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Yoon S. Lee, Walter C. Ermler, and Kenneth S. Pitzer

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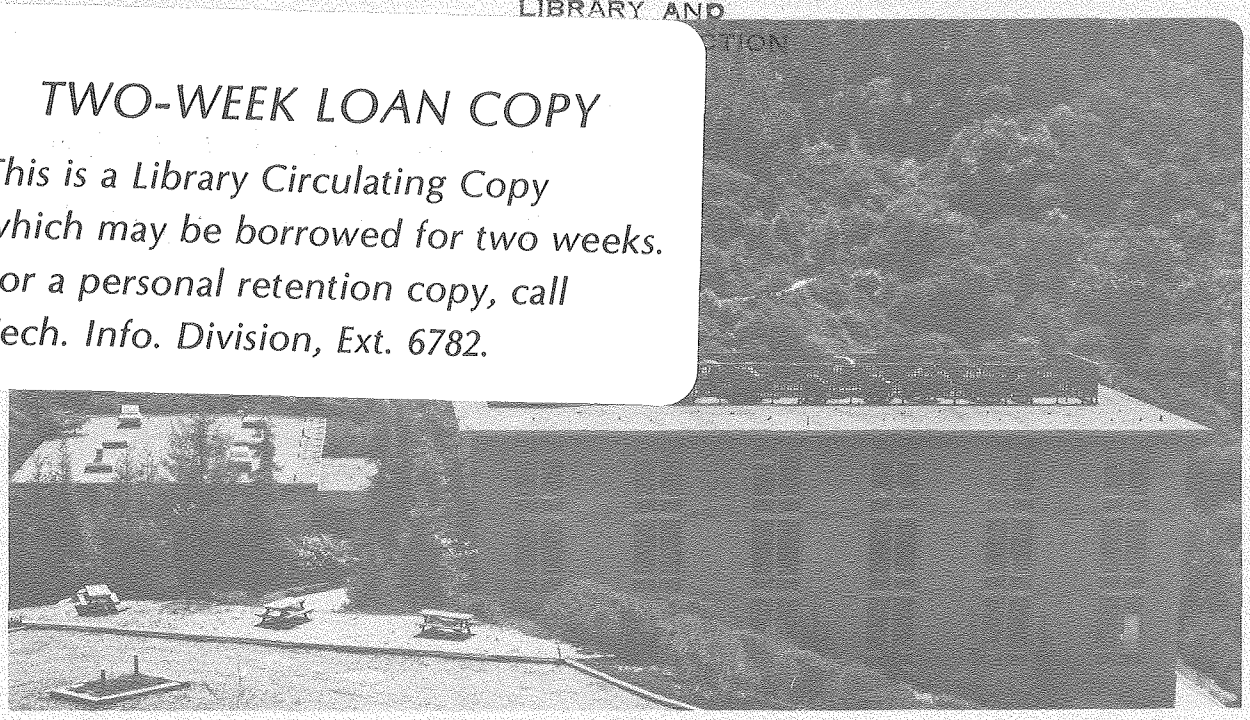

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Ab Initio Effective Core Potentials Including Relativistic Effects. V. S.C.F. Calculations with ω-ω Coupling Including Results for Au_2^+, TℓH, PbS, and PbSe

Yoon S. Lee,[a] Walter C. Ermler,[b] and Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

Abstract

Ab initio self-consistent field calculations are reported for a series of diatomic molecules using relativistic effective core potentials (REP) and basis sets appropriate for ω-ω coupling. The molecular orbitals are expressed as linear combinations of two-component analogs of Dirac spinors. The unique feature of the present approach is the retention of the spin-orbit operator in the generation of the REP's and the propagation of its effects into the molecular wavefunctions in a totally consistent fashion. The nature of bonding in the molecules Au_2^+, TℓH, PbSe, and PbS is discussed with consideration of the orbital energies, spectroscopic constants, and population analyses. Comparisons with recently obtained photoelectron spectra of PbSe and PbS are made. It is noted that the $6p_{1/2}$ and $6p_{3/2}$ orbitals of Tℓ and Pb exhibit markedly different effects in bonding to lighter atoms.

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[a]Present address: James Franck Institute
University of Chicago
Chicago, IL 60637

[b]Present address: Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Hoboken, NJ 07030

I. Introduction

In recent years, there has been increasing interest in the inclusion of relativistic effects in electronic structure calculations of molecules containing heavy atoms. The most straightforward method is the use of the Dirac one-electron operator in the calculations. However, with four-component Dirac spinors a very large number of integrals must be evaluated for all electron Dirac-Hartree-Fock calculations; hence, most methods are based on an approximation that reduces the volume of computation.

In the previous papers,[1-4] of this series we have reported a method of generating relativistic effective core potentials (REP)[1] from atomic Dirac-Hartree-Fock (DHF) calculations and their applications to the diatomic molecules Xe_2[2] and Au_2.[3,4]

In our earlier applications,[2-4] we averaged the $p_{1/2}$ and $p_{3/2}$ potentials (also $d_{3/2}$ and $d_{5/2}$, etc.) with the proper weights so that the spin-orbit splittings are removed from the potentials and standard programs based on LS coupling can be used for the molecular calculations. The use of these averaged relativistic effective core potentials (AREP) in molecular calculations is parallel to various relativistic-effective-core-potential methods developed by other workers.[5-8] These procedures differ in the stage at which the average is taken. Apart from our method, one can start from atomic calculations that have been averaged[5] or employ averaged orbitals in calculating the potentials.[6-8] All of these methods yield potentials that include most of the one-electron relativistic effects of atoms except for the spin-orbit splitting.

Since, in molecules containing heavy atoms, the spin-orbit splitting is often larger than other one-electron relativistic effects, it is theoretically more consistent to avoid this averaging and to carry out molecular calculations in ω-ω coupling. In this report we describe a method for self-consistent-field (SCF) molecular orbital calculations using the non-averaged REP defined in our earlier treatment,[1] thereby retaining the spin-orbit effects. The application of our REP in molecular calculations requires a SCF formalism that is based upon the use of two-component molecular spinors. A brief discussion of the method has been reported in an earlier paper[3] for diatomic molecules with closed-shell configurations. In this paper, we describe this SCF theory more fully and extend it to diatomic molecules having no more than one open shell of a given symmetry. Electronic structure calculations for Au_2^+, TℓH, PbS and PbSe are reported as examples of this procedure together with related calculations on the atoms Hg, Tℓ, Pb, Se, and S.

II. The LCAS-MS SCF theory with the REP and two-component molecular spinors (TCMS)

We use linear combinations of atomic spinors (LCAS) to form molecular spinors (MS). While Dirac spinors have four components, it was shown in earlier papers of this series that the small components were negligible for valence pseudoorbitals and that molecular calculations could, therefore, be based on two component molecular spinors formed from the two large components of the atomic spinors.

When the relativistic effective core potentials (REP) derived by the method described in Ref 1 are used for a diatomic molecular calculation, theHamiltonian of the system is given by [Eq (2) and Eq (3) of Ref 3]

$$\mathcal{H} = \sum_{\mu=1}^{n_v} [- \frac{1}{2}\nabla_\mu^2 + \sum_{\alpha=1}^{2} (- \frac{Z_\alpha}{r_{\alpha\mu}} + U_\alpha^{REP})] + \sum_{\mu>\nu}^{n_v} \frac{1}{r_{\mu\nu}} \tag{1}$$

where n_v is the total number of valence electrons, $r_{\mu\nu}$ is the distance between electrons μ and ν, $r_{\alpha\mu}$ is the distance between the electron μ and the nucleus α, Z_α is the charge of the nucleus α, and U_α^{REP} is the REP due to core electrons of the nucleus α. U_α^{REP} can be approximated by [Eq (4) and Eq (5) of Ref 3].

$$U_\alpha^{REP} = U_{LJ}^{REP}(r_{\alpha\mu}) + \sum_{\ell=0}^{L-1} \sum_{j=|\ell-\frac{1}{2}|}^{\ell+\frac{1}{2}} \sum_{m=-j}^{j}$$

$$[U_{\ell j}^{REP}(r_{\alpha\mu}) - U_{LJ}^{REP}(r_{\alpha\mu})] |\ell jm\rangle_\alpha \langle \ell jm|_\alpha \tag{2}$$

where L and J are, typically, the smallest angular momentum quantum numbers that are not present for the core electrons. The projection operators are defined by

$$|\ell jm\rangle\langle\ell jm| = [\sum_{\sigma=\pm\frac{1}{2}} C(\ell\tfrac{1}{2}j;\ m-\sigma,\sigma)|Y_\ell^{m-\sigma}(\theta,\phi)\phi_{1/2}^{\sigma}\rangle]$$

$$\times [\sum_{\sigma'=\pm\frac{1}{2}} C(\ell\tfrac{1}{2}j;\ m-\sigma',\sigma')\langle Y_\ell^{m-\sigma'}(\theta,\phi)\phi_{1/2}^{\sigma'}|] \tag{3}$$

with the same notation as in Ref 1. In Eq (3) the C's are Clebsch-Gordan coefficients, the Y's are spherical harmonic functions and the ϕ's are Pauli spinors with

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

The projection operators introduce two-by-two matrices into the U_α^{REP} in Eq (2). The symmetry properties of the operator U_α^{REP} and of the eigenfunctions of this operator can be determined from those of the double group.

The symmetry properties of diatomic molecules in the double group representation may be found in the work by Malli and Oreg.[9] However, the molecular spinors which are eigenfunctions of the REP of Eq (2) have only two components while the Dirac spinors have four components. In linear molecules, the angular symmetry of a state of a molecule is defined by the total electronic angular momentum Ω as in the Hund case c[10] and that of i-th molecular orbital by $m_i = \pm\omega_i$. The two orbitals with $m_i = +\omega_i$ and $m_i = -\omega_i$ are degenerate and constitute a shell. Because spin is incorporated in the orbital each molecular orbital can accommodate only one electron. With these characteristics, one can derive the SCF theory for the two-component molecular spinors (TCMS) for diatomic molecules by following the procedures that have been formulated for conventional non-relativistic molecular calculations.[11]

For a molecular state that may be represented by a single Slater determinant, the total wavefunction of the system is approximated by

$$\Phi = \mathcal{A}(\phi^1\phi^2 \ldots \phi^n) \tag{4}$$

where $\mathcal{A}$ is the antisymmetry operator and the ϕ's are one-electron

molecular spinors. The total energy of the molecular state is expressed by

$$E = \langle \Phi | \mathcal{H} | \Phi \rangle \tag{5}$$

provided Φ is normalized. As in the non-relativistic case each one-electron molecular spinor, $\phi_{i\lambda}$, is expanded in a basis set of two-component atomic spinors (TCAS), $\chi_{\lambda p}$,

$$\phi^{\pm}_{i\lambda} = \sum_{p} c^{\pm}_{i\lambda,p} \, \chi^{\pm}_{\lambda p} \tag{6}$$

where λ is the symmetry index ω, i is the index for orbitals of the same symmetry, and + and - refer to the sign of m. The TCAS are defined by

$$\begin{aligned} \chi^{\pm}_{\lambda p} &= \chi_{\lambda p}(n_p, \ell_p, j_p, \pm\lambda) \\ &= R_{\lambda p}(r) \sum_{\sigma=\pm\frac{1}{2}} C(\ell \tfrac{1}{2} j;\ \pm\lambda-\sigma, \sigma)\ Y^{\pm\lambda-\sigma}_{\ell p}\ \phi^{\sigma}_{1/2} \end{aligned} \tag{7}$$

where R(r) is a radial function. When Slater-type-functions (STF) are used as the basis, $\chi_{\lambda p}$ becomes

$$\begin{aligned} &\chi_{\lambda p}(n_p, \ell_p, j_p, \pm\lambda) \\ &= N_p \ r \ n_p^{-1} \ e^{-\zeta_p r} \begin{pmatrix} C(\ell_p \tfrac{1}{2} j_p, \pm\lambda-\tfrac{1}{2}, \tfrac{1}{2})\ Y^{\pm\lambda-\frac{1}{2}}_{\ell_p} \\ C(\ell_p \tfrac{1}{2} j_p, \pm\lambda+\tfrac{1}{2}, -\tfrac{1}{2})\ Y^{\pm\lambda+\frac{1}{2}}_{\ell_p} \end{pmatrix} \end{aligned} \tag{8}$$

where N_p is the normalization factor and the angular parts are rewritten to demonstrate the two-component properties of the basis spinors.

Following the non-relativistic theory for open shells,[11] we express the total energy as

$$E = D_T^\dagger H D_T + \frac{1}{2} D_T^\dagger \mathcal{P} D_T - \frac{1}{2} D_0^\dagger \mathcal{Q} D_0 \tag{9}$$

where H is composed of matrix elements of the one-electron operator [Eq (1)] over TCAS's, D_T and D_0 are the total and the open-shell density matrices, respectively, and $\mathcal{P}$ and $\mathcal{Q}$ are the closed and the open-shell supermatrices. The summations implied in Eq (9) and the definition of density matrices were given by Roothaan and Bagus.[11] The computational methods for one-electron matrix elements are described in Ref (3).

Matrix elements of the supermatrices $\mathcal{P}$ and $\mathcal{Q}$ are defined by

$$\mathcal{P}_{\lambda pq,\mu rs} = J_{\lambda pq,\mu rs} - \frac{1}{2} [K^+_{\lambda pq,\mu rs} + K^-_{\lambda pq,\mu rs}] \tag{10}$$

and

$$\mathcal{Q}_{\lambda pq,\mu rs} = A_{\lambda\mu} J_{\lambda pq,\mu rs} + B_{\lambda\mu} K^+_{\lambda pq,\mu rs} + C_{\lambda\mu} K^-_{\lambda pq,\mu rs} \tag{11}$$

where A, B and C are the open-shell vector-coupling coefficients and J and K are coulomb and exchange integrals. In Eq (10) and Eq (11)

$$J_{\lambda pq,\mu rs} = \int [\chi^+_{\lambda p}(1)]^* [\chi^+_{\mu r}(2)]^* \frac{1}{r_{12}} \chi^+_{\lambda q}(1) \chi^+_{\mu s}(2) \, d\tau \tag{12}$$

and

$$K^{\pm}_{\lambda pq,\mu rs} = \int [\chi^{+}_{\lambda p}(1)]^{*} [\chi^{\pm}_{\mu r}(2)]^{*} \frac{1}{r_{12}}$$

$$\chi^{\pm}_{\mu s}(1)\ \chi_{\lambda p}(2)\ d\tau \tag{13}$$

where the order of signs is preserved. J and K can be calculated from the two-electron integrals over STF's by taking the proper linear combinations.[3,11]

Energy expressions given by equations (9)-(13) were possible because the shell structure was assumed. This equivalence constraint may be expressed as

$$c^{+}_{i\lambda p} \equiv c^{-}_{i\lambda p} \text{ for all } p \tag{14}$$

If the shell structure is not conserved, the number of matrix elements to be included in the energy expression will be increased considerably and yield non-equivalent + and - orbitals for open-shell configurations. When the variational procedure is applied to the energy, one obtains equations that are essentially the same as the non-relativistic equations [Eq (12) - Eq (16) of Ref 11]. Since all the deviations from the conventional SCF equations are included in equations (9) - (14), the SCF equations for the TCMS are omitted.

The open-shell configurations which can be treated with the present formalism are limited to the cases where Ω defined by Eq (11) is adequate for the energy expression; specifically, each open shell must belong to a different symmetry. Table I shows the vector coupling coefficients $A_{\lambda\mu}$, $B_{\lambda\mu}$ and $C_{\lambda\mu}$. Since the only type of relativistic open-shell is one with a single electron, Table I may be used for any open-shell case as long as each open shell belongs to a different symmetry.

Once the proper transformation is carried out for one- and two-electron matrix elements, an existing SCF program can be modified for use with TCMs.

III. Calculations and Results

Relativistic effective core potentials (REP) were generated for the atoms, Hg, Tℓ, Pb, S and Se by the method described in Ref 1. In order to study the effect of the core size, we generated two sets of REP's for Hg, Tℓ and Pb; one treating 5d electrons as valence electrons and the other including those in the core. In addition, non-relativistic effective core potentials were generated for Tℓ for comparison. All of the cases are described in Table II. In each case, a double zeta set of STF's is obtained from the energy optimization of the ground state atoms with numerical AREP's. These basis sets are used for both atomic and molecular calculations. In our molecular studies, it is possible to use different basis functions for orbitals with the same ℓ but different j quantum numbers. However, we choose to use the same basis set for these orbitals with the condition that it be of double-zeta or better quality to allow for the differences in size between the $\ell + \frac{1}{2}$ and $|\ell - \frac{1}{2}|$ components. Also, the selection of different functions for each orbital would greatly increase the size of the basis set with only a slight improvement in accuracy of the results. (See below and Table III).

After the basis set is selected, the procedure for the SCF calculation is the following:

1) Calculation of one- and two-electron integrals over STF basis functions.
2) Transformation of integrals to obtain the matrix elements over TCAS's.
3) Computation of matrix elements of REP's for TCAS's.
4) SCF procedure to obtain molecular wavefunctions, orbital energies, and total energies.

The net effect of the transformation from STF's to TCAS's is to expand all the basis functions with non-zero m values. An example for this expansion is shown in Table III for Tℓ. In the case chosen, the number of basis functions increases from six STF's (four σ and two π functions) to eight TCAS's (six 1/2 and two 3/2 functions). Therefore, some extra computation is necessary compared with the non-relativistic calculations for the same basis functions. This extra computational effort corresponds to a modest integral transformation and the necessity to process the additional integrals at the SCF stage. However, the increase in the computation time is justified since the spin-orbit splittings are properly included in the SCF calculations.

The REP's are used in numerical form in all the calculations. We thereby eliminate the possible error introduced in the process of fitting the potentials with analytic functions. This is possible because the REP integral program can treat both analytical and numerical effective core potentials.[3]

A. Atomic calculations

Atomic calculations were carried out for the low-lying states of neutral atoms and the ground state of the ion for

Hg, Tℓ and Pb with double zeta basis sets of STF's and the averaged REP's (AREP) obtained from the configurations shown in Table II. The results, summarized in Table IV, indicate that the excitation energies of the atomic states are almost the same for n electron REP's (5d electrons in the core) and n + 10 electron REP's (5d electrons in the valence shell). For these types of excitations or ionizations, the 5d electrons seem to behave as core electrons. Therefore, it may be reasonable to exclude 5d electrons from the valence shell in molecular calculations for ground state properties. Based upon these results most molecular calculations were performed without 5d electrons. The excitation energies agree qualitatively with those obtained from experiment.[14] The $np_{1/2}^{1}\ np_{3/2}^{3}$ configuration of S and Se (Table II) used for the generation of REP is close to the average of LS configurations.[15] Excitation energies obtained with these AREP's of S and Se are in good agreement with the nonrelativistic, all electron calculations of Clementi and Roetti[16] as shown in Table V.

B. $(1/2)_g$ state of Au_2^+

The molecular energies were computed for Au_2^+ in its $(1/2)_g$ ground state at several internuclear distances to test the open-shell program with the REP and TCMS. The basis set and the REP are the same as those used in Ref 3 for the 0_g^+ state of Au_2. The total energy on a 21 valence electron basis is given for several interatomic distances in Table VI as are vertical ionization energies calculated by subtracting the energies of Au_2 from those of Au_2^+. These vertical transition

energies are compared with the orbital energies of the least-bound $(1/2)_g$ orbital of Au_2. The agreement between the two sets of values is evidence that the open-shell formalism is correct for a configuration with one open-shell and that Koopman's theorem is approximately valid in this case.

As would be expected, the $(1/2)_g$ state of Au_2^+ has a slightly larger equilibrium bond length (5.18 a.u.) and a smaller vibrational frequency (94 cm^{-1}) compared with the 0_g^+ state of Au_2. The dissociation energy is expected to be smaller for Au_2^+ than for Au_2 although an accurate estimate of D_e is not possible due to the improper dissociation behavior of the SCF approximation. Experimental values of D_e for Au_2^+ are not available.

C. TℓH

The ground state of wavefunction TℓH has been calculated with 3 and 13 electron valence shells and with REP, AREP, and NREP for the Tℓ atom. In each case, a double zeta basis set is derived from the energy optimization of the ground state of Tℓ. In addition to the two s functions, one p function is added to the basis set of the hydrogen. The spectroscopic constants are summarized in Table VII including the results of calculations of Pyykkö and Desclaux[17] and experimental values.[18]

From Table VII it is apparent that relativistic effects reduce the interatomic distance significantly; this may be ascribed to the relativistic contraction of the 6s orbital on Tℓ and to a smaller contraction of the $6p_{1/2}$ orbital. Also it appears that the bond is weakened, but when the spin-orbit

splitting of the atomic states of Tℓ is considered, that conclusion is less clear. The average ^2P energy is 0.024 a.u. higher than the true ground state $^2P_{1/2}$. It is not possible, without ambiguity, to correct the AREP and NREP calculations for this spin-orbit term. But any plausible correction to the AREP result will reduce the true dissociation energy to the $^2P_{1/2}$ atom of Tℓ from the value in Table VII. Hence, one can conclude that the inclusion of spin-orbit effects does decrease D_e for TℓH. The difference in R_e between the 3 and 13 electron bases for Tℓ is surprisingly large. Presumably the outer radius of the 5d orbitals is important in determining R_e and this should be more reliably established when these 5d electrons are included explicitly in the calculation.

The TCMS-MO's have a rather complicated character at the equilibrium internuclear distance. They are much simpler at R = 6.0 a.u.; here the lower valence orbital is almost purely Tℓ - 6s. In the REP basis the higher energy orbital has a population 1.45 on the hydrogen atom with σ bonding participation by $6p_{1/2}$ and $6p_{3/2}$ orbitals. The ratio of populations ($p_{3/2}/p_{1/2}$) is 0.9 at R = 6 a.u. whereas it would be 2.0 in the absence of the spin-orbit term. The decrease in this ratio from 2.0 to 0.9 is caused by spin-orbit interaction, and it introduces a small pπ population. The more interesting aspect is the large ionic character $T\ell^+ H^-$ with the transfer of 0.47 electronic charge. Thus the bonding arises primarily from the upper orbital and is very substantially ionic.

The population analyses at the equilibrium bond distance are given in Table VIII. At this distance the lower energy orbital has become a bonding orbital with a substantial population on hydrogen. The total charge on hydrogen is reduced, but remains substantial (approximately 0.35 e). The Tℓ - 6s participation in the higher energy orbital is antibonding and cancels a large portion of the pσ bonding from the 6p orbitals. Thus, in a simplified description, the covalent bonding comes from the lower orbital with 6s(Tℓ)-1s(H) character, and the remaining contribution to the bonding is primarily ionic. The precise values of the atomic populations should not, of course, be considered accurate measurements of charge transfer due to the approximations inherent in the formalism and to the possible sensitivity of the results to basis set imbalance. (Part of the excess charge on H is undoubtedly due to the presence of the polarization function). However, the bond appears to be more ionic in TℓH than in BH.[19]

The non-bonding character of the 2-1/2 orbital is confirmed by the near constancy of its orbital energy: 0.2892 at r = 3.50, 0.2894 at r = 3.25. In contrast the orbital energy of the 1-1/2 orbital increases from 0.4891 to 0.5016 over the same range.

Since both the ionic bonding and the 6s(Tℓ)-1s(H) bonding character are not appreciably changed by relativistic effects, it is not surprising that the calculated bond energy values in Table VII are nearly equal. The calculated value of D_e on the REP basis is smaller than the experimental value by a

reasonable amount due to the electron correlation, which is not included in the SCF approximation.

D. PbS and PbSe

In addition to the calculations described above on Au_2^+ and T&H, exploratory calculations were made for PbS and PbSe for comparison with photo-electron spectra being measured currently by Shirley and associates.[20] The use of a single relativistic configuration is a rather severe approximation, especially for orbitals primarily located on the S or Se atom, but it does reflect the large spin-orbit term and the other relativistic effects for Pb. A double zeta basis set was used with other details essentially the same as have been described for the other examples. Fortunately, the ground state configuration for the molecules $(1\text{-}1/2)^2\ (2\text{-}1/2)^2\ (3\text{-}1/2)^2\ (4\text{-}1/2)^2\ (1\text{-}3/2)^2$ allows dissociation into neutral atoms $6s^2_{1/2}\ 6p^2_{1/2}$ for Pb and $ns^2_{1/2}\ np^2_{1/2}\ np^2_{3/2}$ for S or Se, although these states are not the true ground states of the atoms.

Tables IX and X show the calculated orbital energies for PbS and PbSe, respectively, at near equilibrium interatomic distances and compare our REP results with those from X_α calculations by Yang and Rabii[21] and the experimental results of Shirley, White, et al.[20] For both molecules the lower frequency photo-electron peak is broad and presumably includes both the lowest $\Omega = 1/2$ state and the $\Omega = 3/2$ state for the positive ion. The agreement of our calculated energies with experiment is as good as could be expected. Also our results show a rapid variation of orbital energies with interatomic distance for the

4-1/2 orbital and hence predict a broad band which would overlap the 1-3/2 band. The detailed band contour does not agree; however, that is not unexpected in view of our approximations. For the second transition removing an electron from the 3-1/2 orbital, the agreement between calculation and experiment is perfect--doubtless in some degree by accident.

The Xα calculations of Yang and Rabii[21] yield the correct order of orbital energies but the quantitative values do not agree. More recent and improved Xα calculations[22] exhibit better agreement.

In Table XI are shown our calculated values of R_e, ω_e, and D_e together with experimental data.[18] The agreement with the experimental values of R_e is quite satisfactory. Since electron correlation is not included in our calculation, it is expected that our calculated D_e will be too small, and this effect will also influence the ω_e values in the same direction.

The $\omega = 3/2$ orbital is, of course, a pure π orbital, and the ion state with this vacancy can be described as $^2\Pi_{3/2}$. The atomic p orbitals with $m = \pm 1/2$, however, contain both σ and π components and the molecular orbitals based thereon, 4-1/2 and 3-1/2, likewise include both σ and π components. If one approaches these same states from a nonrelativistic basis, the $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states are mixed and contribute the σ and π components, respectively. Based upon REP calculations, we estimate the following characteristics for molecular orbitals of PbS and PbSe. Molecular orbitals 4-1/2 and 1-3/2 are π bonding, although the population in the 1-3/2 orbital is almost

entirely on the Se atom. The 3-1/2 orbital is σ-bonding and π-antibonding. The 4-1/2 orbital energy changes rapidly with interatomic distance, as expected for a strongly bonding orbital, whereas the orbital energies for the other orbitals show little change in agreement with their weakly bonding (or antibonding) character.

IV. Discussion

It should be realized that a SCF calculation for a single relativistic (ω-ω) configuration may not be a good approximation even for a molecule with heavy atoms. Such molecules (or atoms) usually fall in the range of intermediate coupling (between L-S and j-j for atoms). Electron-repulsion and spin-orbit terms are of comparable magnitude. Unless the molecular orbitals occupied in the selected configuration allow appropriate adjustment for these two effects, a single configuration will not provide a good description of the ground state of the molecule. If the valence shell of the molecule involves only s-orbitals, then there is no spin-orbit term, and a single configuration suffices, e.g., Au_2 or Au_2^+. With only a single p-orbital involved in TℓH, the molecular orbital can include a linear combination of $p_{1/2}$ and $p_{3/2}$ orbitals from Tℓ and thus provide the needed adjustment for a good initial approximation. But for $T\ell_2$, for example, the ground state cannot be reasonably approximated without CI including at least the two configurations $(1\text{-}1/2)_g^2\ (1\text{-}1/2)_u^2\ (2\text{-}1/2)_g^2$ and $(1\text{-}1/2)_g^2\ (1\text{-}1/2)_u^2\ (2\text{-}1/2)_u^2$ which we have found to be of very nearly equal energy. In addition, in the SCF approximation many

molecules do not dissociate to the proper atomic states. Therefore, configurations accounting for both of these characteristics should be included in most molecular calculations with ω-ω coupling for a reasonable description of even the ground state. Work on the needed programs to include multiple configurations is now in progress. However, the ground states of the molecules presented in this paper are reasonably described near the equilibrium bond distance with our present approximation.

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Table I. Open-shell vector coupling coefficients for the states represented by a single-Slater-determinant

	$A_{\lambda\mu}$	$B_{\lambda\mu}$	$C_{\lambda\mu}$
$\lambda = \mu$	1	-1/2	-1/2
$\lambda \neq \mu$			
$\Omega_i = \lambda + \mu$[a]	0	1/2	-1/2
$\Omega_i = \lvert\lambda - \mu\rvert$[a]	0	-1/2	1/2

[a]If $\Omega_i = \lambda + \mu$ for the interaction of two open shells, the signs of the m's are the same for both orbitals. If $\omega_i = |\lambda - \mu|$, the signs of m's are opposite.

Table II. Separation of the core and the valence electrons for the various atoms

Atom	Potential[a]	Core Electrons	Valence Electrons[a]
Hg	REP2	[Xe] $5d^4_{3/2}$ $5d^4_{5/2}$	$6s^2$
	REP12	[Xe]	$5d^4_{3/2}$ $5d^6_{5/2}$ $6s^2$
Tℓ	REP3	[Xe] $5d^4_{3/2}$ $5d^6_{5/2}$	$6s^2 6p_{1/2}$
	REP13	[Xe]	$5d^4_{3/2}$ $5d^6_{5/2}$ $6s^2 6p_{1/2}$
	NREP3	[Xe] $5d^{10}$	$6s^2 6p$
	NREP13	[Xe]	$5d^{10} 6s^2 6p$
Pb	REP4	[Xe] $5d^4_{3/2}$ $5d^6_{5/2}$	$6s^2 6p_{1/2} 6p_{3/2}$
	REP14	[Xe]	$5d^4_{3/2}$ $5d^6_{5/2}$ $6s^2 6p_{1/2} 6p_{3/2}$
S	REP6	[Ne]	$3s^2$ $3p^1_{1/2}$ $3p^3_{3/2}$
Se	REP6	[Ar] $3d^{10}$	$4s^2$ $4p^1_{1/2}$ $4p^3_{3/2}$

[a] Numerics refer to the total number of valence electrons and a and b are used to distinguish the different atomic configurations.

Table III. Slater type functions (STF) and two-component spinors[a] (TCAS) for 3-electron Tℓ.

STF				TCAS				
n	ℓ	m_ℓ	ζ	n	ℓ	j	m_j	ζ
3	0	0	1.7838	3	0	$\frac{1}{2}$	$\frac{1}{2}$	1.7838
3	0	0	1.7441	3	0	$\frac{1}{2}$	$\frac{1}{2}$	1.1441
4	1	0	1.6897	4	1	$\frac{1}{2}$	$\frac{1}{2}$	1.6897
4	1	0	.9483	4	1	$\frac{1}{2}$	$\frac{1}{2}$	.9483
4	1	1	1.6897	4	1	$\frac{3}{2}$	$\frac{1}{2}$	1.6897
4	1	1	.9483	4	1	$\frac{3}{2}$	$\frac{1}{2}$	.9483
				4	1	$\frac{3}{2}$	$\frac{3}{2}$	1.6897
				4	1	$\frac{3}{2}$	$\frac{3}{2}$	.9487

[a] Tℓ REP3 of Table II

Table IV. Excitation and ionization energies of Hg, Tℓ and Pb calculated with the double zeta basis sets and AREP's (all in a.u.)

Atoms	State	Configuration	Excitation Energies		
			AREP12[a]	AREP2[a]	Exp[b]
Hg	^1S	$6s^2$	0.0	0.0	0.0
	^3P	6s6p	.140	.142	.190
	^1P	6s6p	.238	.241	.246
Hg^+	^2S	6s	.316	.320	.384
			AREP13[a]	AREP3[a]	
Tℓ	^2P	$6s^26p$	0.0	0.0	0.0
$Tℓ^+$	^1S	$6s^2$	.179	.176	.201
			AREP14[a]	AREP4[a]	
Pb	^3P	$6s^26p^2$	0.0	0.0	0.0
	^1D	$6s^26p^2$	.036	.036	.059
	^1S	$6s^26p^2$	.089	.089	.096
Pb^+	^2P	$6s^26p$	.240	.239	.287

[a] Averages are taken from the corresponding REP (Table II)

[b] From Reference 14.

Table V. Excitation energies of S and Se calculated with the double zeta basis sets and AREP's (all in a.u.)

Atoms	States	AREP	All-electron[a]
S	^3P	0.0	0.0
	^1D	.049	.048
	^1S	.126	.120
Se	^3P	0.0	0.0
	^1D	.055	.527
	^1S	.135	.130

[a] From Reference 16.

Table VI. Total valence energies of Au_2^+, vertical ionization energies of Au_2 (calculated from the total valence energies of Au_2 and Au_2^+) and the orbital energies of the least-bound $(1/2)_g$ electron of Au_2 at various interatomic distances. (all in a.u. and based on 11-electron REP's for Au)

R	-E	$E(Au_2^+)$ $-E(Au_2)$	$-E[(\frac{1}{2})_g]$ of Au_2
4.5	70.5181	.260	.281
4.75	70.5266	.254	.274
5.0	70.5300	.249	.267
5.5	70.5292	.238	.255
8.0	70.5022	.202	.211

Table VII. Spectroscopic constants obtained from the SCF calculation of TℓH with various EP's

	Effective Core Potentials					One-center[a]		Exp[b]
	REP13	REP3	AREP3	NREP13	NREP3	R	NR	
R_e(a.u.)	3.47	3.39	3.39	3.67	3.55	3.529	3.795	3.53
D_e(a.u.)	.057	.050[c]	.065[d]	.062[d]	.064[d]			0.072
ω_e(cm^{-1})	1450	1380	1380	1380	1410	1500	1390	1391
$(p_{3/2}/p_{1/2})$[e]	.37	.50	2.0	2.0	2.0	.65	2.0	-
I.P.(a.u.)[f]	.298	.290	.286	.266	.267			

[a] From Reference 17.

[b] From Reference 18.

[c] $E(T\ell\ ^2P_{1/2}) + E(H) - E(T\ell H \text{ at } R_e)$

[d] $E(T\ell\ ^2P) + E(H) - E(T\ell H \text{ at } R_e)$

[e] From the atomic population analysis.

[f] Ionization potential from Koopman's theorem and orbital energies at near-equilibrium distance.

Table VIII. Population analyses for TℓH (R = 3.5 a.u.)

	REP-3			AREP-3			NREP-3		
Orbital	1-1/2	2-1/2	Total	1σ	2σ	Total	1σ	2σ	Total
Tℓ s	1.40	.43	1.83	1.60	.30	1.90	1.17	.70	1.87
$p_{1/2}$	.00	.53	.53	.00	.74	.74	.08	.73	.81
$p_{3/2}$	.02	.27	.29						
H s	.58	.77	1.35	.40	.96	1.36	.75	.56	1.32

Table IX. Orbital energies and ionization energies for PbS (in a.u.)

Orbital	REP[a]	Xα A[b]	Xα B[c]	Exp[d]
4 - 1/2	.326	.227	.334	$.33_8$ (broad)
1 - 3/2	.344	.243	.345	
3 - 1/2	.359	.260	.353	$.36_0$
2 - 1/2	.591	.510	.566	
1 - 1/2	.884	.632	-	

[a] This research, R = 4.25 a.u.

[b] Reference 21.

[c] Reference 22, improved Xα calculation for transition states

[d] Reference 20.

Table X. Orbital energies and ionization energies for PbSe (in a.u.)

Orbital	REP[a]	Xα A[b]	Xα B[c]	Exp[d]
4 - 1/2	.310	.234	.323	$.32_7$ (broad)
1 - 3/2	.317	.235	.323	
3 - 1/2	.348	.258	.338	.350
2 - 1/2	.587	.528	.568	
1 - 1/2	.853	.651		

[a] This research, R = 4.25 a.u.

[b] Reference 21.

[c] Reference 22, improved Xα calculation for transition states

[d] Reference 20.

Table XI. Calculated and experimental quantities for PbS and PbSe

		PbS	PbSe
R_e(a.u.)	REP	4.28	4.55
	Exp[a]	4.321	4.539
ω_e(cm^{-1})	REP	351.	210.
	Exp[a]	429.4	277.6
D_e(a.u.)	REP	0.043	0.033
	Exp[a]	0.128	0.113

[a] From Reference 18.