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RELATIVISTIC QUANTUM CHEMISTRY

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Relativistic Quantum Chemistry

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1. Introduction

Measurements in the classical, the macroscopic world assume the velocity of the probe (light) to be infinite and the interaction between the probe and the object of measurement to be negligible. The laws governing the motions of particles derived on the above assumptions are Newtonian and lead to classical mechanics. In non-relativistic quantum mechanics one assumes the velocity of the probe to be infinite but allows interaction between the probe and the particle by way of Heisenberg's uncertainty principle. For most measurements on the lighter elements in the periodic table, non-relativistic quantum mechanics is sufficient, since the velocity of an electron is small compared to that of light. For the heavier elements in the periodic table (Au, Hg, Pb, Tl, etc.) the picture is entirely different. As a result of heavy nuclear charge for the heavy atoms, the inner electrons attain such high velocities comparable to that of light that non-relativistic quantum mechanics is far from adequate.

Relativistic quantum mechanics neither assumes infinite probe velocity nor ignores the interaction between the probe and the object of measurement. Thus, the difference between non-relativistic quantum results and relativistic quantum results arises from the true velocity of light. One can define relativistic effects, in general, as the difference in the results obtained with the true velocity of light and infinite velocity of light.

Relativistic effects can be further divided into a number of categories such as the mass-velocity correction, Darwin correction, spin-orbit correction, spin-spin interaction, Breit interaction, etc. The mass-velocity correction is the correction to the kinetic energy of the electron arising from the variation of its mass with velocity. One of the consequences of the finiteness of the velocity of light (as can be shown from the laws of the

special theory of relativity) is the variation of the mass of a particle with its speed. This is especially significant as the speed of the particles approach the speed of light. This variation with velocity in turn affects the kinetic energy of the particle. The spin-orbit correction arises from the strong coupling of the spin of the electron with the orbital angular momentum. This is especially large for electronic states of heavier atoms which arise from open shell configurations. The Breit interaction is the two-electron counterpart of the spin-orbit interaction. The Darwin correction is a characteristic outcome of the Dirac relativistic equation and there does not seem to be a simple physical explanation for this effect.

Relativistic corrections make significant impact on the electronic properties of heavy atoms and molecules containing heavy atoms. The inner s orbitals are the closest to the nucleus and thus experience the high nuclear charge of the heavy atoms. Thus, the inner s orbitals shrink as a result of mass-velocity correction. This in turn, shrinks the outer s orbitals as a result of orthogonality. Consequently, the ionization potential is also raised. The p orbitals are also shrunk by mass-velocity correction but to a lesser extent since the angular momentum keeps the electrons away from the nucleus. However, the spin-orbit interaction splits the p shells into $P_{1/2}$ and $P_{3/2}$ subshells and expands the $p_{3/2}$ subshells. The net result is that the mass velocity and spin-orbit interaction tend to cancel for the $P_{3/2}$ shell but reinforce for the $P_{1/2}$.

Spin-orbit interaction plays an important role in the electronic and spectroscopic properties of states arising from open shell electronic configurations. Thus, the contribution of spin-orbit interaction to the ground state of Au is small but to Pb is large. Spin-orbit interaction not only splits the electronic state into substates but mixes states which would

not mix in the absence of spin-orbit interaction. This is well illustrated by the lead atom. The ground state of the Pb atom would be ^3P in the absence of spin-orbit interaction. In addition, the ^1D and ^1S states arise from the $6p^2$ electronic configuration. However, the spin-orbit interaction splits the ^3P state into $^3P_0$, $^3P_1$ and $^3P_2$ states. The $^3P_0$-$^3P_1$, $^3P_0$-$^3P_2$ splittings are large, 7819 cm^{-1} and 10650 cm^{-1}, respectively.[2] The spin-orbit interaction also mixes $^3P_0$ with $^1S_0$ among other states. Similarly, $^3P_2$ mixes with $^1D_2$. This mixing is sometimes referred to as spin-orbit contamination and is quite large for heavy atoms. The $^3P_0$-$^3P_1$, $^3P_0$-$^3P_2$ splittings for the carbon atom are only 16 cm^{-1} and 44 cm^{-1} , respectively.[2] Thus one can see the dramatic contribution of relativistic effects for atoms and molecules containing very heavy atoms. In fact, the rare gas compound RnF is predicted to be ionic, Rn^+F^- based on the spin-orbit interaction of Rn^+.[3]

Spin-orbit interaction alters the spectroscopic properties of molecules containing heavy atoms to a considerable extent. Even if a molecule has a closed shell ground state, the excited states may arise from open shell electronic configurations in which case the spin-orbit interaction not only splits the excited states but mixes different excited states which would not mix in the absence of spin-orbit interaction. This leads to a number of interesting features in the potential energy curves such as shoulders, barriers, double minima, etc., which are attributed to relativistic avoided crossings. This aspect of relativistic effects is discussed in the third section of this chapter. The color of gold is attributed to relativistic effects which splits the 5d shell of gold and raises its energy. The golden color results from the 5d-fermi level transition which contrasts its color in comparison to silver.[8] The Lamb shift, Breit interaction, etc., are more important if one is considering fine structure calculations. They are

normally ignored if one considers electronic and spectroscopic properties in the valence region.

Relativistic effects alter the chemical bonding of molecules containing heavy atoms to a considerable extent. In some cases the bond is strengthened while in other cases it is weakened. Consider the dissociation energies of a few molecules to get some insight into the effect of relativistic corrections on D_e values. The dissociation energy of Au_2 is higher than Ag_2 in contrast to the usual trend of a lower D_e for the heavier elements of a group in the periodic table. This anomaly is caused by relativistic contraction and stabilization of the 6s orbital of Au. On the other hand the relativistic spin-orbit interaction weakens the bond in the case of Pb_2 by 50%. The calculated dissociation energy for Pb_2 with the inclusion of spin-orbit interaction is 50% of the value obtained without spin-orbit interaction.[4]

The lanthanide contraction (the decrease of radii from La to Lu) is usually attributed to incomplete shielding of the 4f shell. However, as pointed out by Pitzer and coworkers[5] this effect is in part attributable to relativistic effects. If one compares the non-relativistic Hartree-Fock and Dirac-Fock results, one obtains a contribution of about 27% from relativistic effects.

In recent years a number of papers have appeared in the chemical literature which deal with relativistic effects in atoms and molecules. Some of the earlier developments in this area have been reviewed by Pyykko[7] and Pyykko and Desclaux[8] and Pitzer[9]. A NATO conference proceedings edited by Malli[10] lists a number of papers by experts in this area on several topics pertaining to relativistic effects in atoms, molecules and solids. More recently, an issue of the International Journal of Quantum Chemistry was devoted to the proceedings of the Finland conference on relativistic

effects.[11] Krauss and Stevens[12] have reviewed the use of effective potentials which include relativistic effective potentials. Christiansen, Ermler and Pitzer[13] have recently reviewed relativistic effects in chemical systems. The above reviews have outlined the various developments and applications in relativistic quantum chemistry. Since the appearance of the above reviews a number of developments and new applications have emerged in this area. Earlier reviews on this topic could not cover all applications in this area in detail as a result of space limitation among other reasons. The present review emphasizes the methods and very recent applications of relativistic quantum chemistry to molecules of spectroscopic interest.

2. Methods of relativistic quantum chemistry

The starting point of most of relativistic quantum mechanical methods is the Dirac equation which is the relativistic analogue of the Schrodinger equation. Before Dirac's formulation, an obvious way of starting relativistic quantum mechanics would be the Einstein energy expression shown below.

$$E^2 = m_o^2 c^4 + p^2 c^2 \qquad (1)$$

One could insert the appropriate quantum mechanical operators for E and p and obtain a differential equation. The resulting differential equation, known as the Klein-Gordon equation, is shown below.

$$(\Box + m_o^2)\ \psi = 0,$$

where

$$\Box = -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{\partial^2}{\partial t^2}$$

where, $\hbar = c = 1$.

The resulting equation is covariant to the Lorentz transformation, a fundamental transformation under which all relativistic equations must be invariant. However, $\rho = \psi\psi^*$ obtained from the Klein-Gordon equation can be negative which leads to difficulties in interpreting ρ, the conventional probability density.

Dirac discovered an equation now well known as the Dirac equation in an attempt to overcome the above-mentioned difficulties of the Klein-Gordon equation. The reasoning behind the derivation of this equation is that in order to prevent the occurance of negative charge densities one must avoid time derivatives in the charge density and the resulting equation must be completely symmetric in the treatment of spatial and temporal coordinates. The resulting equation is shown below for a single electron in a central coulombic field.

$$H_D\psi = E\psi,$$

where

$$H_D = (\vec{\alpha} \cdot \vec{p} + c^2\beta - z/r)$$

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

where the σ_p's are the 2x2 Pauli matrices and I is the 2x2 identity matrix.

The Dirac hamiltonian for a many-electron atom can be written as

$$H_D = \sum_i h_D(i) + \sum_{i<j} \frac{1}{r_{ij}} ,$$

where $h_D(i)$ is the one electron Dirac hamiltonian, $h_D(i) = \vec{\alpha}_i \cdot \vec{p}_i + \beta_i c^2 - \frac{Z}{r_i}$. Note that the above hamiltonian ignores the 2-electron relativistic Breit interaction. Introduction of the Breit interaction as a perturbation shows that it is very small in the valence region. However, the Breit interaction appears to be more important for the properties of core electrons for which this makes significant contribution.

Since the one-particle Dirac hamiltonian involves 4x4 matrices instead of scalar functions and differential operators, the solution of the Dirac equation is a vector of four components. This is referred to as 4-component spinor. It takes the form

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

where

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

$Y_\lambda^{m-\sigma}$ is a spherical harmonic, $\phi_{1/2}^{1/2} = \alpha = \binom{1}{0}$, $\phi_{1/2}^{-1/2} = \beta = \binom{0}{1}$, are the Pauli spinors, $C(\ell\ \frac{1}{2}\ j;\ m-\sigma,\sigma)$ are the Clebsch-Gordan coefficients, and k is the relativistic quantum number. It is defined as

$$k = \begin{cases} j+1/2 & \text{if} \quad j=\ell-1/2 \\ -(j-1/2) & \text{if} \quad j=\ell+1/2 \end{cases},$$

λ is defined as

$$\lambda = \begin{cases} k & \text{if} \quad j=\ell-1/2 \\ -(k+1) & \text{if} \quad j=\ell+1/2 \end{cases} .$$

The Q_{nk}'s are known as the small components and P_{nk}'s are the large components. They satisfy the following coupled differential equations for a central force field v;

$$\frac{dP_{nk}}{dr} + \frac{kP_{nk}}{r} - \left\{ \frac{2}{\alpha} + \alpha(v(r) - \varepsilon_{nk}) \right\} Q_{nk} = 0$$

$$\frac{dQ_{nk}}{dr} - \frac{kQ_{nk}}{r} + \alpha \left[v(r) - \varepsilon_{nk} \right] P_{nk} = 0$$

Thus one can solve the Dirac-Fock equation to obtain the relativistic energies and four-component spinor wave functions.

Desclaux[14] has developed a computer code to solve the many-electron Dirac-Fock equation for atoms in a numerical self-consistent method. In this method the relativistic hamiltonian is approximated within the Dirac-Fock method ignoring the two-electron Breit interaction. The Breit interaction is introduced as a first order perturbation to energy after self-consistency is achieved. Relativistic wave functions and energies calculated this way are available for a number of atoms.[6]

The non-relativistic limit ($c \to \infty$) of the two coupled radial Dirac equation reduces to the Schrodinger equation if the small components Q_{nk} are eliminated. Thus, the small component is a measure of the magnitude of relativistic effects in these systems. While the small components make significant contribution in the core region, the effect of these components in the valence region is ignorable. This was illustrated by a comparison of the

relativistic and non-relativistic radial solutions for the 6s orbital of Pb by Lee, Ermler and Pitzer.[15] We reproduce their comparison in fig. 1. As one can see from that figure the effect of small component is very small in the valence region.

The effect of small components on the properties of molecules have been studied by Schwarz[16] to a high order using the Foldy-Wouthuysen transformation. Schwarz has demonstrated that the contribution of the small components to chemical properties is ignorable. Thus one can ignore the small components if one is considering chemical properties. Examples of 4-component atomic spinors are shown in the review paper by Pitzer.[9]

Relativistic calculations can also be carried out using the Pauli hamiltonian.[1] The Pauli approximation divides relativistic effects into different categories thereby facilitating evaluation of different types of relativistic correction. The Pauli hamiltionian can be written in the absence of magnetic field as

$$H_{BP} = H_o + H_D + H_{MV} + H_{so} + H_{ss}$$

$$H_o = \text{non-relativistic hamiltonian}$$

$$H_D = + \frac{\alpha^2}{8} [\nabla^2 V] \qquad \text{(Darwin)}$$

$$H_{MV} = - \frac{\alpha^2}{8} \sum_i P_i^4 \qquad \text{(mass velocity)}$$

$$H_{so} = \frac{\alpha^2}{2} \left[\sum_i \frac{z}{r_i^3} (\vec{L}_i \cdot \vec{S}_i) - \sum_{i \neq j} \frac{1}{r_{ij}^3} (\vec{r}_{ij} x \vec{P}_i) \cdot (\vec{S}_i + 2\vec{S}_j) \right] \qquad \text{(spin-orbit)}$$

where α is the fine structure constant, and

$$V = -Z \sum_i \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}$$

The Pauli hamiltonian is ideally suited for carrying out relativistic corrections as first order perturbation to a non-relativistic hamiltonian. In recent years, several authors have considered inclusion of the Pauli terms in variational (SCF) calculations.[17-19] Wadt, Hay and coworkers[20-24] use the Pauli hamiltonian in deriving relativistic effective core potentials. The choice of appropriate basis sets is crucial in using the Pauli hamitonian in polyatomic relativistic calculations. Gaussian basis functions with large exponents are important. It has been noted[17,25] that the mass-velocity term of the Pauli hamiltonian leads to divergence in the region close to the atomic nucleus. Cowan and Griffin[17] avoid this divergence in their numerical SCF calculations by restricting the wave function near the nucleus by a two-term series expansion. For Gaussian basis sets the total Pauli kinetic energy contributions for the s functions with exponents of the order of $1/\alpha^2$ or larger become negative, resulting in unrealistic wave functions and energies if corrections above first order in α^2 are included. Nevertheless, this can be avoided if one contracts heavily such high exponent s functions with functions having much smaller exponents.

Several authors have considered a number of approximate solutions to the Dirac equation. One such method is the use of the Foldy-Wouthuysen transformation[19] (see, for example, Morrison and Moss[25]). Upon application of a unitary transformation of the form shown below to the Dirac hamiltonian, one can transform the Dirac hamiltonian to a form for which the solutions have only the large two components.

$$H = \exp(is)\, H_D \exp(-is),$$

where s is an hermitian operator. Kuttzelnig[26] has also recently emphasized the importance of the Foldy-Wouthuysen transformation in order to avoid a variational collapse for finite basis sets with the Dirac hamiltonian. Desclaux and coworkers[27] have formulated a relativistic one-center approach based on the Dirac hamiltonian; this method, however, is applicable only for hydrides.

Kim[28] has formulated a relativistic Hartree-Fock-Roothaan equation for the ground states of closed shell atoms using Slater-type orbitals. Relativistic effects in atoms have been reviewed by Grant.[29] Malli and coworkers[30-33] have formulated a relativistic SCF method for molecules. In this method four-component spinor wave functions are obtained variationally in a self-consistent scheme using gaussian basis sets.

Lee and McLean[34,35] have considered full-relativistic all-electron solutions to the Dirac equation for AgH and AuH. In this method, 4-component, all-electron spinors are obtained using a LCAS-MS (linear combination of atomic spinor-molecular spinor) method. These authors employ a Slater type basis for AgH and AuH. However, such relativistic all-electron calculations do not seem to be practical for molecules other than diatomic hydrides at present.

The Breit two-electron correction[36] arises from the relativistic magnetic retardation between two electrons. The Breit operator, which describes this interaction, is

$$H_{Br} = -\frac{e^2}{2r_{12}}\left[\vec{\alpha}_1 \cdot \vec{\alpha}_2 + \frac{(\vec{\alpha}_1 \cdot \vec{r}_{12})(\vec{\alpha}_2 \cdot \vec{r}_{12})}{r_{12}^2}\right]$$

where α_1 and α_2 are Dirac matrices, r_{12} is the distance between the electrons 1 and 2. The eigenfunction of H_{Br} is thus a 16-component spinor, since each electron has a 4-component spinor function. The Breit interaction is of the order α^2 (α is the fine structure constant). Although its contribution is significant in the core, the effect of Breit correction in calculating chemical and valence-level spectroscopic properties appears to be small. The Breit interaction is normally introduced as a first order perturbation to the Dirac hamiltonian. Further, inclusion of Breit interaction in the Dirac hamiltonain would lead to results that are not consistent with the laws of quantum electrodynamics since the Breit interaction is not Lorentz-invariant. The effect of Breit interaction on chemical properties have not yet been studied in full detail. Stevens and Krauss[37,38] have developed a semiempirical scaling method which corrects for two-electron screening of the valence spin-orbit by core. The total Breit correction to the spin-orbit splittings are about 15% in the first row and 5% in the second row.

Pyykkö and coworkers[39,40] have formulated a relativistic extended Hückel method for molecules. This method incorporates relativistic effects by a systematic parametrization using Desclaux's atomic relativistic Dirac-Fock calculation.[6] The Dirac-Fock atomic energies and the off-diagonal elements are proportional to the product of the overlap matrix element in the relativistic $|\ell\ sjm\rangle$ basis. Pyykkö and coworkers[40-44] have applied this method to a number of molecules.

Dirac-Slater multiple $\chi\alpha$ (DS-MS $x\alpha$) method is an approximate way of introducing relativistic corrections. Case and coworkers[42-46] have used this method in a number of studies. This method has been recently reviewed by Case[42] and earlier by Pyykkö.[7] The readers are referred to these two reviews for further details.

We now briefly consider the symmetry aspects of relativistic quantum chemistry. With the introduction of spin-orbit interaction, the appropriate group of the hamiltonian is the double group of the molecular point group. This arises from the fact that spin is no longer a good quantum number. The double group contains twice the number of operations in the molecular point group. In this group, rotation by an angle $\varepsilon + 2\pi$ is not considered equivalent with the rotation by ε. The group has two sets of irreducible representations. The first set is for the integral spins which correspond to the ordinary irreducible representations of the point group but extended to the double group. For half-integral spins additional representations are generated which are not members of the set of irreducible representations of the point group. The first use of the double group is in correlating non-relativistic electronic states into relativistic states. An equivalent correlation is the correlation of the states without and with spin-orbit interaction. For example, consider the $^3B_1$ state of PbH_2. Since the spin-orbit interaction on Pb is quite large, this state would be split apart into finer relativistic states. The states which result from $^3B_1$ are obtained by first correlating the spin state (triplet, $D^{(1)}$) into the C_{2v}^2 group and then multiplying the resulting spin representations with the spatial symmetry. The correlation of the triplet into C_{2v}^2 gives rise to $A_2 + B_1 + B_2$ representations which upon multiplication with B_1 results in $B_2 + A_1 + A_2$. Thus the $^3B_1$ state of PbH_2 is split into three states in the presence of spin-orbit interaction which are of A_1, A_2 and B_2 symmetry. If one considers the $^2B_1$ state of PbH_2^+ one obtains a different picture. The doublet correlates with the $E_{1/2}$ representation in the C_{2v}^2 group. The overall symmetry is thus $E_{1/2}$, which is not a part of the character table of C_{2v}. Oreg and Malli[47,48-49] have considered symmetry aspects of the construction of spinors for polyatomics

which are symmetry-adapted in the double group of the molecule. These methods have been used in the Dirac-Fock theory of openshell as well as closed shell molecules.[51]

An important and reliable method for carrying out relativistic quantum calculations is the relativistic effective potential method. A number of groups have considered the generation of both relativistic and non-relativistic effective potentials. Krauss and Stevens[12] have recently reviewed the use of effective potentials in quantum chemistry. Readers are referred to that review for additional details pertaining to this topic. In this review we consider the methods of relativistic effective potentials.

The objective of the effective potential method is to represent the interaction of the valence electrons with the core electrons by an effective potential thereby reducing the number of electrons significantly in quantum calculations. The effective potentials must prevent the collapse of the valence electrons into the core. Effective potentials can be relativistic or non-relativistic depending on the nature of the wave function from which they are generated. Relativistic effective potentials can be generated by either semiempirical or ab initio methods. We first briefly review the ab initio methods.

Many of the effective potentials (relativistic or non-relativistic) are generated using the Phillips-Kleinman transformation.[50] In this method, the explicit core-valence orthogonality contraints are replaced by a modified valence hamiltonian. If one replaces the potential generated by core electrons by a potential V_c then one can write the one-electron valence wave equation as

$$(h + V_c)\ \phi_v = E_v \phi_v,$$

where $\langle\phi\,|\phi_c\rangle = 0$, $H\,\phi_c = E_c\phi_c$. Phillips and Kleinman[50] suggested that ϕ_v can be written as

$$\phi_v = \chi_v - \sum_c \langle\chi_v|\phi_c\rangle\,\phi_c$$

It can be easily seen that for any χ_v, ϕ_v is orthogonal to ϕ_c thereby satisfying $\langle\phi_v|\phi_c\rangle = 0$. If one substitutes the above expression for ϕ_v into the one-electron eigenequation one obtains

$$(h + V_c + V_{Ep})\,\chi_v = E_v\chi_v,$$

$$V_{Ep} = \sum_c [E \quad - E_c]\,|\,\phi_c\rangle\langle\,\phi_c|$$

V_{Ep} thus obtained is often referred to as the Phillips-Kleinman pseudo potential; while χ_v is known as the pseudo orbital. $|\phi_c\rangle\langle\phi_c|$ is the projection operator corresponding to the core orbital ϕ_c. Thus the operator $\sum_c |\phi_c\rangle\langle\phi_c|$ is the projection operator of the core orbitals. If the V_{Ep}'s are derived based on a non-relativistic atomic wave function, they are known as non-relativistic effective core potentials. There are also several non-relativistic model potentials which are not strictly derived from ab initio methods. For a review of these potentials, see Krauss and Stevens.[49]

Ab initio relativistic effective core potentials can be derived from a number of methods. We briefly review these methods. Lee, Ermler and Pitzer[15] have formulated a method for deriving effective potentials from the numerical Dirac-Fock calculations of the atoms. We start with this method.

The solution of the Dirac-Fock equation is a set of 4-component spinors. If the spinors are partitioned as core and valence spinors then one

can write the overall many-electron relativistic wave function for a single configuration as

$$\psi = A\ [(\psi_1^c \psi_2^c \ldots \psi_m^c)(\psi_1^v \psi_2^v \ldots \psi_n^v)],$$

where A is the antisymmetrzer, $\psi_1^c \ldots \psi_m^c$ are core orbitals, m being the number of core electrons and ψ_1^v, $\psi_2^v \ldots \psi_n^v$ are the valence orbitals with n being the number of valence electrons. The total Energy E_T can be partitioned into core, valence and core-valence interaction energies. In symbols,

$$E_T = E_c + E_v + E_{cv}$$

It can be shown that

$$E_v + E_{cv} = \langle \psi_v^R | H_v^{Rel} | \psi_v^R \rangle,$$

$$H_v^{Rel} = \sum_i \{ h_D(i) + \sum_c (J_c(i) - K_c(i) \} + \sum_{i<j} \frac{1}{r_{ij}},$$

where the indices i and j run over valence electrons. For an orthonormal set of valence orbitals it can be shown that the DHF equation for a single electron is given by

$$[h_D + \sum_c [J_c - K_c]]\ \psi_v = \varepsilon_v \psi_v + \sum_c \psi_c \varepsilon_{cv},$$

where ε_{cv}'s are the off-diagonal Langrarge multipliers given by

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

If one defines the core projector and the pseudo orbital in the same way as done in the Phillips-Kleinman method, for relativistic spinor wave functions one obtains relativistic pseudo orbitals and relativistic effective potentials which are given by

$$\chi_v^R = \psi_v^R + \sum_c a_c \psi_c^R , \quad \psi_v^R = (1-P)\chi_v^R, \quad P = \sum_c |\psi_c\rangle\langle\psi_c|$$

$$V^{RPK} = - PH_v^{rel} - H_v^{rel} P + PH_v^{rel} P + \varepsilon_v P,$$

where

$$(H_v^{Rel} + V^{RPk}) \chi_v^R = \varepsilon_v \chi_v^R$$

$$(h_D + U^{core}) \chi_v^R = \varepsilon_v \chi_v, \text{ if } U^{core} = \sum_c (J_c - K_c) + V^{RGPK}$$

The relativistic effective potentials thus formulated involve 4-component spinor projectors. As mentioned earlier the effect of small components in the valence regions is rather small and one can neglect the small components in considering chemical and spectroscopic properties. Alternatively one can make the Foldy-Wouthuysen transformation[19] to eliminate the small components and obtain a correction to the large comonent; for valence spinors this correction is so small that it can be neglected. Thus one can use the nonrelativistic kinetic energy operator along with the relativistic large components in an equation from which valence-level, relativistic core potentials are generated. Thus, for a single valence electron

$$(- \frac{1}{2} \nabla^2 - \frac{z}{r} + U^{EP}) \chi_v' = \varepsilon_v \chi_v'$$

where χ'_v is a two-component pseudowavefunction containing only the large radial components.

With more than one valence electron, this equation becomes

$$[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + U^{EP} + W(\chi'_v, \chi'_{v'})]\ \chi'_v = \varepsilon_v \chi'_v$$

where $W(\chi'_v, \chi'_{v'})$ is the sum of Coulomb and exchange interactions of a given pseudo-orbital χ'_v with all other valence pseudo-orbitals $\chi'_{v'}$.

The effective core potentials U_v^{EP} are not the same for pseudo-orbitals of different symmetry. Thus one can express the REP's as products of angular projectors and radial functions. In the Dirac-Fock approximation, the orbitals with different total j but which have the same ℓ value are not degenerate, and thus, the potentials derived from the Dirac-Fock calculations would be j-dependent. The REP's can thus be expressed by introducing the ℓj-dependent radial potentials $U_{\ell j}^{REP}$, as

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

where $|\ell jm\rangle$'s are Pauli 2-component spinors.

The expression for the relativistic effective potentials involves an infinite sum over ℓ. This requires calculations of the radial potentials for all the excited states of the atom, which is impractical. However, the radial functions $U_{\ell j}^{REP}$ cease to change significantly with ℓ and j after these numbers exceed those of electrons in the core. Consequently, it is a good approximation to stop at a maximum ℓ and j values denoted by L and J, respectively. The modified relativistic effective potential can be written as

$$U^{REP} = U^{REP}_{LJ}(r) + \sum_{\ell=0}^{L-1} \sum_{j=|\ell-1/2|}^{\ell+1/2} \sum_{m=-j}^{j} [U^{REP}_{\ell j} - U^{REP}_{LJ}] \cdot |\ell jm\rangle\langle\ell jm|.$$

One can test alternate values by a series of actual calculations. It is our experience that L should be at least one higher than the maximum ℓ value in the core. Thus for example, desirable minimal values of L for Sn and Pb are 3 and 4, respectively.

Pitzer and coworkers[15,52-55] have carried out relativistic calculations on a number of diatomics such as Xe_2, Xe_2^+, TlH, Au_2, Au_2^+, PbS, $PbSe^+$, etc. These calculations were carried out with LCAS-MS (linear combination of atomic spinor-molecular spinor) approach with the relativistic effective potentials. Many of these calculations were at the level of single configuration SCF. In the earlier calculations, the spin-orbit coupling was ignored at the SCF stage and introduced using a semiempirical procedure.

These early calcuations used effective potentials obtained by the Phillips-Kleinman method[50] (see the review of Krauss and Stevens[12]) wherein the pseudo-orbitals are taken to be linear combinations of the atomic orbitals of the same ℓ and j. This method tends to underestimate the repulsive region of the potential energy curves. There is no reason that the pseudo-orbital must be linear combinations of core and valence orbitals. Christiansen, Lee and Pitzer[56] have proposed a method for constructing pseudo-orbitals in which the pseudo orbital is represented as

$$P^{PS}_{\ell} = \begin{cases} r \sum_{i}^{N} C_i r^i, & \text{for } r \le r_m \\ \phi_{\ell}(r), & \text{for } r \ge r_m , \end{cases}$$

where r_m is a match radius, and ϕ_ℓ is the all-electron Dirac-Fock orbital. In this method the coefficients C_is are determined by matching the value and the first three derivatives of the P_ℓ and ϕ_ℓ at r_m with the condition that P_ℓ is

normalized. The match radius is minimized subject to the condition that P_ℓ can have only one maximum and two inflection points. Pseudo orbitals derived this way are called shape-consistent because the resulting pseudo-orbital is identical to the Hartree-Fock (Dirac-Fock) orbital in the valence region. In Fig. 2, we reproduce a comparison of this pseudo-orbital and the corresponding orbital obtained using the Phillips-Kleinman method for the chlorine atom as done by Christiansen, Lee and Pitzer (CLP).[56] As one can see from that figure the maximum of the Phillips-Kleinman orbital is at smaller radius than the all-electron orbital or that of the CLP orbital.

The relativistic effective potentials obtained with the methods described above are numerical potentials. However, for polyatomic calculations a gaussian analytic fit of such potentials is more desirable since multicentered integrals over gaussians can be obtained easily. Kahn, Baybutt and Trulhar[57] have suggested the following gaussian expansion of numerical potentials.

$$U_{LJ}^{REP}(r) - U_{\ell j}^{REP}(r) = \frac{1}{r^2} \sum_{i=0}^{N} C_i \, r^{ni} \exp(-\alpha_i r^2)$$

where C_i's, n_i's, and α_i's are chosen so as to obtain the best fit for the numerical potentials.

The relativistic effective potentials can be averaged with respect to spin. The averaged relativistic effective potentials can be written as

$$U_{(r)}^{AREP} = U_L^{AREP}(r) + \sum_{\ell=0}^{L} \sum_{m=-\ell}^{\ell} [U_\ell^{AREP}(r) - U_L^{AREP}(r)] \, |\ell m\rangle\langle \ell m|,$$

where

$$U_{\ell}^{AREP} = \frac{1}{2\ell+1} [\ell\ U_{\ell,\ell-1/2}^{REP}(r) + (\ell+1)\ U_{\ell,\ell+1/2}^{REP}(r)]$$

The resulting potentials involve the ordinary spherical harmonic projector as opposed to 2-component spinor projectors. These potentials include all relativistic effects except the spin-orbit interaction. These potentials resemble non-relativistic effective potentials in their form and can thus be introduced into non-relativistic SCF or MCSCF calculations. Schwarz and coworkers[58] and Ermler et al.[59] have suggested that the spin-orbit operator can be obtained as the difference of different j but same ℓ. The resulting spin-orbit operator is simply the difference of $\ell+1/2$ and $\ell-1/2$ relativistic effective potentials. The spin orbit operator thus derived can be written as

$$H^{SO} = \sum_{\ell=1}^{L-1} \Delta U_{\ell}^{REP}(r) \left\{ \frac{\ell}{2\ell+1} \sum_{-\ell-1/2}^{\ell+1/2} |\ell,\ell+1/2,m\rangle \times \langle\ell,\ell+1/2,m| \right.$$

$$\left. - \frac{\ell+1}{2\ell+1} \sum_{-\ell-1/2}^{\ell-1/2} |\ell,\ell-1/2,m\rangle\langle\ell,\ell-1/2,m| \right\},$$

$$\Delta U_{\ell}^{REP}(r) = U_{\ell,\ell+1/2}^{REP}(r) - U_{\ell,\ell-1/2}^{REP}(r)$$

The spin-orbit operator derived this way can be ab initio in that if it is derived from relativistic ab initio potentials. It can be introduced in molecular calculations. Pacios and Christiansen[60] have published gaussian analytical fits of averaged relativistic effective potentials and spin-orbit operators for Li through Ar. The relativistic potentials of other elements

are also being tabulated.[61]

The relativistic effective potentials derived from the numerical Dirac-Fock wave functions have been employed in a number of quantum calculations with considerable success. We will review a number of such calculations and results in the next section. We now consider other methods of generating relativistic effective potentials.

Hay, Wadt and coworkers[20-24,62,63] derive relativistic effective potentials from the Pauli hamiltonians after omitting the spin-orbti term. Cowan and Griffin have suggested a procedure for the inclusion of the mass-velocity and Darwin terms of the Pauli hamiltonian into a variational SCF calculation. Since Hay and Wadt do not include spin-orbit interaction in their effective potentials, these potentials are analogous to spin-averaged relativistic potentials. Hay and Wadt[22-24] have published recently gaussian fits of relativistic effective potentials without spin-orbit interaction for all the elements in the periodic table. Also, included in these papers are the optimized gaussian basis sets of these elements for polyatomic calculations. The results of the Hay-Wadt potentials compare reasonably well with the averaged relativistic effective potentials derived from the Dirac-Fock calculations. However, these potentials do not provide for an ab initio spin-orbit operator which can be introduced variationally either in a MCSCF or a CI scheme. The spin-orbit interaction is introduced in the final step as a perturbation using the semiempirical method.[21]

Schwarz and coworkers[58,64-65] have developed a relativistic model potential method. In this method the relativistic effective potential is expressed as follows:

$$V_{rel}^{eff} = V_{rel} + \sum_{\ell,j,m_j}^{core} |\ell j m_j > V_{\ell j}(r) <\ell j m_j|,$$

where $V_{rel}(r)$ and $V_{\ell j}(r)$ are parametrized as

$$V_{rel}(r) = \frac{-Zeff + A\exp(\alpha r)}{r},$$

$$V_{\ell j}(r) = B_{\ell j} \exp(-\beta_{\ell j} r),$$

where Zeff is the effective charge of the atomic core. The parameters α, $\beta_{\ell j}$, A, $B_{\ell j}$, are obtained so that the effective hamiltonian reproduces valence-electron spectrum of the alkali-like systems. The resulting effective potentials are spin-dependent and they include spin-orbit interaction. Schawarz and coworkers[65] have developed a complex two and four-index transformation over two-component spinors which enable introduction of these potentials in MCSCF or CI calculations. These authors[66-70] have applied the relativistic model potential method to a number of molecules containing heavy atoms. More recently, Mark, Marian and Schwarz[71] have considered the use of relativistic Dirac-Breit approach to estimate the fine structure splittings of F_2 and F_2^+. Schwarz and Chu[72] have considered relativistic contributions to ionization energies and bond lengths with semiempirical as well as ab initio Dirac Fock calculations. Esser[73] has recently developed a relativistic MRCI method for many electron wave functions. He has presented the unitary group formalism and applications to heavy atoms such as Pb, Hg, etc.

We now briefly review a number of methods of relativistic calculations using effective potentials. As mentioned earlier Pitzer and coworkers carried out their earlier relativistic calculations using a single configuration SCF spinor scheme.[52-55] Christiansen and Pitzer[74] introduced REPs in MCSCF-LCAS-MS spinor calculations. These calculations were carried out by a modification of the BISON-MCSCF code to accomodate relativistic two-component spinors. The

first calculation along these lines was carried out on the ground state of the TlH molecule.[74] This MCSCF calculation included 5 spinor configurations. Christiansen and Pitzer[75-78] have carried out such MCSCF calculations on $T\ell_2$, $T\ell_2^+$[75] and polarizabilities of the Rb and Cs atoms.[76] Other calculations which compare effective potential and all-electron methods have also been carried out.[79,80] This MCSCF-spinor scheme is restricted in that it could accomodate only 10 configurations. This was, however, adequate for the ground state properties of molecules such as TlH. Christensen and Pitzer[74] obtained 80% of the experimental dissociation energy using this method.

While the MCSCF spinor approach with up to 10 configurations provides a reasonable picture of bonding for some of the molecules such as TlH, for other molecules like Pb_2, this approach is far from adequate. This is a result of large mixing of configurations arising from both correlation and spin-orbit interaction. Thus an approach which can accomodate a large number of configurations is more desirable. Further, the method should enable calculations of several excited states. Christiansen, Balasubramanian and Pitzer[81] have developed a relativistic configuration interaction method. In this method the relativistic effective potentials are averaged with respect to the spin at the SCF stage. Thus at this stage relativistic effects such as mass-velocity correction, Darwin correction, etc., are included, but, the spin-orbit interaction is not introduced at this stage. However, this spin-orbit operator is obtained as the difference of $\ell+1/2$ and $\ell-1/2$ potentials as described earlier. The spin-orbit integrals over MO's with this SO operator obtained this way are introduced as one-electron integrals at the CI stage. The spin-orbit integrals over real cartesian basis sets can be imaginary and thus, the introduction of these integrals at the SCF or MCSCF stage would lead to a complex Fock operator. Although the CI integrals are imaginary, the CI

matrices are diagonalized only once. This procedure could be called relativistic CI method or SOCI method. This provides for a method of introducing spin-orbit interaction variationally rather than the conventional perturbative scheme. Further, this method allows for mixing of configurations which would not mix in the absence of spin-orbit interaction. The method has been tested on a number of diatomics in the past few years. These results will be reviewed in the next section. R. Pitzer and Winter[82] are considering relativistic CI calculations of UF_6, NpF_6 and PuF_6 with this method.

4. Applications to molecules containing heavy atoms

In this section we consider applications of relativistic quantum methods to calculations of properties of molecules containing heavy atoms. In recent years a number of authors have made relativistic calculations of the electronic and spectroscopic properties of a number of molecules using the methods outlined in the earlier section. There are excellent reviews on applications of relativistic calculations to a number of molecules[7-13,42,83-84]. While we review some of these calculations for completeness, additional details on these calculations can be found in these reviews. In the present chapter we review more recent developments in this area. We will divide molecules into several categories and discuss the calculations in each category. Sections 4A and 4B consider homonuclear and hetero diatomics, respectively, while Section 4C considers polyatomics and miscellaneous applications. The heteronuclear diatomics that we consider here include hydrides, halides, and oxides.

A. Homonuclear diatomics containing very heavy atoms

One of the first relativistic calculations on very heavy diatomics were carried out by Pitzer and coworkers[53] on the ground state of Au_2. For this molecule, the spin-orbit contribution is small in comparison to other relativistic contributions such as mass velocity and Darwin corrections. The Au_2 molecule exhibits primarily σ_s bonding arising from the overlap of s orbitals. An important result of this calculation is that the Au_2 bond is stronger than Ag_2 bond as a result of the relativistic contraction of the s orbital. Ermler, Lee and Pitzer[55] carried out calculations of several excited states of Au_2. For the excited states the spin-orbit interaction plays a more important role; it was introduced by a semiempirical procedure. These calculations employ the Phillips-Kleinman potentials which tend to underestimate the repulsive region of the potential energy curves, thus predicting short bond lengths. Zeigler et al.[85] have carried out Hartree-Fock-Slater calculations of Au_2 as well as other heteronuclear diatomics containing Au and Ag. Ross and Ermler[86] have recently reported calculations on Ag_2, Au_2, and other Ag, Au-containing molecules. They have carried out SCF, MCSCF and CI calculations on these molecules with the revised Christiansen-Lee-Pitzer potentials. These calculations have shown that the relativistic bond contractions for Au_2 and Ag_2 are about 0.2 Å and .05 Å, respectively. These calculations employ a triple-zeta s, double-zeta p and double-zeta d basis, but the f functions which seem to play a significant role for these systems are not included. Further, core-valence correlations which were not included, may be important for these systems. As a result of these approximations their calculated dissociation energies with MCSCF and CI schemes are 1.00 eV and 1.47 eV, for Ag_2 and Au_2, respectively, in comparison to the experimental value of 2.08 eV for Au_2. McLean[87] has also carried out

non-relativistic all-electron calculations for Ag_2.

Christiansen and Pitzer[75] carried out MCSCF calculations on $T\ell_2$ and $T\ell_2^+$ in ω-ω coupling scheme. They carried out calculations on 3 low-lying ω-ω states and 3 λ-s states. These calculations revealed that the ground state of $T\ell_2$, is the 0_u^- state and is essentially repulsive with only a shallow minimum at long distance. The 0_g^+ and 1_u states are slightly higher in energy. The $T\ell_2^+$, ion, however, has a 1/2g state which is bound by 0.58 eV at this level of calculations. Christiansen[88] carried out relativistic configuration interaction calculations on $T\ell_2$ with the method described in reference 81. These extensive calculations also produced only weak binding for the ground state of $T\ell_2$. Christiansen[88] also recalculated the experimental dissociation energy by correcting the partition function of $T\ell_2$. The revised experimental D_e for $T\ell_2$ is about 0.37 eV (±0.15). Pitzer[83] has reviewed the earlier calculations on $T\ell_2$ and Au_2.

The Pb_2 and Sn_2 molecules are considerably more complex than Au_2 and $T\ell_2$ in that even the atom needs to be treated in an intermediate coupling scheme. Both correlation and spin-orbit contributions are large for these systems, but the spin-orbit contribution for Pb_2 is much larger than for Sn_2. Balasubramanian and Pitzer[4,89] have carried out relativistic CI calculations on Pb_2 and Sn_2. Results of our calculations on Pb_2 and Sn_2 are shown in figures 3-6. Our calculations enabled interpretation of experimentally observed laser-induced fluorescence spectra of Pb_2[90-91]. The experimentally observed X, A, and C states were assigned to 0_g^+, 1_g, and 0_u^+ states. The B state was reassigned to the 0_u^- state. The ground 0_g^+ and low-lying 1_g state are type c analogues of $^3\Sigma_g^-$ $(\sigma_g^2\pi_u^2)$. However, the assignment of any state of Pb_2 to any particular spin-orbit component of a λ-s state has limited meaning because of large spin-orbit contamination of several λ-s

states. In fig. 7 we show the fractional CI populations of various λ-s states as a function of internuclear distances for the 0_g^+ ground state. As one can see from these figures, λ-s populations in Pb_2 change dramatically as a function of internuclear distance. It is further interesting to note that at a short distance, the 0_g^+ states of both Pb_2 and Sn_2 exhibit an avoided crossing resulting from π_u^4 (0_g^+) with $\sigma_g^2\pi_u^2$ $(0_g^+, 1_g)$ configurations. This results in a shoulder in the 0_g^+ curve at short distance. The Sn_2 is described reasonably well in λ-s coupling. As one can see from figure 7, the spin-orbit contamination for Sn_2 is rather small and thus the ground state is $^3\Sigma_g^-$ (0_g^{+-}). The J = 0 state of the Pb atom is 88% (^3P_o) and 12% (^1S_o). Similarly, the J = 2 state of Pb atom is 70% ($^3P_2$) and 30% ($^1D_2$). The corresponding percentages for the J = 0 and J = 2 states of Sn are 97% (^3P_o), 3% (^1S_o) and 97% ($^3P_2$) and 3% ($^1D_2$). Thus correlation is more important for Sn than spin-orbit interaction, while both correlation and spin-orbit interaction are important for the Pb compounds. For the Pb_2 dimer the spin-orbit interaction destabilizes the bond by almost 50%. The calculated D_e values for Pb_2 and Sn_2 (0.88 eV and 1.86 eV) are in good agreement with the experimental values[92-94] (0.88 eV and 1.94 eV). After the completion of these calculations, an experimental value of R_e for the ground state of Pb_2 was reported by Sontag and Weber.[96] The calculated value of R_e = 2.97 Å agrees very closely with the subsequent experimental value of 2.930 Å.

Pacchioni[96] has recently carried out calculations on the low-lying states of Sn_2 and Pb_2. This author gives the impression that he is the first to carry out a comparative ab initio CI calculation on these systems. We would like to clarify this further. First, his calculation starts with the Hafner-Schwarz model potentials in comparison to our relativistic ab initio potentials derived from numerical Dirac-Fock solutions of the atoms.

Pacchioni's calculations ignore spin-orbit interaction. Our calculations include spin-orbit interaction in a relativistic CI scheme in comparison to the non-relativistic CI of Pacchioni. Thus, he obtains a D_e approximately twice the experimental value which he corrects by a semiempirical scheme to arrive at a value close to our calculated value with a relativistic CI. Our calculations have clearly demonstrated the need to carry out an intermediate coupling CI calculation for Pb_2 as a result of large spin-orbit contamination. Calculations without spin-orbit, such as Pacchioni's have little relationship to the real Pb_2 molecule.

Christiansen[97] has recently carried out relativistic CI calculations on the ground state of Bi_2. His calculations have shown that although the ground state of Bi_2 is dominantly $^1\Sigma_g^+$ (arising from the $\sigma_g^2\pi_u^4$ triple bonding configuration), it is significantly contaminated by $^3\Pi_g$ (about 25%). The calculated D_e value of Bi_2 (2.3 eV) is in reasonable agreement with the experimental value of 2.04 eV. The computed R_e value is about 0.16 bohr longer than the experimental value. This seems to be the general trend in a limited relativistic CI scheme which is adequate to describe other properties but somewhat less accurate in calculating bond distances and dissociation energies. It is believed that this discrepancy in calculated bond distances arises from the d-correlation. More extensive calculations are warranted to confirm the origin of calculated longer bond lengths.

Celestino and Ermler[98] have carried out calculations on Hg_2 and TℓHg. Calculations on Hg_2 were carried out with a full 4-electron CI within 16 of the 22 valence and virtual orbitals. The spin-orbit interaction is ignored at the CI stage but introduced after CI using a semiempirical scheme. For the TℓHg molecule, CI calculations included full correlation of 5 outer electrons with some restrictions. These authors have carried out calculations on a

large number of low-lying states.

Stevens, Basch, and Krauss[99] have carried out calculations on a number of light diatomics such as P_2 and Cl_2 among other molecules like SiO, CH_4, etc., to test the reliability of effective potentials. They have also generated ab initio effective potentials and compatible basis sets for the first and second row atoms.[99] Other calculations on homonuclear diatomics which use relativistic methods include Cu_2[100], and I_2[101]. Relativistic ab initio calculations have been carried out on noble gas dimers and ions such as Xe_2^+, Xe_2, etc.[80,102-105].

B. Heteronuclear diatomics containing very heavy atoms

Among the heteronuclear diatomics containing heavy atoms, a number of hydrides have been studied. Desclaux and Pyykko have studied a number of hydrides using the one-center numerical Dirac-Fock method.[27,106-109] These calculations provide an insight into the magnitude of relativistic effects on the bond lengths; however they are not useful for dissociation energies as they break down at long distances.

Hay et al.[110] have carried out effective potential calculations on AuH which yield the relativistic bond contraction of 0.26Å. The dissociation energy of AuH is increased by 0.5 eV as a result of relativistic contributions. They also presented calculations for AuCl, HgH and $HgCl_2$. Zeigler, Snijders and Baerends[85] have carried out perturbational relativistic calculations on a number of heteronuclear diatomics such as HgH^+, CdH^+, ZnH^+, AuH, AgH, CuH, CsH.

Lee and McLean[34,35] have carried out all-electron Dirac-four component spinor LCAS-MS-SCF calculations on AgH and AuH. The relativistic effects increase the dissociation energies by 0.08 eV and 0.42 eV in these molecules,

while the bond lengths contract by 0.08 Å and 0.25 Å these values for AuH confirm the earlier effective potential calculations[110].

Lee, Ermler and Pitzer[55] have carried out SCF calculations in ω-ω coupling on TlH, PbSe and PbS among other diatomics. Christiansen and Pitzer carried out MCSCF LCAS-MS spinor calculations on TlH.[74]

Christiansen, Balasubramanian and Pitzer[81] have carried out relativistic configuration interaction calculations on the six low-lying states of TlH. In these calculations, spin-orbit interaction is introduced at the CI stage with the spin-orbit operator derived as a difference of ℓ+1/2 and ℓ-1/2 relativistic effective potentials. The properties of the two lowest 0^+ states are in very good agreement with the experimental results. In addition, these calculations yielded shallow minima in certain excited states of TlH in agreement with provisional interpretation of spectra. The calculated equilibrium bond length (1.99 Å) is somewhat longer than the experimental value of 1.87 Å. This discrepancy was in part attributed to the lack of d correlation. However, this is yet to be confirmed. The calculated dissociation energy (1.81 eV) is in reasonable agreement with the experimental value of 1.97 eV.

Balasubramanian and Pitzer[111,112] also made relativistic CI calculations on a number of low-lying states of PbH and SnH which enabled interpretation of the electronic spectra of these molecules. The low-lying electronic states of PbH (3/2 (II),5/2) exhibit interesting avoided crossings. The 3/2(II) state is $^4\Sigma^-_{3/2}$ at short distances, but at long distances it becomes a mixture of $^2\Pi_{3/2}$, $^2\Delta_{3/2}$ and other λ-s states. The 5/2 state is $^2\Delta_{5/2}$ at short distances, but it becomes $^4\Pi_{5/2}$ at very long distances.

Balasubramanian[113] has recently reported relativistic CI calculations on four low-lying ω-ω states of BiH arising from the $\sigma^2\pi^2$ electronic configuration. These calculations enabled the assignment of the $X(0^+)$, A(1) and $B(0^+)$ states which were observed experimentally. The potential energy curve of the 2 state exhibits a barrier resulting from the avoided crossing of $^1\Delta_2$ with $^5\Sigma_2^-$. The experimental D_e value of this molecule is uncertain since it is estimated from the predissociation of the $E(0^+)$ state into $^2D_{3/2}$ + $^2S_{1/2}$ atoms. In another investigation more extensive relativistic CI calculations have been carried out[114] on 10 low-lying ω-ω states of BiH (0^+, 1, 2, 0^+(II), 1(II), 2(II), 0^-, 0^+(III), 3, 0^+(IV)). Potential energy curves of the excited states of this molecule exhibit very interesting properties such as shoulders, barriers, etc. Fig. 8 shows the potential energy curves of some of the low-lying states of BiH. In fig. 9 we show the relativistic CI population of the 0^+(IV) ($E0^+$) state of BiH. As one can see from fig. 9, this state exhibits a number of avoided crossings. The spin-orbit contaminations of these states are quite large. In another investigation Balasubramanian[115] has carried out relativistic CI calculations of 8 low-lying states of BiH^+ (1/2, 3/2, 1/2(II), 1/2(III), 3/2(II), 3/2(III), 5/2, and 5/2(II). The ionization potential of BiH^+ was calculated to be 8.08 eV. The exctied states of BiH^+ show interesting relativistic avoided crossings. The calculated D_e of BiH^+ is about 1.05 eV in comparison to the neutral molecule whose D_e value is about 2.2 eV. Since the π orbital of BiH is essentially non-bonding one might expect the D_e values of BiH and BiH^+ to be about the same. However, at the dissociation limits, the spin-orbit stabilization of the $^4S_{3/2}$ of the neutral atom is substantially smaller than that of the $^3P_0$ state of the ion. The ground state of the Bi neutral atom ($^4S_{3/2}$) cannot be split but is lowered by 0.03266 hartree-atomic

units when the spin-orbit operator is included. The ground state of Bi^+ ($^3P_0$) is stabilized by 0.0859 atomic units in comparison to ^3P without the spin-orbit term. The D_e values of BiH and BiH^+ obtained without spin-orbit interaction are 2.06 eV and 2.17 eV, respectively. Thus the D_e value of BiH^+ is lowered considerably by spin-orbit interaction.

Chapman, Balasubramanian and Lin[116] have carried out relativistic CI calculations on the six low-lying states of HI. These calculations enabled the assignment of absorption continua near 46,000 cm^{-1}, 23,000 cm^{-1} as well as bands which extend from 55,000 cm^{-1}. Calculations of a number of low-lying states of HBr (0^+, 0^+(II), 0^+(III), 1, 1(II), 0^-, 0^-(II), 2, 2(II), 0^-(III)) have just been completed.[117] These calculations were carried out with an extended triple zeta basis set since the 0^+(III) and 2(II) states dissociate into Rydberg atoms. These calculations have not only enabled the assignment of experimentally observed bands but also predicted several new transitions which are yet to be observed.

Wang and Pitzer[118] have carried out relativistic CI calculations on the five low-lying states of PtH as well as PtH^+. The calculated dissociation energy is about 2.45 eV in comparison to the experimental value of 3.44 eV. There are three states of nearly equal energy. In each case there is a sigma bond and a single vacancy in the 5d shell of Pt. The calculations indicate the $^2\Delta_{5/2}$ state to be lowest with the $^2\Sigma_{1/2}$ higher by 1008 cm^{-1} and the $^2(\Pi + \Delta)_{3/2}$ above $^2\Delta_{5/2}$ by 2742 cm^{-1}. But these differences are so small that further refinement of the calculations might change the order. All three states are known experimentally,[119] but the present measurements leave many uncertainties. A tentative value of 1300 cm^{-1} has been given for T_e of the 3/2 state with the 5/2 state at zero.

Balasubramanian and Pitzer[120,121] have carried out relativistic CI calculations on eleven low-lying states of PbO and SnO with the objective of interpreting chemiluminescent spectra resulting from Pb + O_3, Sn + N_2O and other reactions. These calcualtions enabled the assignement of a number of experimentally observed bands. Calculations of low-lying states of isoelectronic PbS and SnS have also been carried out.[122] Balasubramanian[123] reported relativistic CI calculations on the low-lying states of PbO^+, SnO^+, PbS^+, and $PbSe^+$. These calculations confirmed the breakdown of Koopman's theorem for SnO and PbO which had previously been noted by Dyke et al.[124] For SnO and PbO, Koopman's theorem predicts the $^2\Sigma^+$ state to be the ground state, while the actual ground state of these molecules is $^2\Pi_{3/2}$. Actually, at very short distances the $^2\Sigma^+$ state is lower than the $^2\Pi$ state. At near equilibrium geometries this ordering is reversed which results in an avoided crossing in the 1/2 state of PbO^+ and SnO^+. The breakdown of Koopman's theorem was explained based on orbital relaxation effects. However, for $PbSe^+$, it was noted that the orbital relaxation effects are not large enough to affect the ordering. Thus Koopman's theorem correctly predicts the $^2\Pi$ state to be the ground state of $PbSe^+$.

Balasubramanian[125] carried out relativistic CI calculations on the low-lying states of TlF. There is considerable experimental interest in the photoionization of vapors of relatively non-volatile materials such as the thallous halides. The thermodynamic and spectroscopic dissociation energies of this molecule do not agree, which seems to suggest the existence of barriers in the excited states. Relativistic CI calculations of the potential energy curves of 9 low-lying states of TlF arising from $^1\Sigma^+$, $^3\Pi$, $^1\Pi$, $^3\Sigma^-$, $^3\Sigma^+$, and $^3\Delta$ were carried out.[125] These calculations confirmed the existence of barriers in the excited states of TlF which arise from relativistic avoided

crossings. Calculations on a number of low-lying states of ICl and ICl^+ have also been carried out.[126,127] These calculations enabled interpretation of the electronic spectra of these molecules.

Relativistic CI calculations of the low-lying states of PbF were recently carried out.[128] The assignments of the experimentally observed A and B states were ambiguous as a result of the existence of a number of low-lying states. Relativistic CI calculations of these states enabled the assignment of A and B states to $^2\Sigma^+_{1/2}$ and $^2\Sigma^+_{1/2}$(II). The calculations of the B state, which is a Rydberg state, were carried out with an extended triple zeta basis set. The ground configuration $^2\Pi$ is split into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states with a spin-orbit splitting of about 7895 cm^{-1}. Basch and Topiol[129] have carried out calculations on AuCl and PtH in addition to $HgCl_2$.

Laskowski and Langhoff[130] have carried out calculations on CrI using averaged relativistic effective potentials. Similar calculations have been carried out on CsO[131] as well as CsH[132]. Krauss and Stevens[133,134] carried out SCF calculations on UO, UH, UF and their ions. Krauss and Stevens[135] have investigated the electronic structure of FeO and RuO using relativistic effective potentials. Relativistic configuration interaction calculations of low-lying states of BiF have been completed.[136]

C. Relativistic Calculations of Polyatomics and Miscellaneous Applications

Relativistic calculations of a number of polyatomic molecules have been carried out by both semiempirical and ab initio methods. Many of the earlier calculations have been reviewed by Pyykkö[7] as well as by Christiansen, Ermler and Pitzer[13]. The semiempirical methods include the relativistic extended Hückel method, relativistic $\chi\alpha$ method etc. Most of the ab initio calculations on polyatomics intially omit the spin-orbit interaction. This is introduced at a later stage as a perturbation or by a semiempirical scheme.

One of the very interesting earlier calculations on polyatomics was carried out by Wadt[137] on ThO_2 and UO_2^{+2} . While the UO_2^{+2} ion is linear, ThO_2 is bent. There is a greater 5f participation in UO_2^{+2} in contrast to ThO_2, and this seems to be the reason for the change in structure. Wadt notes that earlier semiempirical calculations on these molecules yielded results which do not agree with his accurate ab initio calculations.

Another interesting molecule is the cyclooctatetraene sandwich complex, $U(C_8H_8)_2$. The 5f contribution is important to the stability of uranium-containing molecules. Semi-empirical calculations have been carried out on this molecule as well as other actinocene compounds.[138],[139]. Relativistic calculations on UF_6, NpF_6 and PuF_6 have been reported.[140-144]

Case and coworkers[45],[46] have reported calculations on Pt clusters and their reactivity with CO using relativistic $\chi\alpha$ methods. Noell and Hay[145] have carried out SCF calculations on Pt complexes such as $Pt(NH_3)$ using the REP's generated from Pauli hamiltonians. Hay[146] has also studied the Pt-ethylene complex. Similar calculations have been carried out by Basch and Cohen[147] on PtCO.

Collignon and Schwarz[148] have studied the changes of molecular structures as a result of relativistic effects. They have carried out calcuations on $PbCl_2$, PbH_2, Pb_2H_4, TeH_2, PoH_2 and $^{114}EH_2$ using relativistic SCF pseudopotential method. Spin-orbit interaction changes the bond angle by less than a degree in these systems with the exception of $^{114}EH_2$ where the bond angle is increased by 2.3°.

Relativistic calculations have made an impact on biological compounds recently. Miller et al.[149] have recently investigated the binding of cis-$Pt(NH_3)_2^{+2}$ to the bases of DNA (guanine (G), cytocine (C), adenine (A) and thymine (T)). Electronic and geometrical structures of $Pt(NH_3)_2Cl_2$, $Pt(NH_3)_3X$

and $Pt(NH_3)_2XY$ (X,Y = H_2O, OH^-) have also been investigated recently by Basch, Krauss and Stevens.[150]

Pitzer and Winter[144] have developed a computer code for including the ab initio spin-orbit operator in polyatomic calculations. In this method the spin-orbit integrals are evaluated using the difference of $\ell+1/2$ and $\ell-1/2$ potentials over gaussian basis sets. The procedure is being tested on $UFUF_6$, NpF_6 and PUF_6 .

Ross, Ermler and Christiansen[151] have recently carried out ab initio EP calculations of spin-orbit coupling in the group III A and group VII A atoms. The spin-orbit splittings are computed with the operator represented as the difference of $\ell+1/2$ and $\ell-1/2$ effective potentials. Comparisons were also made with the all-electron Dirac-Fock results as well as the first order perturbation calculations. These authors have shown that the first order perturbation results could be in error by 9% in comparison to the Dirac-Fock results and that the EP spin-orbit operator yields accurate results.

Self-consistent Dirac-Slater calculations of molecules and embedded clusters have been recently reviewed by Ellis and Goodman.[152] Relativistic band structure calculations have also been carried out.[153] Dirac scattered wave calculations have been carried out on a number of inorganic complexes such as $W(CO)_6$[154] and $W_2Cl_8^{-4}$.[155] The electronic structure and geometries of X_2H_2 (X = O, S, Se and Te) have also been investigated recently.[156]

Malli[157] has investigated recently the use of Dirac-type functions (DTF) as basis sets for relativistic Dirac-Fock-Roothaan calculations for atoms. The well-known Slater-type functions with non-integral principal quantum numbers are special cases of DTF's. Recently, self-consistent relativistic Thomas-Fermi equations for heavy atomic ions have been formulated.[158] Matsuhita et al.[159] have reported ab initio spin-orbit splittings of

the ^3P ground state of the Se atom using the Pauli spin-orbit term. They obtain spin-orbit splitting as a perturbation to MRSDCI wave function. The relativistic Pauli integrals over gaussian basis sets are evaluated by the procedure proposed by Chandra and Buenker.[160,161] Similar calcuations have also been made on CBr.[162]

Balasubramanian and coworkers[163] have carried out relativistic CI calculations on the collision of Kr with Br^+. The collisions of rare gas atoms with heavy halogen ions are the topics of a number of investigations. (For a brief review of recent progress in experimental and theoretical works in this area see reference 164). Krauss, Stevens and Basch[165] have very recently carried out EP calculations on AgH and AuH. Their results are in very good agreement with all-electron Dirac-Fock calculations.

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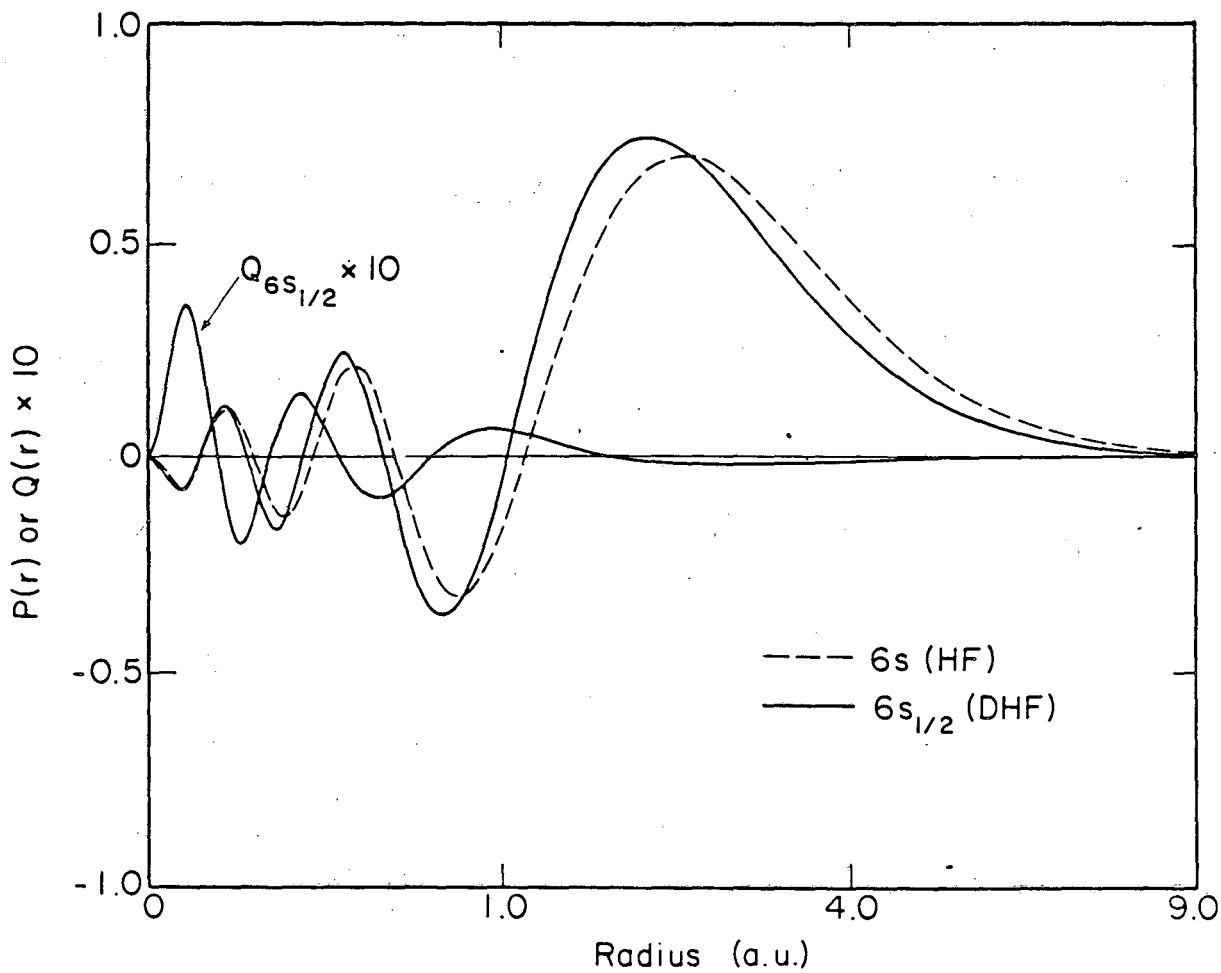

Fig. 1. Relativistic (DHF) and nonrelativistic (HF) radial components of 6s wavefunctions of Pb. Only the small component of DHF is labeled.

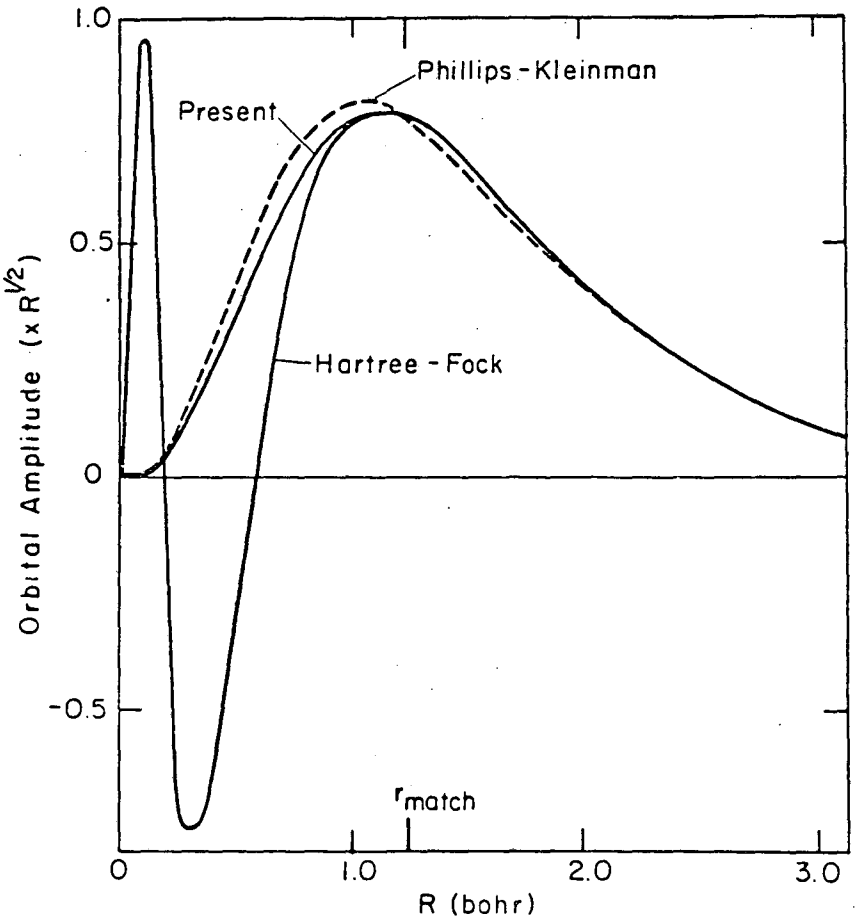

Fig. 2. A comparison of chlorine 3s pseudoorbitals generated with the Christiansen-Lee-Pitzer method and the Phillips-Kleinman pseudo-orbital and the all-electron Hartree-Fock orbital.

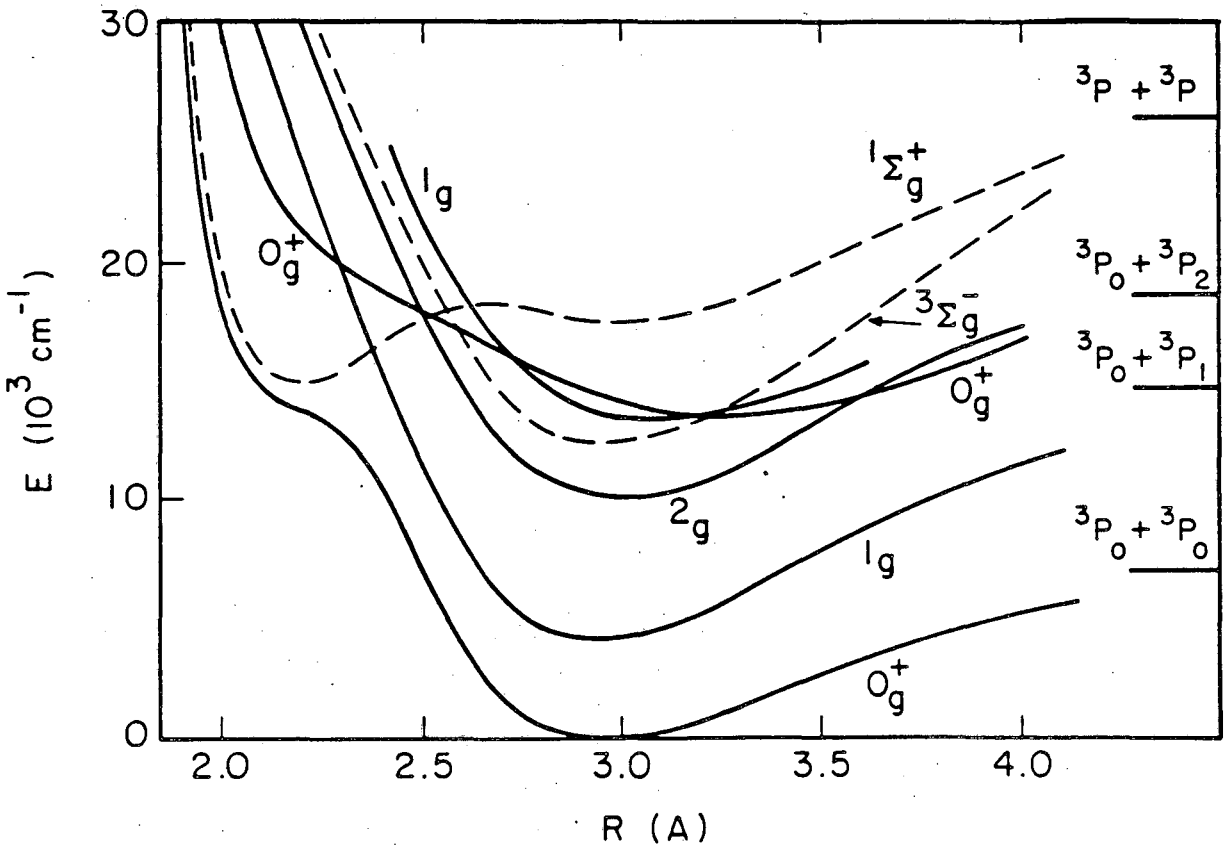

Fig. 3. Calculated potential curves for the g states of Pb_2. The dashed curves are computed without the spin-orbit term.

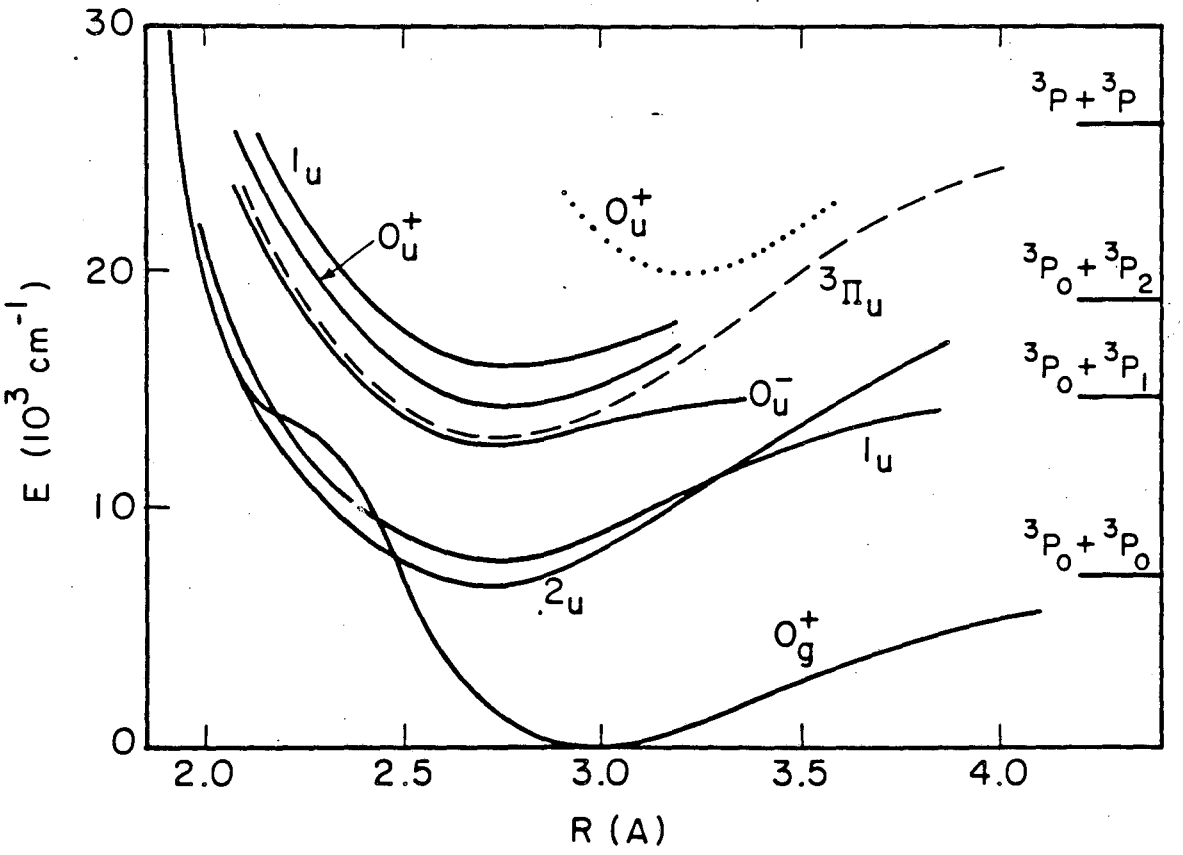

Fig. 4. Calculated potential curves for the u states and the ground 0_g^+ state of Pb_2. An estimated curve at the experimental T_e is also given for the upper 0_u^+ state.

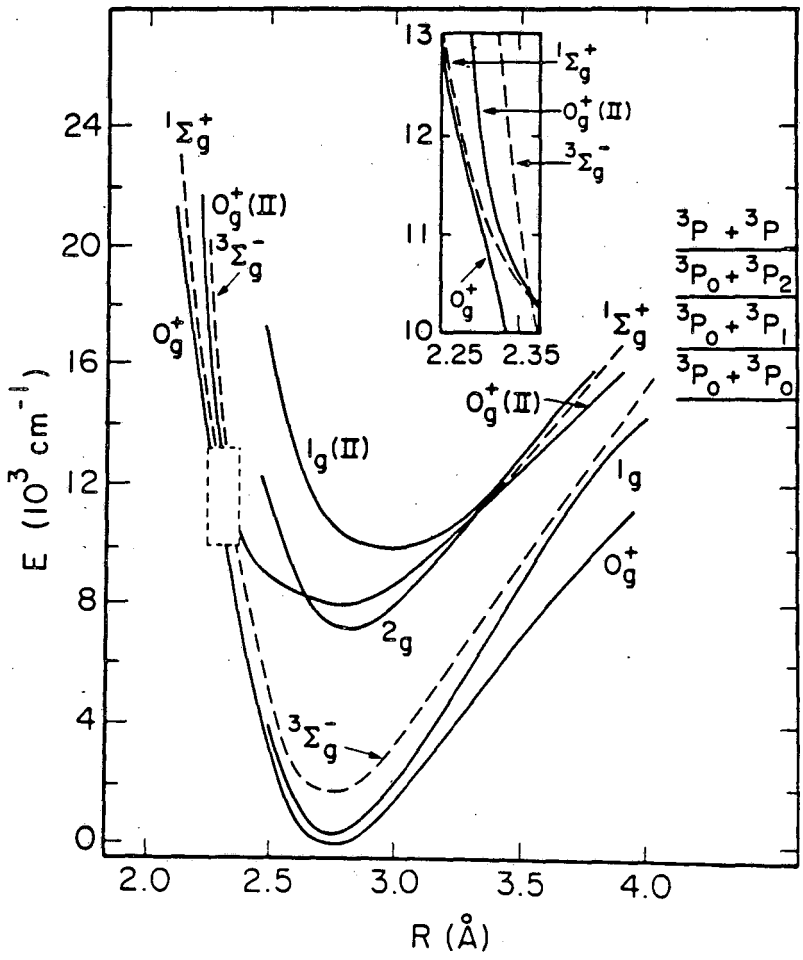

Fig. 5. Calculated potential curves for the g states of Sn_2. An inset shows the details of the avoided crossing of the two 0_g^+ curves, and the crossing of the related $^1\Sigma_g^+$ and $^3\Sigma_g^-$ curves without SO.

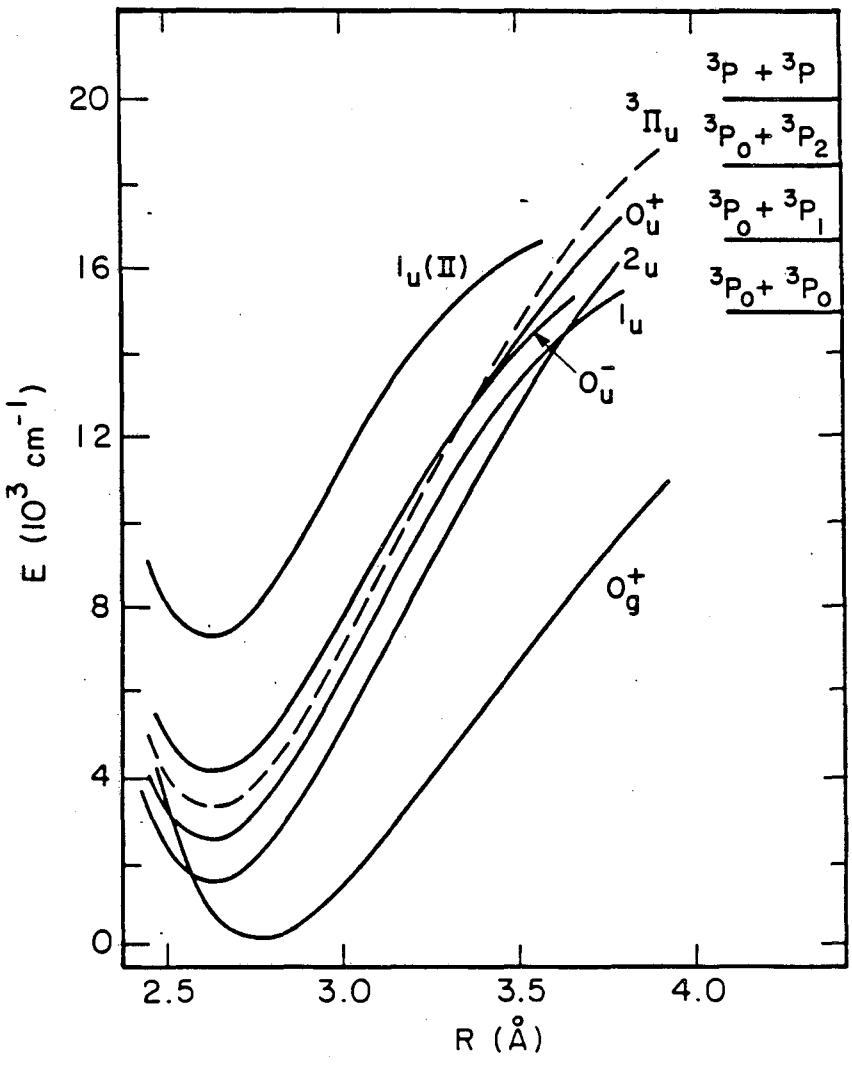

Fig. 6. Calculated potential curves for the u states and the ground 0_g^+ state of Sn_2.

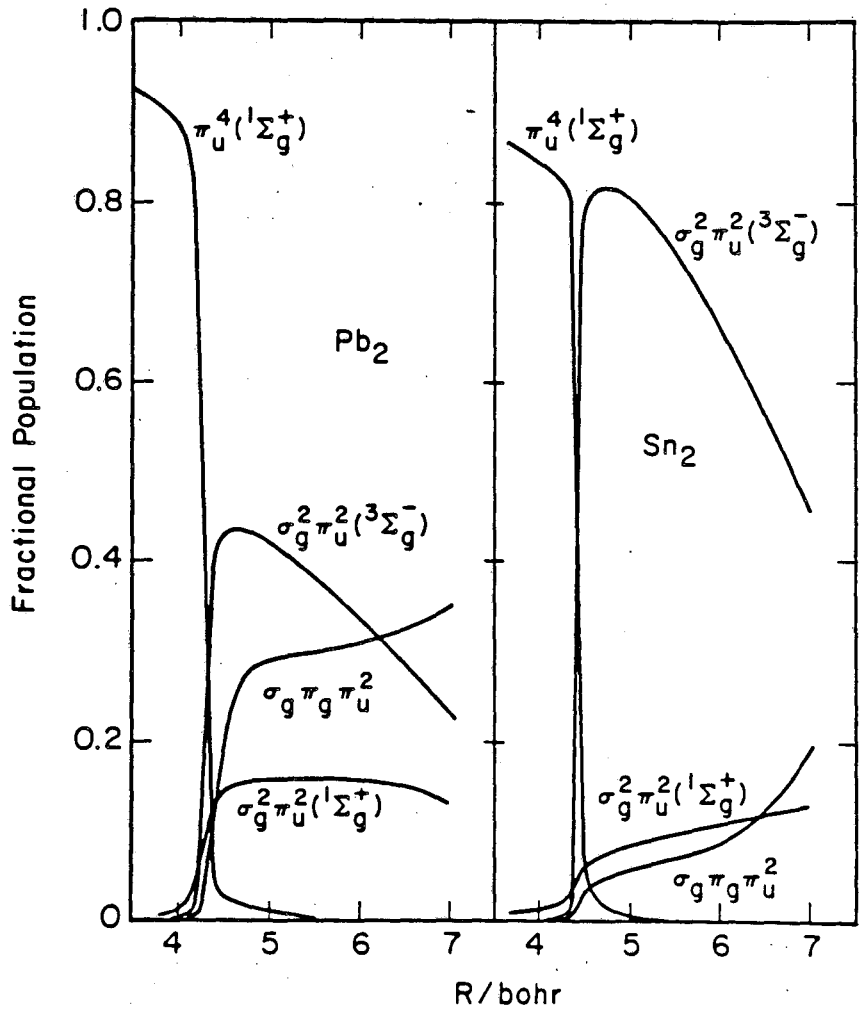

Fig. 7. Fractional populations of various Λ-S configurations for Pb_2 and Sn_2.

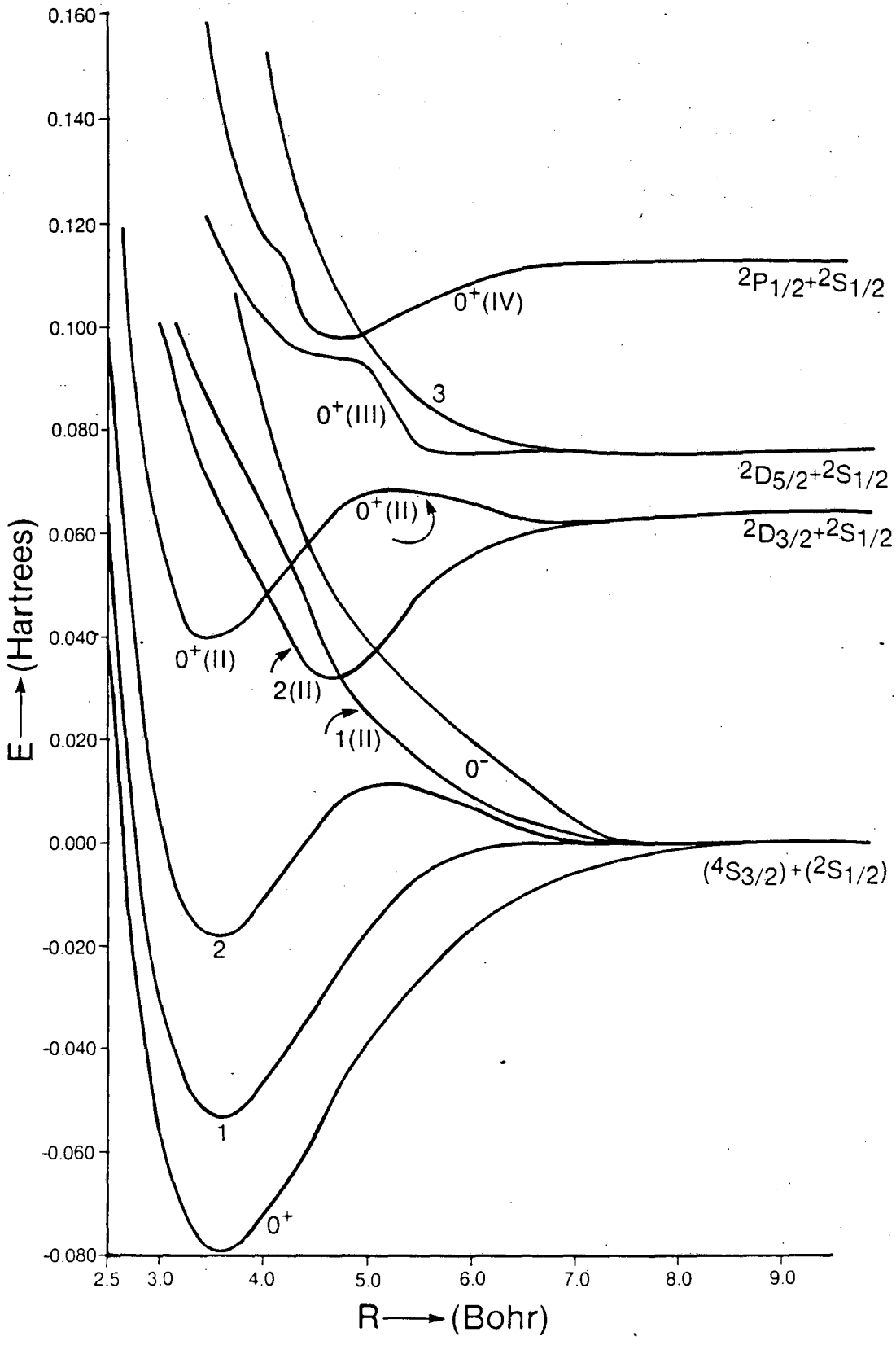

Fig. 8. Potential energy curves of 10 low-lying states of BiH.

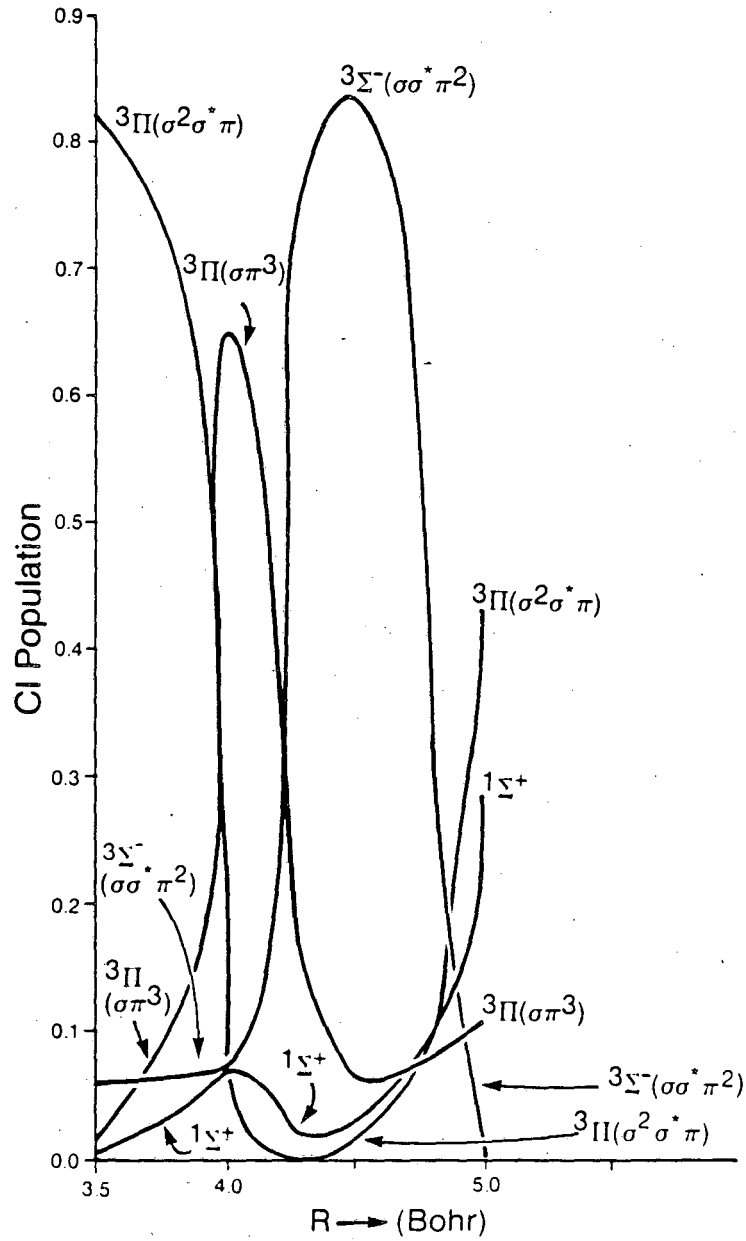

Fig. 9. CI population of the 0^+(IV) ($E0^+$) state of BiH as a function of internuclear distance.

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