	-.9650	0.0000	-1.9000	-.0800

n	ζ	b($f_{5/2}$)	b($f_{7/2}$)
0	3101.058	31279.1311	2113.0941
0	1656.440	36852.5108	2283.5929
0	400.180	-2321.1665	-274.3619
0	211.511	-824.5441	245.9050
0	172.220	-879.5308	-277.2614
0	60.100	-55.3613	-80.4418
0	18.000	-4.1024	-19.4455
0	8.721	24.5051	22.8176
0	5.317	-40.6120	-39.1541
0	1.451	-4.5579	-4.6926
0	.300	-.1695	-.1701
0	.045	-.0010	.0005
-1	7251.500	327.6640	21.6016
-1	5425.000	364.5751	11.4488
-1	1177.970	-1251.9758	-60.4323
-1	185.410	131.1954	-6.0645
-1	12.910	-20.0562	-16.9169
-1	1.010	-.7633	-.7442
-2	165000.000	-2.7700	-.0800

Table B4. EP of Au (1 valence electron) - ETF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	150.000	10407.1070	-61062.0179	-10939.5762	-46960.4244	-6076.6009
0	70.000	-120022.4606	-96493.6711	-49002.1026	-157811.9114	-246022.8670
0	39.000	-40147.4848	-36740.9434	-32993.2168	-80935.7650	-138147.2638
0	10.000	-1242.1066	-920.6448	-1044.6210	803.3328	1422.4442
0	7.500	940.2014	984.5105	642.3319	-513.1141	-994.5427
0	5.500	-301.2724	-422.2172	-119.3052	178.9839	271.6038
0	4.000	2.6310	33.3237	-101.3955	-75.3272	-106.7079
0	2.300	20.5461	16.9608	37.9047	8.0910	10.8046
0	1.300	-3.0050	-3.0048	-3.3372	.0443	.5614
0	.750	.0490	.0017	.1406	.1050	.2198
0	.300	-.0001	.0021	-.0015	-.0009	-.0008
-1	900.000	-154.0037	-443.6706	40.3236	-1315.8596	-103.6626
-1	275.000	19.5814	-1157.4110	-70.5142	-781.9291	36.0542
-1	91.000	-2744.3411	-1751.1612	-2307.1914	-3541.0067	-8385.5191
-1	35.000	2707.6360	2288.4102	2207.0755	3726.7340	8227.4697
-1	10.000	70.8471	91.3005	47.0017	-17.7949	-35.1148
-2	1000.000	0.0000	-1.0000	-.2500	-2.7000	-.1600

n	ζ	$b(f_{5/2})$	$b(f_{7/2})$	$b(g_{7/2})$	$b(g_{9/2})$
0	150.000	-43847.0179	1256.7147	-81844.0979	330.1006
0	70.000	-33005.4005	-17710.5341	-69517.8306	-33319.1691
0	31.000	-9958.4055	-6414.2194	-16159.9320	-11512.8764
0	10.000	146.7154	-106.9314	104.4157	212.6671
0	7.500	-414.4490	-260.7161	-871.0691	-918.4922
0	5.500	212.6604	170.9108	407.3474	403.2508
0	4.000	-71.7056	-67.2047	-119.4515	-170.1372
0	2.300	-34.3180	-31.1401	-30.9404	-27.7034
0	1.300	-1.3099	-2.0150	-1.0140	-1.1901
0	.750	.0316	.0419	.0542	.0505
0	.300	-.0010	-.0013	-.0011	-.0012
-1	900.000	-1783.2390	-103.0200	-2298.4206	-104.3903
-1	275.000	-1021.9280	-38.0475	-1352.6749	-42.1121
-1	93.000	-426.7002	-451.6551	-609.8613	-774.1659
-1	35.000	700.0947	407.4072	1050.0399	722.7318
-1	10.000	-79.7026	-63.8182	-49.5718	-55.3699
-2	1000.000	-2.9700	-.1550	-2.9600	-.1590

Table B5. EP of Au (11 valence electrons) - ETF

n	ζ	b($s_{1/2}$)	b($p_{1/2}$)	b($p_{3/2}$)	b($d_{3/2}$)	b($d_{5/2}$)
0	200.000	-55132.0075	101942.9100	49104.9071	-29791.2213	-41060.1247
0	139.000	-1126007.6516	-408214.0601	240906.1741	-930727.6606	-779167.3713
0	61.900	350739.7434	254496.0761	-133125.7849	186134.0291	263179.0757
0	43.600	101372.4578	64945.6690	-292760.4214	43437.4932	66220.5404
0	34.800	129870.3808	104071.4087	-50335.4471	84312.0326	119667.5520
0	20.000	80375.0031	60132.1503	-31564.2020	42244.5709	50744.4156
0	10.700	3652.9430	4137.0930	-4195.6788	1721.0716	2804.7040
0	7.800	538.6643	331.9913	4101.2495	-238.0065	-947.0413
0	2.500	92.5487	55.8331	66.2310	-13.4315	-11.0400
0	1.000	-.6607	-.1412	.1060	-.2032	-.2342
-1	445.000	-201.4161	836.8354	461.5938	135.9102	-102.0095
-1	162.000	-24194.2127	-12099.4944	6909.6166	-11339.3045	-10724.1707
-1	107.000	34347.7443	16718.3050	-10707.4408	16590.1512	24097.0113
-1	17.000	-8191.0033	-5020.0944	891.1280	-4340.8703	-6193.1419
-1	11.000	-1662.9434	-1401.5869	2184.4263	-195.2109	-1148.0599
-1	4.500	-83.6511	-45.9327	-310.6402	49.6120	61.0105
-2	150.000	-.6700	-1.0009	-.1300	-2.0300	-.1400

n	ζ	b($f_{5/2}$)	b($f_{7/2}$)	b($g_{7/2}$)	b($g_{9/2}$)
0	200.000	21134.9640	11410.2109	52809.6434	21790.3790
0	139.000	100111.6229	123399.0455	300211.1219	332139.1202
0	61.900	-41332.3185	-34933.0361	-115149.1816	-115133.9061
0	43.600	-14177.2401	-14306.6127	-33100.0133	-32391.7207
0	34.800	-11102.4035	-11431.5069	-46239.0018	-46720.6570
0	20.000	-14581.1453	-13073.1665	-32441.0002	-33404.2200
0	10.700	-4011.1203	-3907.9384	-6368.6419	-6361.9907
0	7.800	972.6191	957.2140	1649.9913	1599.9959
0	2.500	-0.1344	-6.8211	-8.6614	-1.6190
0	1.000	-.0581	-.0104	-.0011	-.0093
-1	445.000	446.3165	51.3115	121.6671	67.8364
-1	162.000	2300.0300	2515.8457	6645.2110	7131.2003
-1	107.000	-3467.6167	-3651.5703	-4106.0198	-10315.1200
-1	17.000	23.5609	21.1522	1260.5763	1336.9716
-1	11.000	1075.2421	970.4012	1803.9714	1841.5909
-1	4.500	-52.1610	-53.5201	-131.9001	-137.1714
-2	150.000	-2.9900	-.1540	-3.4500	-.1500

Table 86. EP of Au (17 valence electrons) - ETP

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	82.400	577464.3903	-1306478.3492	-39019.4410	56424.4506	69357.1897
0	45.000	281164.6310	-74000.0632	-24060.8779	20560.7013	19948.7770
0	24.500	84279.4689	-37815.5887	-22695.1711	-14.4659	-8640.2092
0	17.800	3990.4357	24246.9927	3207.9171	1505.7875	2411.1764
0	8.000	-420.6447	-2111.0912	-1240.1174	-104.0484	-537.8038
0	6.500	785.9511	1997.0062	1197.9174	248.4532	572.0006
0	4.600	-385.2819	-469.1228	-32.0274	45.2074	-105.9445
0	1.970	102.1644	112.3312	-41.2462	-17.2406	55.0087
0	2.030	67.6081	-7.4043	7.9700	-.6249	-12.0427
0	5.026	.0430	.0167	-.0441	-.5051	-.2724
-1	339.000	-599.1719	-667.8876	-42.3743	-239.4072	-24.1216
-1	250.500	1845.7190	-57.9283	-40.1037	-59.0076	52.0837
-1	170.700	-5310.6199	709.4336	419.3039	-419.7103	-415.5224
-1	119.000	14149.2492	-3452.0064	-1139.3870	1314.6297	1705.4954
-1	45.000	-4560.1441	217.4354	-600.0555	-858.0564	-1580.4739
-1	19.500	-7411.3637	2678.4018	1374.5202	-336.1562	119.0652
-2	500.000	-.0700	-1.0300	-.1280	-2.0400	-.1500

n	ζ	$b(f_{5/2})$	$b(f_{7/2})$	$b(g_{7/2})$	$b(g_{9/2})$
0	82.400	792.6404	-30041.2651	2422.0001	-21094.7914
0	45.000	-8005.9611	-24117.0739	-6487.7749	-17607.8969
0	24.500	-9005.2410	-12819.4217	-4026.1493	-12501.3422
0	17.400	364.6343	60.1161	915.7214	844.2579
0	8.000	-841.0409	-1166.2009	-1179.6334	-1151.4296
0	6.000	603.5839	870.0025	691.1099	674.6001
0	4.400	-130.6554	-291.6021	-294.1761	-201.9972
0	1.570	93.2513	94.4855	47.6317	91.0937
0	2.630	-13.7143	-14.6907	-13.0978	-11.0167
0	1.046	-.6660	-.0634	-.0108	-.0250
-1	339.000	-260.4319	8.2532	-270.4854	-1.0910
-1	250.500	-271.7866	-152.6106	-301.0992	-100.3174
-1	170.700	146.6202	378.2546	140.5369	242.6662
-1	119.000	-207.5788	-1060.5244	-164.8581	-650.9381
-1	45.000	-667.9502	-195.0140	-572.4774	-385.4060
-1	19.500	574.8139	893.8474	471.3749	781.9851
-2	500.000	-2.6700	-.1500	-3.9600	-.1600

Table B7. EP of Au (19-valence electrons) - ETF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	50.400	-250150.5376	-272569.7687	-177293.4046	-72778.1642	-121613.1159
0	45.600	310982.5242	343648.5653	221013.5945	87125.9468	144200.5565
0	34.200	-98506.9479	-115610.1826	-70904.9025	-28012.6444	-43030.3270
0	22.000	3159.6551	4880.2727	1675.6085	-926.1176	-1977.1688
0	13.800	-37.6719	-662.8158	677.0520	655.3370	977.2616
0	9.230	-164.0773	-38.3844	-602.4090	-286.2867	-324.0627
0	5.200	354.4650	275.9426	387.2481	268.3691	272.1922
0	4.000	-82.0156	-59.9916	-77.1426	-65.7408	-61.5367
0	1.700	.5132	.3430	.3214	.4411	.3922
-1	631.000	146.3805	200.5777	123.3224	176.0379	115.5844
-1	324.000	-247.1178	-673.0245	-200.9140	41.4274	-162.3994
-1	157.000	1147.4624	1112.5985	481.3069	358.9098	542.5936
-1	113.000	-2172.8640	-1831.1627	-1553.1640	-650.5118	-932.5354
-1	46.400	1102.6925	1114.0256	737.0005	218.7338	404.8111
-2	280.000	-.6700	-1.0300	-.1200	-2.0200	-.1500

Table B8. EP of Au as 33-Electron Atom (STF)

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	94.600	-5739.3569	-203505.0981	-28410.1162	18936.0773	88581.2196
0	50.700	7671.8779	-71252.9283	-2907.2001	8970.4274	36252.1507
0	13.000	874.5670	-163.2324	1344.0777	1091.4831	1505.5665
0	9.000	-445.3606	-3.8440	-881.6528	-385.8125	-437.1619
0	6.000	456.3453	304.6532	520.2618	350.2276	358.5798
0	3.000	-7.7512	.5569	-5.0601	-6.1672	-5.3149
-1	918.000	-565.6734	-850.7471	-666.4730	-267.0547	1649.7253
-1	550.000	301.3901	258.1169	344.7486	338.1029	-813.8507
-1	140.000	-195.4412	-3367.9336	-532.3716	315.6497	1545.8045
-1	43.200	157.2892	3273.9393	471.5705	-284.0469	-1297.8050
-1	14.000	-29.5498	44.2343	-46.8761	-107.7971	-180.3610
-2	200.000	-.0800	-1.0500	-.1250	-2.0300	-.1440

	ζ	$b(f_{5/2})$	$b(f_{7/2})$
0	94.600	-111711.9268	-122697.6558
0	50.700	-38222.7536	-43434.4726
0	13.000	-694.8698	-813.8225
0	9.000	191.6533	243.3335
0	6.000	-108.2117	-117.2041
0	3.000	-5.4833	-5.4115
-1	916.000	-2358.4297	-1500.2877
-1	550.000	1565.1514	785.4738
-1	140.000	-1864.9436	-2060.6307
-1	43.200	1621.4621	1834.1648
-1	14.000	-3.2351	8.0145
-2	200.000	-3.0000	-.1500

Table B9. EP of Au (1 valence electron) - GTF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	1847.100	1435.1224	-7163.7402	824.4270	-2140.2219	-10981.0964
0	560.000	-6194.7667	13711.0634	-1299.1204	18465.1642	30145.8649
0	223.000	-4067.5276	9460.7940	-1466.2763	12963.6082	21508.7380
0	80.900	-1691.7851	4717.3456	-804.3849	6232.8509	11387.8245
0	42.000	-31.7686	253.5568	-1.5343	430.2287	777.6972
0	8.910	4.2475	.8150	10.9810	-4.4967	-4.8958
0	1.590	2.6196	-9.0932	-7.2393	-21.1103	-20.9831
0	1.240	-9.7644	4.8462	-1.6711	25.9360	35.3210
0	.950	0.0503	2.8090	5.6149	-9.6604	-12.5565
0	.300	-.5538	-.5391	-.2802	.0016	.1413
-1	41500.000	-18.6271	-170.0740	-27.0062	-74.2143	93.0046
-1	13007.000	-12.0933	-13.9900	-26.2155	-10.6813	101.1525
-1	5145.000	-4.4113	73.2565	-52.5519	144.6024	188.8421
-1	1288.400	-266.5603	740.9513	-88.2314	748.4619	1482.1031
-1	210.300	144.5726	-321.1754	52.9071	-487.8530	-669.3090
-1	61.400	192.9931	-565.3048	74.9206	-777.5197	-1406.1492
-2	150000.000	0.0000	-1.0000	-.2500	-2.0000	-.1500

n	ζ	$b(f_{5/2})$	$b(f_{7/2})$	$b(g_{7/2})$	$b(g_{9/2})$
0	1847.100	10011.9139	8955.6620	12003.0916	6502.5905
0	560.000	-28878.9135	-36134.0032	-30981.2858	-33990.6045
0	224.000	-20445.1215	-25512.7404	-20190.1010	-23531.4317
0	80.900	-4556.4409	-10421.1099	-10651.0248	-9119.0271
0	42.000	-616.6509	-710.6681	-809.3044	-750.7591
0	8.980	-53.1554	-61.0796	-109.8878	-110.4609
0	1.590	-28.4716	-24.6354	-54.7918	-50.1935
0	1.240	26.6147	23.3013	50.0027	49.7399
0	.950	-16.6345	-14.3705	-23.6855	-23.1252
0	.300	-.0781	-.9297	-.5648	-.6228
-1	41500.000	-315.7864	-170.9051	-348.8140	-164.7963
-1	13007.000	-259.5117	-133.1494	-260.7801	-120.6013
-1	5145.000	-221.2316	-336.4030	-291.1360	-301.4512
-1	1288.400	-1460.3800	-1655.0420	-1778.6540	-1408.9697
-1	210.300	798.2806	1030.9010	1048.7899	981.5111
-1	63.400	993.3132	1224.1588	1254.0386	1076.3017
-2	150000.000	-2.9900	-.1950	-1.9600	-.1990

Table B10. EP of Au (11-valence electrons) GTF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	3500.000	481.3616	2014.9994	-706.8771	-923.6213	-493.7414
0	987.000	-544.4345	606.6585	349.6466	-130.9542	-147.9267
0	450.000	-536.2821	-732.4855	-70.0611	582.4496	323.9008
0	170.000	439.6673	63.8604	34.3131	-149.0565	-140.1292
0	70.000	125.6432	124.0009	-19.2150	-67.9194	-115.6359
0	30.000	52.1910	40.2037	54.4878	34.0606	50.1019
0	11.100	1.5600	26.1394	2.6052	4.5442	4.4197
0	7.000	11.5502	7.6060	30.3380	13.3264	12.3053
0	3.360	2.6645	1.5147	-1.2036	3.3505	4.1033
0	1.410	5.5021	5.3315	3.3551	-1.8061	-1.4072
0	.721	1.1459	4.2766	4.7780	-.5143	-.4029
0	.300	.3461	.2915	.5703	-.2807	-.3110
-1	270000.000	-64.1125	-108.2466	44.5056	351.0524	9.7640
-1	31100.000	-1.7410	-215.1150	-42.8730	-210.2990	-20.4082
-1	6650.000	39.4429	6.0971	-47.8164	-65.7189	-16.5054
-1	315.000	62.4000	51.1142	29.6291	-56.1612	-35.9940
-1	84.500	-28.0236	-22.9718	-6.1224	-13.8803	-23.0600
-2	150000.000	-.0700	-1.0900	-.1330	-2.0300	-.1460

	ζ	$b(f_{5/2})$	$b(f_{7/2})$	$b(g_{7/2})$	$b(g_{9/2})$
0	3500.000	-1103.6736	-302.8488	-1039.4734	-113.6005
0	987.000	-131.5666	-42.6530	1.0766	84.1071
0	450.000	661.5181	442.0270	734.2050	434.1517
0	170.000	-115.4450	-119.4236	62.1264	15.0750
0	70.000	-113.6759	-106.7502	-81.0320	-92.4505
0	30.000	-91.7419	-124.1263	-147.4115	-142.6666
0	11.100	-38.1641	-48.1207	-70.7924	-77.6640
0	7.000	5.5454	6.0341	-1.9916	-8.7228
0	3.360	-2.4094	-2.0548	-13.0097	-15.4412
0	1.410	-2.2110	-2.0584	-1.6447	-3.8388
0	.721	-.4121	-.2483	-.5031	-.5212
0	.300	-.1066	-.1091	-.3114	-.0416
-1	270000.000	547.2501	6.6421	844.0617	5.4505
-1	31100.000	-290.2642	-28.0413	-360.9033	-26.9411
-1	6650.000	-72.4553	-14.5907	-85.3598	-11.9084
-1	315.000	-57.4811	-45.7697	-53.3174	-38.7446
-1	84.500	-19.2640	-18.9143	-36.1384	-12.1536
-2	150000.000	-2.4900	-.1540	-3.4500	-.1580

Table B11. Ep of Au (17 valence electrons) - GTF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	5166.000	-4010.8466	-41712.9408	-45777.4345	-5617.7070	-380.9637
0	1203.000	11556.3951	150661.5038	14641.2144	64464.8075	10073.2078
0	450.000	-2240.6511	7111.5942	4161.6510	2838.6595	-576.2027
0	210.000	-147.6141	734.2343	687.7412	-.4051	-474.0028
0	77.500	76.7240	-90.7899	-105.6097	-132.7016	-270.3137
0	32.000	58.4562	100.7265	123.2597	78.1354	90.1092
0	14.650	26.1667	-22.8578	-40.7417	.3661	6.7074
0	6.300	29.6433	48.2503	52.1866	12.1822	32.4974
0	1.730	13.6357	1.3010	3.0897	2.0817	2.5746
0	.600	4.3318	-.3742	-.0719	-.1149	-.3417
0	.350	.0463	.1116	.2519	-.3486	-.2101
-1	7249.000	33.5456	198.4626	-2.1520	175.1970	30.3642
-1	3562.000	156.1171	1666.5812	196.3164	530.3394	43.4228
-1	1798.000	283.3049	2926.8052	295.2983	1532.6051	201.1473
-1	1052.000	-634.2000	-4054.0289	-411.7959	-2532.6070	-454.5714
-1	286.000	131.7366	-262.9332	-167.1136	-137.0424	5.4136
-2	150000.000	-.0700	-1.0500	-.1280	-2.0400	-.1500

n	ζ	$b(f_{5/2})$	$b(f_{7/2})$	$b(g_{7/2})$	$b(g_{9/2})$
0	5166.000	-4311.3120	-1311.8663	-990.5715	-382.7639
0	1203.000	82559.5590	11008.1230	98133.6445	11412.7048
0	450.000	3504.2045	323.7176	2103.6552	-1249.1935
0	210.000	18.1240	-260.6288	-216.0078	-503.3916
0	77.500	-315.4775	-294.1480	-215.7606	-255.1721
0	32.000	-46.0502	-75.6103	-92.7254	-94.8790
0	14.650	-43.2260	-55.2734	-79.3307	-11.6933
0	6.300	8.9319	1.5273	-23.5911	-24.1872
0	1.730	.5936	.0566	-4.2913	-4.1000
0	.600	-.5170	-.2290	-.3164	-.3516
0	.350	-.0438	-.0664	-.0741	-.0042
-1	7249.000	243.8240	28.0235	313.1000	32.0134
-1	3562.000	588.5122	75.5446	613.1470	48.4094
-1	1798.000	1575.6549	273.7302	2370.5306	292.2190
-1	1052.000	-3204.7619	-457.4213	-3867.8297	-628.4202
-1	286.000	-151.3407	-39.6246	-115.4426	36.2608
-2	150000.000	-2.9900	-.1500	-3.9600	-.1600

Table B12. EP of Au (10 valence electrons) - GTP

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	434.000	39.8898	-1357.4639	255.2750	459.1720	240.4948
0	119.000	-1074.0351	-1380.3516	-452.7408	556.2987	255.6750
0	58.500	-249.3531	-300.4179	-18.6902	318.4185	227.5420
0	19.500	67.3322	37.8110	20.1600	37.3672	53.7582
0	6.300	41.2423	34.0094	29.7716	28.3747	27.8296
0	3.020	9.7687	6.8809	14.3761	6.2497	7.1941
-1	349000.000	184.7641	-329.0292	178.9118	1117.4844	56.3634
-1	36100.000	-82.4940	-215.1460	-69.0564	-211.7471	-23.3444
-1	12200.000	146.0769	-70.1630	104.9425	31.8086	2.1519
-1	8300.000	-197.7226	50.7043	-142.0962	-85.6067	-12.3574
-1	63.500	103.6613	119.3673	35.5048	-83.2514	-66.0791
-2	150000.000	-.0700	-1.0300	-.1200	-2.0200	-.1500

Table B13. EP of Au (33 valence electrons) - GTF

n	ζ	$b(s_{1/2})$	$b(p_{1/2})$	$b(p_{3/2})$	$b(d_{3/2})$	$b(d_{5/2})$
0	700.000	448.6607	301.4170	200.7117	-483.9060	-1237.8321
0	332.000	994.4173	400.3150	549.3324	-389.8623	-178.5829
0	140.000	11.3659	-6.3986	12.9470	-427.6568	-679.1200
0	38.600	66.7285	128.8330	109.1684	-34.8698	-75.2952
0	8.600	21.7210	54.4295	32.6592	.4998	-3.3622
0	4.710	33.3491	12.7050	22.0338	29.9257	29.7349
0	2.770	5.6914	9.7342	11.6259	3.4011	4.3857
-1	11.900	17.4315	2.9246	6.2435	21.7291	26.5201
-1	953.000	76.9177	83.6306	40.6674	-26.2857	-20.9216
-1	3090.000	-46.1454	52.8219	-41.6067	-66.0238	-45.6425
-1	22300.000	-63.6244	-109.2419	-54.5629	-163.3883	-30.3795
-1	65700.000	15.9185	-168.8357	6.0730	-46.6652	-11.0422
-2	150000.000	-.0800	-1.0500	-.1250	-2.0300	-.1440

n	ζ	$b(f_{5/2})$	$b(f_{7/2})$
0	700.000	-802.8767	-563.9701
0	332.000	-216.0503	-229.9127
0	140.000	-325.4685	-305.6888
0	38.600	-115.3664	-115.7969
0	8.600	-37.6765	-37.9266
0	4.710	18.0018	18.3822
0	2.770	-12.5753	-12.8716
-1	11.900	-2.3196	-2.1466
-1	953.000	-17.8469	-17.8560
-1	3090.000	-72.1232	-27.4761
-1	22300.000	-249.7527	-30.0653
-1	65700.000	-51.6752	-7.6792
-2	150000.000	-3.0600	-.1500