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ELECTRONIC STRUCTURE OF MOLECULES

USING RELATIVISTIC EFFECTIVE CORE POTENTIALS

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INTRODUCTION

The application of ab initio techniques to molecular electronic structure has enabled the quantum chemist to make reliable predictions of molecular geometries and spectroscopic properties, to calculate excitation and ionization energies, and to characterize transition states and energy barriers in chemical reactions. Investigations of the electronic properties of molecules containing heavier atoms (such as transition-metal or actinide compounds) has been hampered by (1) the increase in computational effort (by roughly N^4) with the number of electrons (N) in heavier atoms and (2) the importance of relativistic effects, even on valence electrons, with increasing Z.

In this review we outline our approach in studying molecules containing heavy atoms with the use of relativistic effective core potentials (RECP's). These potentials play the dual roles of (1) replacing the chemically inert core electrons and (2) incorporating the mass velocity and Darwin terms into a one-electron effective potential. This reduces the problem to a valence-electron problem and avoids computation of additional matrix elements involving relativistic operators. The spin-orbit effects are subsequently included using the molecular orbitals derived from the RECP calculation as a basis.

The present approach retains the one-component formalism familiar to chemists for electronic structure calculations while, at the same time, implicitly includes the dominant molecular relativistic effects. The resulting simplicity of this approach enables one to use without further modification the well-developed techniques of quantum chemistry for molecular problems—including normal evaluation of 1- and 2-electron integrals, SCF, and MC-SCF techniques for obtaining orbitals, and configuration interaction (CI) methods for treating electron correlation. The computational expense is considerably reduced by the drastically fewer number of basis functions needed to describe the valence orbitals of the system and the concomittant reduction in number of two-electron integrals. The only additional requirements in carrying out a RECP calculation are (1) evaluation of the multi-center one-electron integrals between atomic basis functions (χ_a) of the potentials, $\langle\chi_a|V_c|\chi_b\rangle$; and (2) evaluation of matrix elements between molecular orbitals $\langle\phi_i s_i|V_{so}|\phi_j s_j\rangle$ where s_i denotes the associated electron spin (α or β).

In the following sections we discuss one-component relativistic Hartree-Fock orbitals, the derivation of RECP's from these orbitals, and various levels of treatment for the spin-orbit coupling operator. Applications of RECP's to calculation of molecular potential energy curves, excitation energies and geometries are then discussed.

The work discussed here was carried out by the author and his collaborators Willard R. Wadt, Robert D. Cowan, and Richard L. Martin at Los Alamos and Luis R. Kahn at Battelle Columbus Laboratories.

METHODS

Relativistic Hartree-Fock Wavefunctions

The traditional approach to relativistic effects in atoms, the Dirac-Hartree-Fock (DHF) method, describes each atomic orbital in terms of 4-component spinors—a "large" and "small" component for $j = \ell - 1/2$ and a similar pair for $j = \ell - 1/2$. Thus a 6p shell in an atom would be described by four radial functions, large and small components associated with $6p_{1/2}$ and $6p_{3/2}$. Cowan and Griffin have developed an alternative 1-component approach—relativistic Hartree-Fock (RHF)—which still retains the important relativistic mass-velocity and Darwin terms. Spin-orbit coupling parameters are then computed from the RHF wavefunctions using the Blume-Watson method. The use of a single-component radial function for each shell (i.e., one radial function for the 6p shell) results in a significant simplification in the atomic case and also makes the RHF wavefunctions more amenable for use in molecular calculations.

The RHF equations are derived as follows. From the local potential approximation to the DHF equations by Desclaux one obtains

$$P_k' = -\frac{k}{r} P_k + \frac{\alpha}{2} \left(\epsilon - V(r) + \frac{4}{\alpha^2}\right) Q_k \qquad (1)$$

$$Q_k' = \frac{\alpha}{2} (V(r) - \epsilon)\, P_k + \frac{k}{r}\, Q_k \qquad (2)$$

where P and Q are the "large" and "small" components, respectively, and

$$k = \begin{cases} \ell & \text{when } j = \ell - \frac{1}{2} \\ -\ell-1 & \text{when } j = \ell + \frac{1}{2} \end{cases}$$

From solving (1) for Q_k, evaluating Q'_k, and substituting in (2), one obtains an equation in terms of P and P'. Replacing the k-dependent term by the (2j+1)-weighted average, - 1/r, yields the RHF equations

$$[H_{NR} + H_{MV} + H_D]\, P_i(r) = \epsilon_i P_i(r) \qquad (3)$$

$$H_{NR} = -\frac{d^2}{dr^2} + \frac{\ell_i(\ell_i+1)}{r^2} + V_i(r) \qquad (4)$$

$$H_{MV} = -\frac{\alpha^2}{4} [\epsilon_i - V_i(r)]^2 \qquad (5)$$

$$H_D = -\delta_{\ell,0} \frac{\alpha^2}{4} \left[1 + \frac{\alpha^2}{4}(\epsilon_i - V_i(r))\right]^{-1} \frac{dV_i}{dr} \frac{dr^{-1} P_i}{dr} \qquad (6)$$

The potential $V_i(r)$ in H_{NR} in Eq. (4) is the coulomb and non-local exchange potential normally used in nonrelativistic Hartree-Fock calculations; in the mass-velocity and Darwin terms [Eqs. (5) and (6)] V_i is replaced by the "local exchange" form using the $\rho^{1/3}$ density expression.

The radial characteristics and energies of the Au atom valence orbitals are compared for nonrelativistic Hartree Fock (HF), RHF and DHF wavefunction in Table 1. The relativistic shifts apparent in the j-weighted average DHF wavefunctions are well reproduced by the RHF wavefunctions. One sees the typical orbital contraction and stabilization for low ℓ (s orbitals) and the orbital expansion and destabilization for high ℓ (d and f orbitals). Comparisons of excitation energies in the Au atom from HF, RHF, and averaged DHF results (Table 2) reveal virtually identical excitation energies for RHF and DHF calculations. The large relativistic shifts are evident for these valence electron transitions, since the nonrelativistic results give the incorrect ordering (compared to RHF and experiment) for the 5d→6s and 6s→6p transitions.

Table 1. Comparison of Orbital Sizes and Energies for the Uranium Atom. (Ref. 1)

	HF[a]	RHF[b]	DHF[c]	DHF (average)
		$\langle r^2 \rangle$ (bohr^2)		
$5f_-$ $5f_+$	1.94	2.57	2.53 2.67	2.61
$6d_-$ $6d_+$	9.63	12.4	11.1 13.7	12.7
7s	28.8	21.5	21.8	21.8
$6p_-$ $6p_+$	4.11	3.73	3.13 4.08	3.76
		Orbital Energy (a.u.)		
$5f_-$ $5f_+$	-0.634	-0.331	-0.352 -0.297	-0.320
$6d_-$ $6d_+$	-0.267	-0.188	-0.208 -0.172	-0.186
7s	-0.167	-0.201	-0.199	-0.199
$6p_-$ $6p_+$	-1.04	-1.086	-1.363 -0.959	-1.094

[a] Nonrelativistic Hartree-Fock.
[b] Relativistic Hartree-Fock (Cowan-Griffin).
[c] Dirac-Hartree-Fock.

Relativistic Effective Core Potentials

The numerical relativistic orbitals of Cowan and Griffin form the starting point for obtaining the relativistic effective core potentials (RECP) according to the procedure of Kahn, Hay and Cowan.[2] One seeks to obtain valence "pseudo-orbitals," $\tilde{\phi}_{n\ell}$, and RECP's V_ℓ, which satisfy the valence Hartree-Fock equation,

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U_\ell(r) + \hat{W}_{val} \right] \tilde{\phi}_{n\ell} = \epsilon_{n\ell}\, \tilde{\phi}_{n\ell}$$

which may be compared to the original equation satisfied by the RHF orbitals, ϕ_{nl}

Table 2. Excitation Energies for the Au Atom. (Ref. 13)

	Excitation Energy (eV)			
	HF	RHF	DHF (avg)	Expt
$5d^{10}\ 6s^1(^2S)$	0.00	0.00	0.00	0.00
$5d^9\ 6s^2\ (^2D)$	5.13	1.86	1.86	1.74
$5d^{10}\ 6p^1\ (^2P)$	2.71	4.24	4.24	4.95

$$\left[-\frac{1}{2}\nabla^2 - \frac{z}{r} + W_{core} + W_{rel} + W_{val}\right]\phi_{n\ell} = \varepsilon_{n\ell}\,\phi_{n\ell}$$

In these equation W_{val} ($\tilde{W}_{val}$) represents the coulomb and exchange contributions of the other valence orbitals (pseudo-orbitals); W_{rel} represents the relativistic mass-velocity and Darwin terms. Once the pseudo-orbitals are defined, the RECP can be obtained by inverting Eq. (7). The $\tilde{\phi}_{nl}$ have been defined in two different manners: two different manners:

(1) Linear combinations of RHF orbitals. In this approach[7,8] a smooth, nodeless pseudo-orbital $\tilde{\phi}_{nl}$ is defined in terms of the RHF orbitals

$$\tilde{\phi}_{n\ell}(r) = \sum_k b_{k\ell}\,\phi_{k\ell}(r) \tag{9}$$

where the coefficients b_{kl} are defined by minimizing a "smoothness" functional related to the kinetic energy.

(2) Conservation of valence density. In this approach,[6] the pseudo-orbital is required to be as similar as possible to the RHF orbital in the valence region ($r > R_c$)

$$\tilde{\phi}_{n\ell}(r) = \begin{cases} \phi_{n\ell}(r) & r > R_c \\ \chi_{n\ell}(r) & r < R_c \end{cases} \tag{10}$$

where $\chi_{n\ell}$ is a polynomial which is smoothly matched to $\phi_{n\ell}$ and its derivatives across R_c. The latter approach has been more successful in reproducing all-electron molecular results with nonrelativistic ECP's, apparently by virtue of providing a more faithful representation of the valence charge density, and therefore should also provide a more reliable basis for molecular results using relativistic ECP's.

After obtaining RECP's for each angular momentum value $\ell = 0,1,\ldots L$, where L is the lowest value not present in the core (e.g., 5g for Au), the total potential is given as

$$U_{core}(r) = U_L(r) + \sum_{\ell=0}^{L-1} |\ell\rangle[U_\ell(r) - U_L(r)]\langle\ell| \qquad (11)$$

where the closure property of projection operators has been invoked and an implicit sum over $-\ell < m < \ell$ is also implied in the above equation.

The potentials are fit to analytic Gaussian forms

$$\sum_k d_k r^{n_k} e^{-\alpha_k r^2} \qquad n_k = 0,1,2 \qquad (12)$$

which are convenient for evaluation of multi-center matrix elements[3] $\langle\chi_a|V_c|\chi_b\rangle$ needed in molecular calculations.

Spin-Orbit Coupling

The effects of the spin-orbit coupling operator are included using the total energies E_I and wavefunctions Φ_I of the electronic states calculated using the RECP's,

$$H_{I,J} = \delta_{I,J} E_I + \langle\Phi_I|V_{s-o}|\Phi_J\rangle \quad . \qquad (13)$$

where Φ_I can represent either a single-configuration Hartree-Fock wavefunction or a multi-configuration MC-SCF or configuration interaction (CI) wavefunction comprised of one-electron orbitals ϕ_i. The Hamiltonian in Eq. (13) is then diagonalized to obtain the energies and wavefunctions in the presence of the spin-orbit operator.

The spin-orbit operator can be treated in three increasingly more sophisticated (and more computationally demanding) levels.

(1) *Atoms-in-molecules method.* When the molecular states retain, to a good approximation, their atomic parentage, the semi-empirical atoms-in-molecules approach can be easily applied. The spin-orbit Hamiltonian matrix can be written as

$$\underset{\sim}{H}_{s-o}(\underset{\sim}{R}) = \underset{\sim}{\delta}\, E_I(R) + \underset{\sim}{V}_{s-o} \qquad (14)$$

where $E_I(R)$ is the potential energy curve of the I^{th} molecular state, R denotes the nuclear coordinates and V_{s-o} depends only on the spin-orbit splittings of the constituent atomic fragments. For example, for the states of XeF dissociating to $Xe^+ + F^-$ (see Fig. 1), H_{s-o} has the form[4]

$$H_{s-o} = \begin{bmatrix} E_1(R) & -\sqrt{2}\lambda & 0 \\ -\sqrt{2}\lambda & E_2(R)+\lambda & 0 \\ 0 & 0 & E_1(R)-\lambda \end{bmatrix} \qquad (15)$$

where E_1 and E_2 are the total energies of the 2 $^2\Sigma^+$ and 2 $^2\Pi$ states, respectively, and λ is one-half the empirical Xe^+ $^2P_{1/2}$ - $^2P_{3/2}$ splitting. Good agreement between all-electron and ECP calculations and also between theory and experiment is evident from the spectroscopic properties given in Table 3.

(2) Effective spin-orbit operator. For the majority of molecules, the delocalization, hybridization and charge transfer effects occurring in chemical bonding will distort the orbitals from their atomic character and require a more sophisticated spin-orbit treatment. These effects can be successfully incorporated by the effective spin-orbit operator approach, in which matrix elements over the one-electron orbitals, $\langle\phi_i|V^{eff}_{s-o}|\phi_j\rangle$ are used to construct the spin-orbit matrix in Eq. (13) over state functions $\langle\Phi_I|V_{s-o}|\Phi_J\rangle$. The effective operator V^{eff}_{s-o} has the form[3]

$$V^{eff}_{s-o} = \frac{\alpha^2}{2} \sum_{i_k,k} \frac{Z^{eff}}{r^3_{ki_k}} \underline{\ell}_{ki_k} \cdot \underline{s}_{i_k} \qquad (16)$$

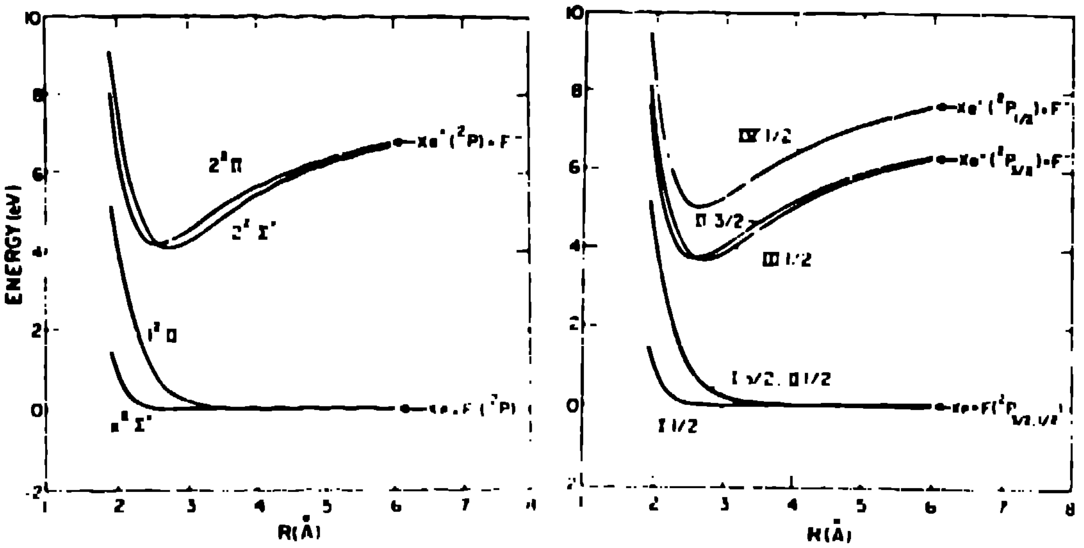

Fig. 1. Electronic states of XeF without spin-orbit coupling (left) and with spin-orbit coupling (right) using the atoms-in-molecules procedure.

Table 3. Spectroscopic properties of the $III_{1/2}$ state of XeF. (Ref. 7)

	D_e(eV)	R_e(Å)	ω_e(cm^{-1})	Emission energy (eV)
AE	5.07	2.68	303	3.65
VE(NR)	5.17	2.63	311	3.56
VE(R)	5.15	2.63	311	3.52
Expt	5.31	(2.49)	309	3.52

where α is the fine-structure constant, k indexes the nuclei and i_k indexes the electrons on center k. The parameter Z_k^{eff} is adjusted to reproduce the relevant atomic spin-orbit constants ζ_k. Also, only 1-center terms are used to evaluate the above 1-electron operator. In all-electron applications Z_k^{eff} can be viewed as an effective nuclear charge. In ECP calculations, where the valence orbitals are nodeless with zero amplitude at the nucleus, the resulting values of Z_k^{eff} must be taken to be very large (compared to the actual Z) to match the experimental atomic spin-orbit parameters and hence lose any physical significance. Nevertheless the effective operator approach has proved extremely useful in accounting for the effects of spin-orbit coupling for valence electrons in molecules.

In Table 4 recent calculations by Wadt[9] compare the use of the effective operator method in all-electron and valence-electron calc-

Table 4. Silicon atom spin-orbit constants (in cm^{-1}) calculated using Hartree-Fock wavefunctions over Gaussian basis sets and an effective one-electron one-center spin-orbit operator adjusted to reproduce the Si(^{3}P) constant, VE=valence electron, AE(FC) = all-electron with $1s^22s^22p^6$ core frozen from Si(^{3}P). (Ref. 9)

	AE(FC) (11s8p)/[4s4p]	VE (3s4p)	VE (5s7p)	Expt
Si [$3s^23p^2$] ^{3}P	148.9	148.9	148.9	148.9
Si^+[$3s^23p^1$] ^{2}P	192.6	179.81	179.8	191.3
Si^+[$3s^24p^1$] ^{2}P	27.2	27.3	32.7	40.0
Si^{3+}[$3p^1$] ^{2}P	295.0	240.2	250.2	306.9

ulations on the Si atom and its ions. The values of Z^{eff} for the HF orbitals and pseudo-orbitals, respectively, were chosen to match the quantity $Z^{eff} \langle r^{-3} \rangle_{3p}$ to the Si spin-orbit constant, $\zeta = 2/3 \left[{}^3P - {}^3P_0 \right]$. Since the calculations covered large changes in the radial extent of the Si 3p orbital they provide an excellent test of the method. The good agreement (within 20 percent) between all-electron, valence-electron and experimental results supports the validity of the approach; in the next section the method is tested in a molecular example.

(3) Breit-Pauli spin-orbit operator. The spin-orbit term in the Breit-Pauli Hamiltonian is given by

$$V_{so} = \frac{\alpha^2}{2} \sum_{i,k} \frac{Z_k}{\sigma_{ki}^3} \underline{\ell}_{ki} \cdot \underline{s}_i + \sum_{i,j}{}' \left(\frac{\underline{r}_{ij}}{r_{ij}^3} \times \underline{p}_i \right) \cdot (s_i + 2s_j) \tag{17}$$

A rigorous application of this operator to molecular problems requires multi-center integral evaluation of 1-electron and 2-electron operators and is applicable only to all-electron calculation to a few molecular systems. Langhoff[10] has used the full Breit-Pauli operator to calculate rare gas-oxygen matrix elements and to compare to the all-electron results using the 1-center, 1-electron effective spin-orbit operator discussed above. The results are shown in Fig. 2 for the coupling matrix elements $\langle {}^3\Sigma^- | V_{s-o} | {}^1\Sigma^+ \rangle$ and $\langle {}^3\Pi | V_{s-o} | {}^1\Sigma^+ \rangle$ for ArO, KrO and XeO. Excellent agreement is obtained between the results using the effective operator and the Breit-Pauli Hamiltonian and enhance the validity of the simpler approach

APPLICATIONS

Relativistic Effects in Transition Metal Atoms

A recent comprehensive study of relativistic effects in transition metal atoms and ions by Martin and Hay[11] revealed large effects in excitation and ionization energies. The relativistic shifts for excitation energies involving the s^2d^n, s^1d^{n+1}, and d^{n+2} states of the neutral species computed using Cowan-Griffin RHF wave functions are shown in Fig. 3. The simultaneous stabilization of s orbitals and destabilization of d orbitals arising from the relativistic terms in the Hamiltonian becomes increasingly apparent in the larger relativistic shifts observed as one proceeds from the first through third transition series. The effects of relativity were found to be several eV in the third transition series and surprisingly significant (as large as 0.6 eV) for the first transition series

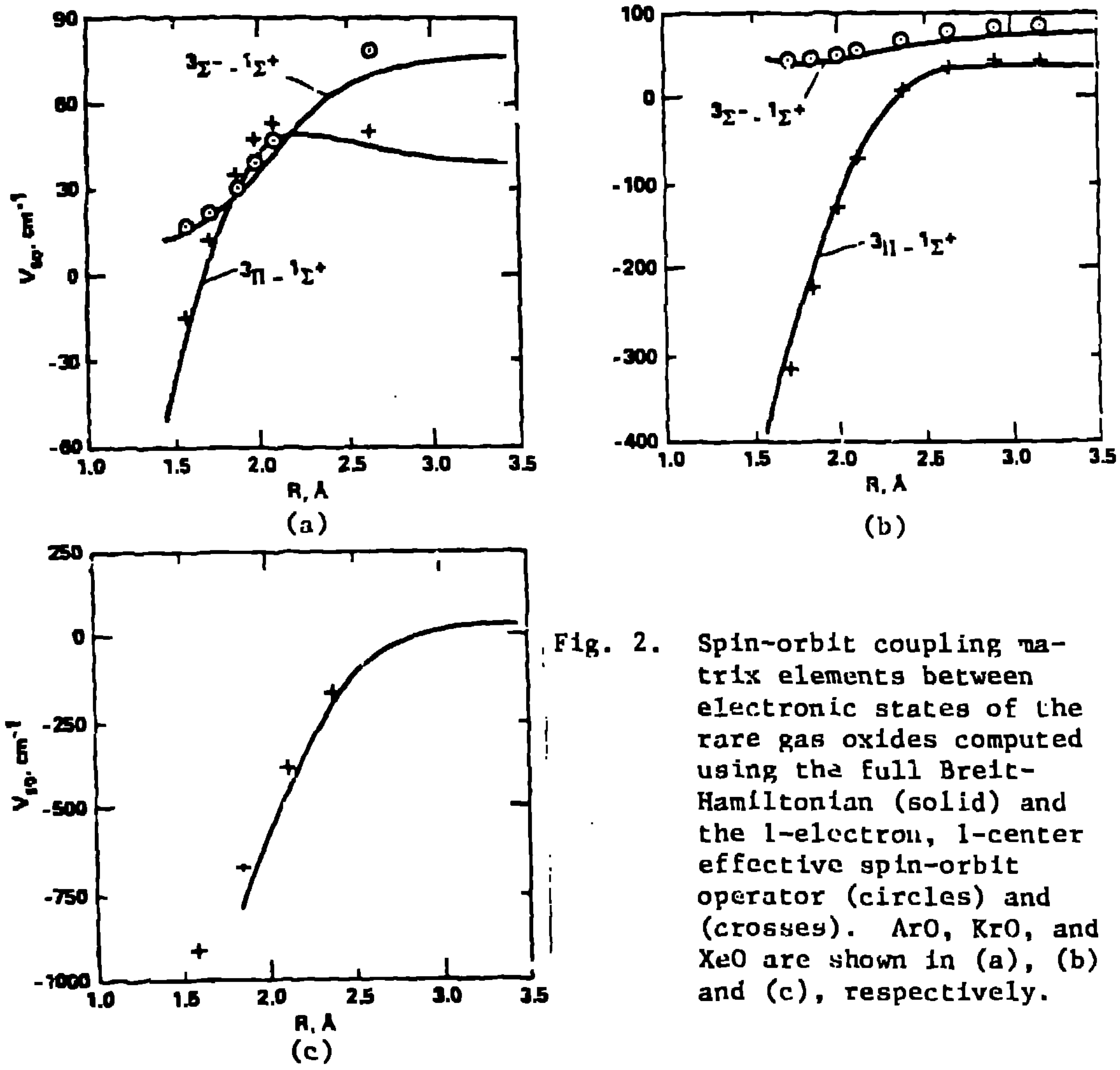

Fig. 2. Spin-orbit coupling matrix elements between electronic states of the rare gas oxides computed using the full Breit-Hamiltonian (solid) and the 1-electron, 1-center effective spin-orbit operator (circles) and (crosses). ArO, KrO, and XeO are shown in (a), (b) and (c), respectively.

Relativistic Effects in Chemical Bonds

The importance of relativistic effects in chemical bonding of molecules has been studied using a variety of theoretical approaches including 1-center Dirac-Fock,[12] relativistic ECP,[13] and full Dirac-Fock[14] methods. Hay et al.[13] used RECP's to investigate the ground states of the AuH and AuCl molecules and to compare with the results using nonrelativistic ECP's (Fig. 4). With a properly dissociating 2-configuration (GVB-1) wavefunction the predicted bond length from the RECP calculations differed by only 0.01Å from the experimental value (1.52Å) as shown in Table 5. By contrast the nonrelativistic ECP calculation gave a bond length over 0.3Å too long! A relativistic contraction of 0.16Å was also observed in the ionic AuCl species (Table 6). One interpretation ascribes the shortening of the bond in AuH to the relativistic contraction of the

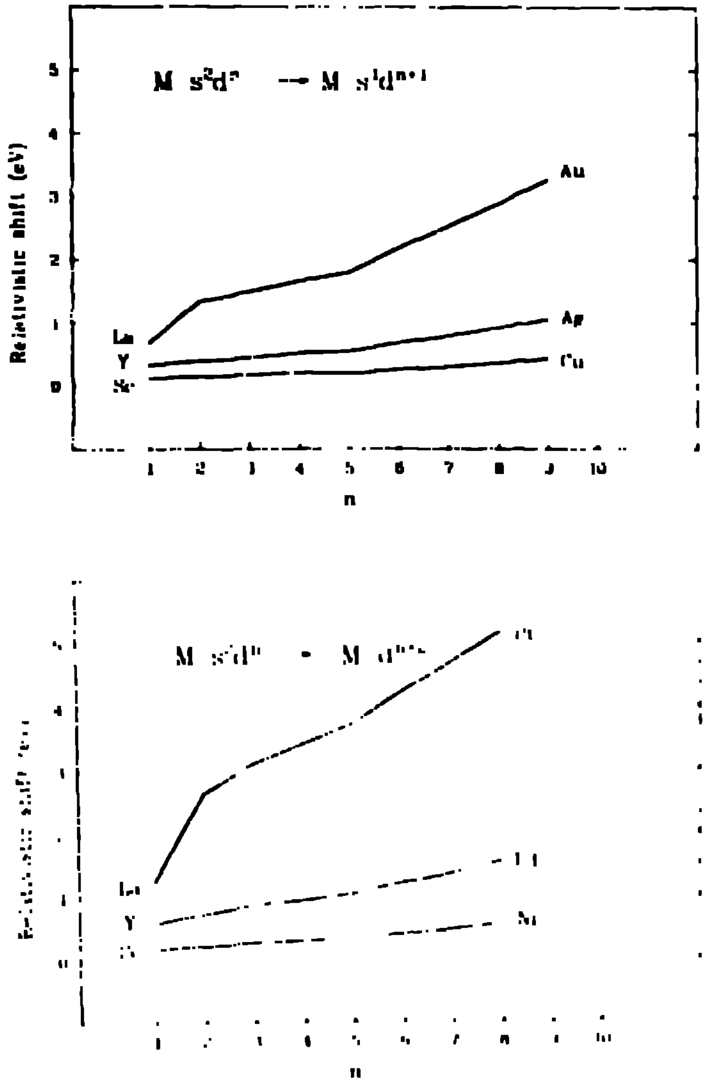

Fig. 1. Relativistic shifts in excitation energies for transition metal atoms obtained from comparing HF and relativistic HF calculations.

6s orbital in Au, as $\langle r \rangle_{6s}$ is reduced from 1.7 to 1.4 a_0 and the $5d^{10}$ core of Au does not participate in the bonding.

A similar relativistic contraction (0.16Å) is observed in AuCl (Table 6). The relativistic calculations give a larger dissociation energy for AuH compared to the nonrelativistic results, while the reverse is true in AuCl. The decrease in the bond energy of AuCl can be correlated with the increase in energy of the ionic $Au^+ + Cl^-$ asymptote relative to the covalent limit upon inclusion of relativistic effects in the atom.

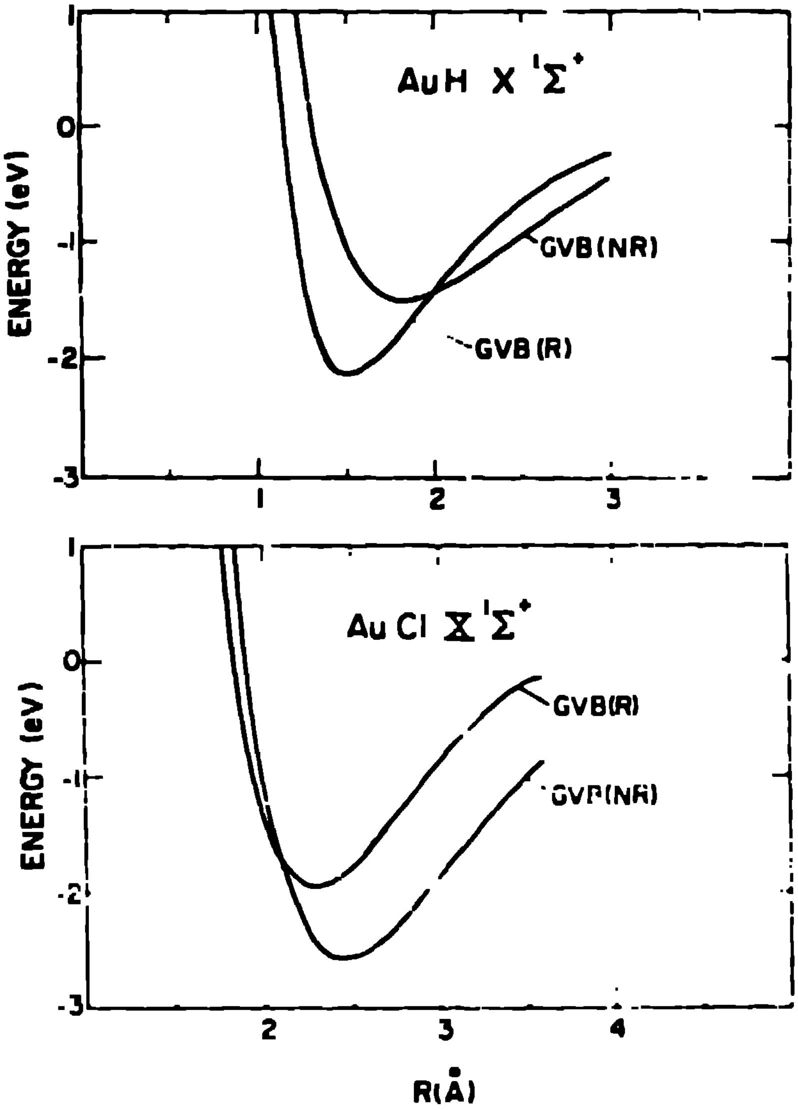

Fig. 5. Potential energy curves for the ground states of AuH and AuCl computed from nonrelativistic (NR) and relativistic (R) ECP calculations.

Electronic Structure of Transition Metal Complexes

The advent of relativistic ECP's makes calculations feasible for the first time on third row transition metal complexes. Theoretical studies of platinum complexes using RECP's have explored (1) the structures and energetics of Pt(II) hydride and chloride complexes,[illegible] (2) the oxidative addition of H_2 to a Pt(0) complex,[illegible] and (3) the binding of ethylene in Zeise's salt,[illegible] $PtCl_3(C_2H_4)^-$. The geometric parameters of Zeise's salt computed from Hartree-Fock

Table 5. Spectroscopic Properties of AuH. (Ref. 13)

AuH $X^1\Sigma^+$	R_e (Å)	D_e (eV)	ω_e (cm^{-1})
Nonrel. ECP			
HF	1.763	0.99	1387
GVB-1	1.82[illegible]	1.52	1203
POL-CI	1.807	1.57	12.17
Rel. ECP			
HF	1.508	1.55	2014
GVB-1	1.514	2.14	199[illegible]
POL-CI	1.522	2.2[illegible]	18[illegible]
Exptl	1.5237	[illegible]	2[illegible]
1-Center Dirac-Fock			
Nonrel.	1.765	--	2296
Rel.	1.65[illegible]	--	2[illegible]

wavefunctions using a RECP on Pt are compared with the values obtained from neutron diffraction in Fig. 5. The perpendicular orientation of the ethylene ligand relative to the PtCl$_3$ plane is correctly predicted to be the stable form, with the planar conformation calculated to lie 15 kcal/mol higher in energy. The other geometrical parameters, including the bending of the CH$_2$ groups away from the metal, are also well reproduced by the calculations.

Both Zeise's salt and the related PtCl$_4^{2-}$ species have (5d)^8 formal configurations, where the 5d$_{x^2-y^2}$ orbital oriented along

Table 6. Spectroscopic Properties of AuCl. (Ref. 13)

AuCl ($X^1\Sigma^+$)	R_e (Å)	D_e (eV)	ω_e (cm^{-1})
Nonrel. ECP			
GVB-1	2.44[illegible]	[illegible]	2[illegible]
Rel. ECP			
GVB-1	2.[illegible]8[illegible]	1.96	298
POL-CI	[illegible]	2.[illegible]	306
Exptl		1.[illegible] ± 0.1	19[illegible]

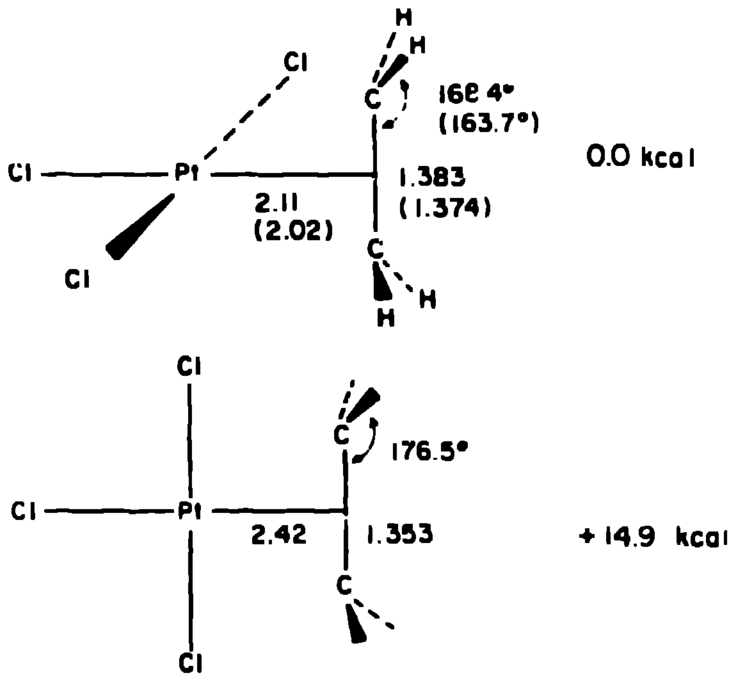

Fig. 5. Calculated geometrical parameters (with experimentally observed values in parentheses) for Zeise's salt.

the metal-ligand axes is nominally vacant. The lowest excited states in both systems arise from d-d excitations from the (xz, yz), xy or z^2 orbitals into the x^2-y^2 orbitals leading to states of E_g, A_{2g}, and B_{1g} symmetry, respectively, in $PtCl_4^{2-}$. The results of CI calculations[41] are shown in Fig. 6 where triplet and singlet states of these symmetries are identified. Spin-orbit coupling has been included using the effective operator method discussed earlier, and in this case the procedure involves setting up and diagonlizing the 17 x 17 spin-orbit Hamiltonian matrix over the above set of singlet and triplet states. The CI + spin-orbit results are compared with experimentally observed levels, which are in reasonably good agreement with the predicted levels, although there is still considerable controversy over some of the assignments.

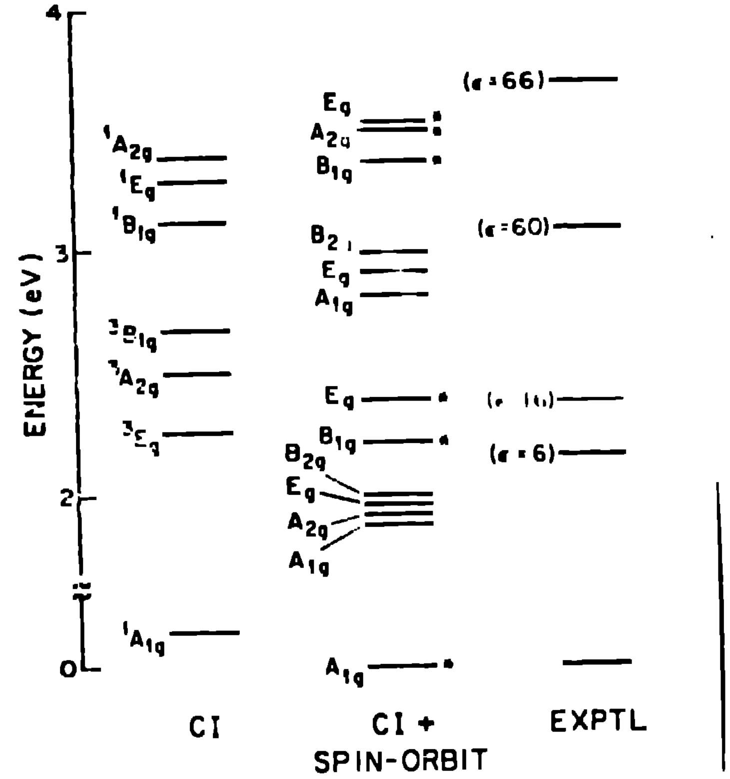

Fig. 6. Electronic states of PtCl^{2-} obtained from CI calculations with and without spin-orbit coupling.

Actinide Compounds

The electronic structure of actinide compounds including UF_6,[19] UF_5,[20] UO_2^{2+},[21] and ThO_2[21] has also been explored with the aid of the RECP method. In Figs. 7-9 some aspects of the electronic structure of UF_6 are depicted. To a zeroth-order approximation, one may regard UF_6 as having formal charges of U^{+6} and F^{-1} and thus having a $(5f)^0$ configuration in the ground state. (Mulliken population analyses of the ground state wavefunction of UF_6 actually show considerable "back-bonding" into the 5f orbitals.) The highest occupied levels arise from symmetry combinations of the F 2p orbitals (Fig. 7) while the lowest unoccupied levels correspond to the seven U 5f levels. Spin-orbit coupling has only a modest effect on the level ordering with the exception of the $2t_{1u}$ orbital which contains significant U 6p character and is split into two components—8u and 6u in the octahedral double group representation—separated by over 2 eV. Excited states may then be viewed in terms of charge-transfer excitations from the 36 F 2p levels (including spin-degeneracies) into the 14 U 5f levels leading to 504 states in all. These transitions account for the entire uv absorption spectrum of UF_6 between 3 and 10 eV (Figs. 8 and 9), where the results of CI + spin-orbit calculations[22] are shown for these 504 states classed according to the dominant excitations.

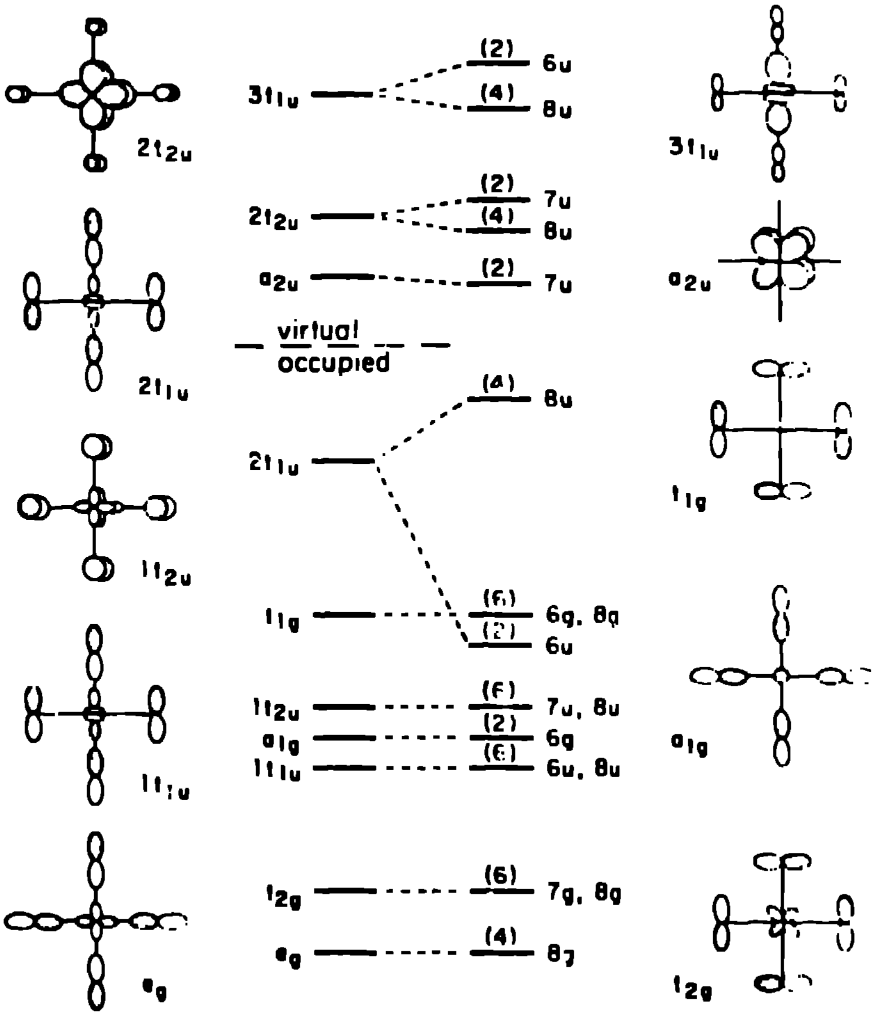

Fig. 7 Schematic diagram of the highest occupied and lowest unoccupied orbitals of UF_6.

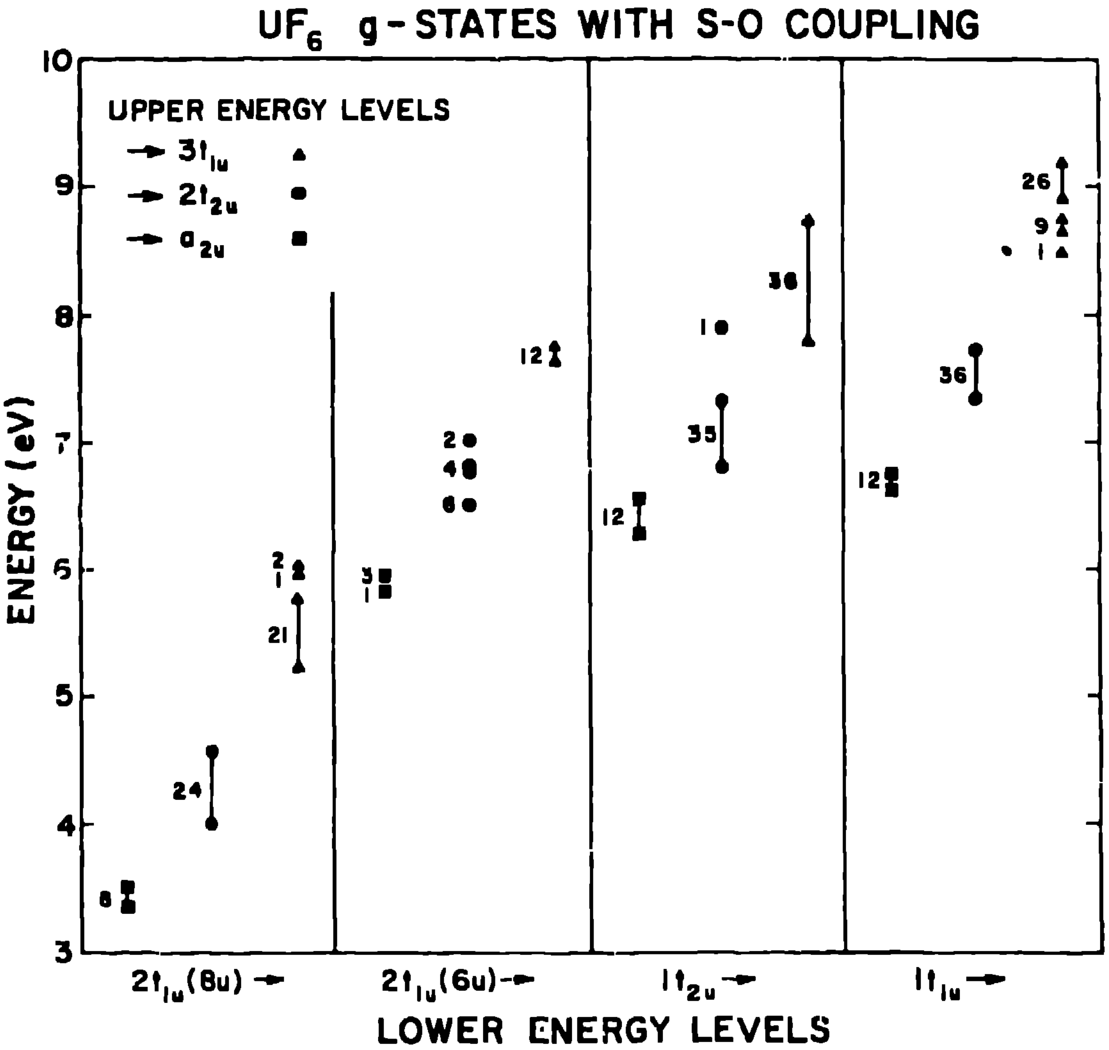

Fig. 8. Excited states of UF$_6$ with spin-orbit coupling (g states) grouped according to orbital parentage.

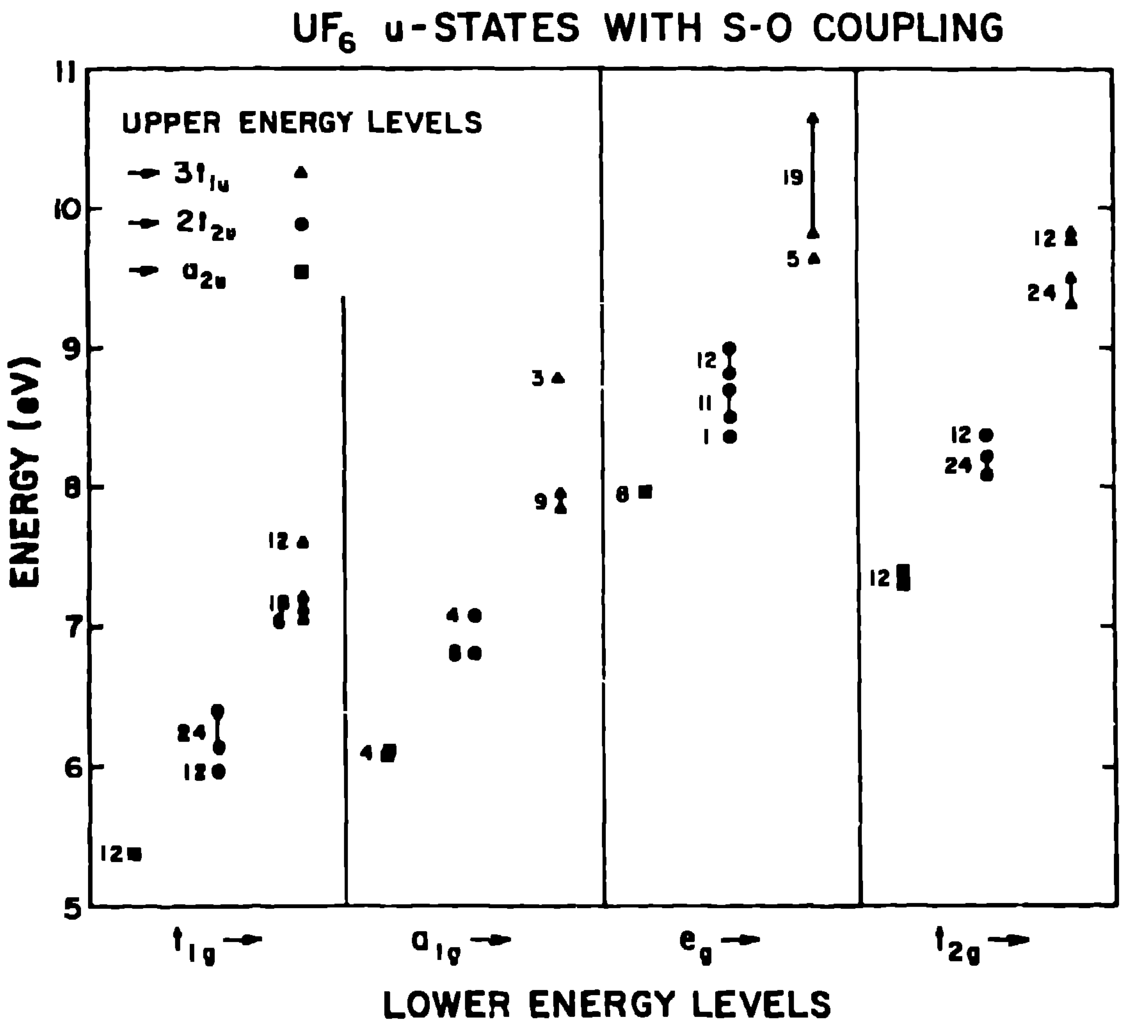

Fig. 9. Excited states of UF$_6$ with spin-orbit coupling (u states) grouped according to orbital parentage.

SUMMARY

Starting with one-component Cowan-Griffin relativistic Hartree-Fock orbitals, which successfully incorporate the mass-velocity and Darwin terms present in more complicated wavefunctions such as Dirac-Hartree-Fock, one can derive relativistic effective core potentials (RECP's) to carry out molecular calculations. These potentials implicitly include the dominant relativistic terms for molecules while allowing one to use the traditional quantum chemical techniques for studying the electronic structure of molecules. The effects of spin-orbit coupling can then be included using orbitals from such calculations using an effective 1-electron, 1-center spin-orbit operator. Applications to molecular systems involving heavy atoms, show good agreement with available spectroscopic data on molecular geometries and excitation energies.

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