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FROM RELATIVISTIC MULTICONFIGURATION SCF CALCULATIONS

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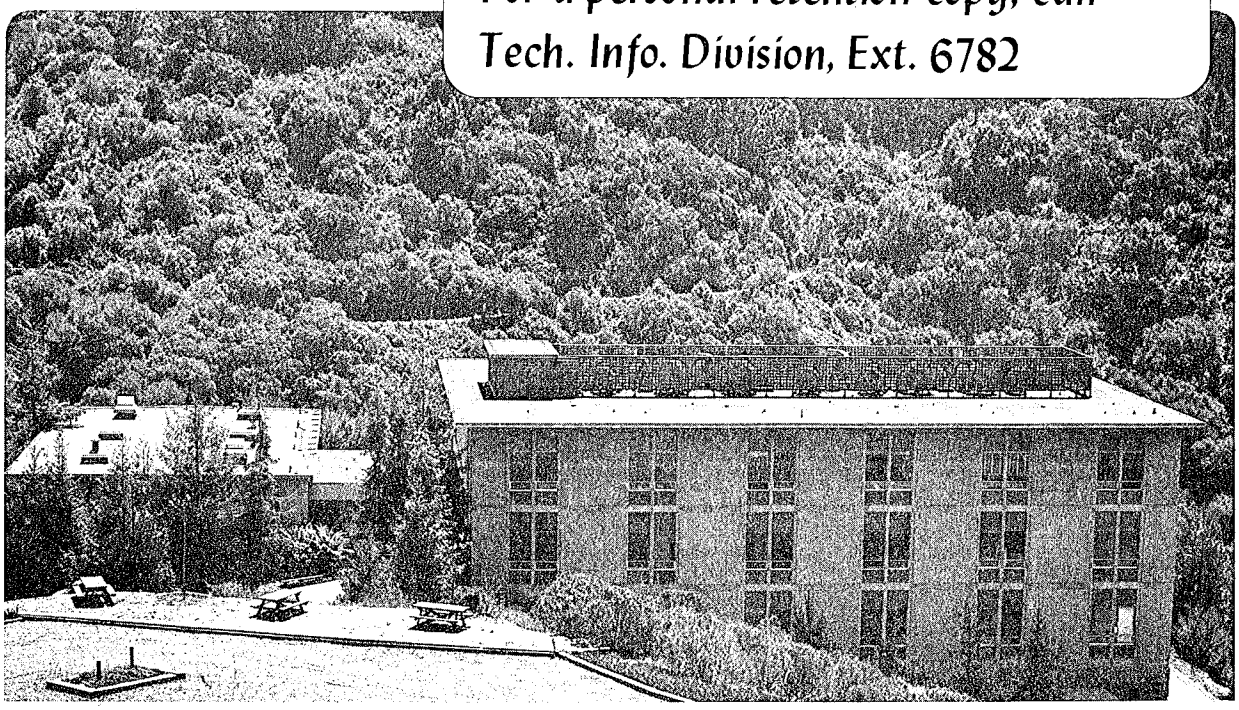

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Electronic Structure for the Ground State of TlH from Relativistic Multiconfiguration SCF Calculations

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Abstract

The dissociation curve for the ground state of TlH was computed using a relativistic ω-ω coupling formalism. The relativistic effects represented by the Dirac equation were introduced using effective potentials generated from atomic Dirac-Fock wavefunctions using a generalization of the improved effective potential formulation of Christiansen, Lee and Pitzer. The multi-configuration SCF treatment used is a generalization of the two-component molecular spinor formalism of Lee, Ermler and Pitzer. Using a five configuration wavefunction we were able to obtain approximately 85% of the experimental dissociation energy. Our computations indicate that the bond is principally sigma in form, despite the large spin-orbit splitting in atomic thallium. Furthermore the bond appears to be slightly ionic ($Tl^{+}H^{-}$) with about 0.3 extra electron charge on the hydrogen.

Introduction

In recent years several relativistic effective-potential formalisms have been proposed[1-5] and employed in electronic structure studies of molecules containing heavy elements. In most of these, relativistic contributions, except for spin-orbit, are introduced into the molecular calculations via the effective potentials, (EP). The spin-orbit effects are added later as some sort of perturbation. However, for molecules containing some of the sixth row elements such as Tl or Pb the spin-orbit contributions may be substantially larger than correlation effects and perturbation methods may be inadequate. Thus it seems preferable to include the spin-orbit effects in the SCF step of the calculation. This is the procedure employed in the two-component molecular spinor formulation of Lee, Ermler and Pitzer.[1] Hafner and Schwarz give an excellent description of a similar method.[2] In these procedures the molecular SCF computations are done directly in ω-ω coupling. Unfortunately, both procedures employ EP formalisms of questionable reliability. Furthermore, little has been done within the ω-ω framework to include molecular correlation effects. Therefore, though quite adequate for qualitative studies, these methods could be misleading if quantitative molecular results are desired.

In the present work we have extended the molecular spinor formalism of Lee, *et al*. in two important ways. First, we have generalized the previous ω-ω SCF procedure to include a multiconfiguration SCF treatment (MCSCF). This allows us to include the major effects of electron correlation and to obtain proper dissociation in all cases. In addition we have replaced the previously used Phillips-Kleinman type EP formalism[6] with the frozen-core EP method reported recently by Christiansen, Lee,

and Pitzer[7] which was shown to be much more reliable for the calculation of potential curves or dissociation energies. In that work we were able to show that by retaining in the valence portion of the pseudoorbital, the true form of the original atomic orbital, ab initio effective potentials can be generated which reproduce all-electron results to a high degree of accuracy. Calculations using EPs based on Phillips-Kleinman pseudoorbitals sometimes give results which differ seriously from those of all-electron calculations.[8-11] Our recent paper identified the cause of this unreliability and demonstrated a procedure which eliminates the problem.

Since most of the important mathematical details of our calculations have been stated in references 1 and 7, they will not be repeated here.

For a first test of this procedure we chose the thallium hydride molecule, for which good spectroscopic data are available.[12,13] In our molecular calculations we treat explicitly only the outer-most thirteen electrons of thallium, (the 5d, 6s electrons and single $6p_{1/2}$ electron). The $p_{1/2}$-$p_{3/2}$ spin-orbit splitting is approximately one electron volt. Thus TlH should be an excellent test of our relativistic MCSCF formalism. Also the relativistic contraction of the 6s atomic spinor causes a substantial energy gap between the 6s and 6p atomic spinor energies, resulting in the so-called inert pair effect for the 6s electrons. Thus, in terms of molecular bonding with hydrogen, Tl is somewhat similar to the alkali metals with essentially only one valence electron. However, in this case the electron is assigned to a p rather than s type spinor. It is well established for the ground states of the light alkali metal dimers and hydrides[14] that one can obtain a good approximation to the experimental bond energies by correlating only the two valence electrons

using a relatively small MCSCF wavefunction. We expect that this may also be true for the thallium dimer and hydride.

The behavior in chemical bonding of $p_{1/2}$ and $p_{3/2}$ spinors , with a large spin-orbit energy difference, is a matter of great interest. A $p_{1/2}$ orbital is one-third sigma and two-thirds pi in its character, and in a diatomic molecule such as Tl_2, the molecular orbitals can be either sigma bonding and pi antibonding, or the reverse. For TlH any pi bonding or antibonding effects will be very small, but the behavior of the p orbital in sigma bonding is still of considerable interest. We are currently studying Tl_2 where the pi bonding or antibonding aspects will also become important.

Method and Calculations

The effective potentials for the present calculations were generated as in reference 7, only for Tl it is necessary that we use numerical atomic Dirac-Fock spinors[15] rather than Hartree-Fock spin orbitals to form our pseudo-orbitals (in this case pseudospinors). Since the two small components of the four component Dirac spinors have essentially negligible amplitudes in the valence region, they are neglected in the pseudospinors. Thus our valence pseudospinors have only two components, greatly simplifying our molecular calculations. The $5d_{3/2}$, $5d_{5/2}$, $6s_{1/2}$, and $6p_{1/2}$ pseudospinors were obtained from a ground state atomic calculation. The $6p_{3/2}$, $5f_{5/2}$, $5f_{7/2}$, $5g_{7/2}$, and $5g_{9/2}$ pseudospinors were obtained from atomic calculations where the single 6p electron was transferred from the $p_{1/2}$ spinor into the various excited spinors. In all, we used nine atomic pseudospinors and ultimately nine relativistic EPs in our molecular calculations.

As before (see Equations 1-3, Ref. 1), the complete effective potential for thallium has the general form.

$$U_{T\ell}^{EP} = U_{LJ}(r) + \sum_{\ell=0}^{L} \sum_{j=\ell-\frac{1}{2}}^{\ell+\frac{1}{2}} \sum_{m=-j}^{j} [U_{\ell j}(r) - U_{LJ}(r)] \,|\ell jm\rangle\langle \ell jm|$$

where $L = 4$ and $J = 9/2$ and the $U_{\ell j}$ are the EPs derived from the individual pseudospinors with angular quantum numbers ℓ and j. The projection operator on the right insures that the $U_{\ell j}$ operate only on spinors of the proper angular symmetry. Previous work[1] has indicated that provided the L and J quantum numbers are not present for the core electrons (which precludes any radial "exclusion" effects due to core orbitals of the same symmetry), then U_{LJ} is probably a good approximation to the potentials of higher angular symmetry.

For the determination of the pseudospinors from the spinors, a few minor refinements were added to the procedure described in reference 7.

As suggested by P. J. Hay,[16] in addition to limiting the maximum number of inflexions in the radial pseudoorbital or pseudospinor to two, we also require that there be no more than three inflexions in the first derivative. This has only a slight effect on the match point (the radial point outside which the spinor and pseudospinor are identical, see reference 7), but ultimately results in a smoother potential. Also, we found that for some of the more diffuse excited spinors, one could substantially reduce the value of the match point by adjusting the lead power in the analytical portion of the radial pseudospinor. This adjustment seems to have little effect for the more tightly bound spinors.

The basis set for Tl was double-zeta in form (2s, 2p, and 2d) made up of Slater type functions. The exponents were obtained by optimizing the energy of the Tl ground state using the EPs after averaging out the spin-orbit effects. This will, of course, result in somewhat less than double-zeta quality for the individual spinors, but it greatly reduces the number of molecular integrals which need to be generated (to within our program limitations). In these calculations we have assumed that the important bonding spinor on Tl, the $p_{1/2}$, will be adequately polarized by the excess 6s and 5d functions. Unfortunately, at the time of these calculations our molecular integral programs were limited to maximum n quantum numbers of 4. Although this is probably adequate for Phillips-Kleinman[6] type calculations where the pseudoorbitals contain substantial core character, higher n values might have been more appropriate for the present work. The hydrogen basis set was double-zeta plus polarization as in Lee *et al.*[1] Therefore, we expect that the overall quality of our molecular basis set is somewhat less than double-zeta plus polarization.

Once the exponents have been selected, the Slater type spin orbitals are then transformed into two-component atomic spinors to be used as basis functions in our molecular calculations. The molecular spinor formalism employed here is essentially that of Lee et al.[1] However, we wish to correlate the two bonding electrons. For the 0^+ state this requires double excitations from the bonding spinor into the correlating spinors. It can be easily shown that the coupling between configurations is of the form, $K^+_{ij} + K^-_{ij}$, where the + refers to integrals resulting from the exchange of electrons with angular momentum of the same sign, and the - signifies angular momentum of opposite sign. The i and j refer to the two spinors by which the configurations differ. Thus, for the 0^+ state, the correlation coupling is analogous to that of non-relativistic singlet sigma states as in the ground state alkali metal hydrides. We modified a version of the Bison MCSCF code of Das and Wahl[17] to perform the SCF calculations. To our knowledge this is the first time a molecular MCSCF calculation in ω-ω coupling using accurate relativistic EPs has been attempted.

Results and Discussion

Using the effective potentials and basis sets described above, we computed total molecular energies for the ground state of TlH using single determinant (essentially closed-shell Dirac-Fock), two determinant (to obtain proper dissociation), and five determinant MCSCF wavefunctions formed from two-component spinors. In the five-determinant calculation, various plausible configurations were introduced into exploratory calculations and the five most important were used in the final calculations. In addition to the two configurations required for proper dissociation,

it was found that two configurations generated by double excitations to $\omega = \frac{1}{2}$ spinors and one configuration with a double excitation to an $\omega = 3/2$ spinor made substantial contributions. The internuclear separation was varied from three to fifteen atomic units (a.u.). The resulting molecular dissociation curves are listed in Table I. Spectroscopic constants for the single determinant and MCSCF wavefunctions are listed in Table II along with single determinant values from previous calculations and the experimental values. Plots of our dissociation curves are given in Figure 1.

First, note the large discrepancy between our single determinant dissociation energy and the value obtained using EPs generated from Phillips-Kleinman type pseudospinors.[1] Our single determinant calculation gives about 47% of the experimental dissociation energy as opposed to about 79% for the Phillips-Kleinman type calculation. Non-relativistic, all-electron, single-determinant calculations usually give only about one half or less of the dissociation energy.[14] This discrepancy is very similar to that seen in the earlier non-relativistic EP calculations on F_2 and Cl_2 where Phillips-Kleinman EPs gave substantially larger dissociation energies than the corresponding all-electron calculations.[9] Note also that both our single configuration and MCSCF calculations predict bond lengths which are slightly too long relative to experiment. Though we have no proof, we suspect that this is the result of our slightly inadequate basis set. The fact that the MCSCF bond length is slightly longer than the single determinant value closely parallels previous non-relativistic calculations.[14]

With our five determinant MCSCF wavefunction we were able to obtain more than 85% of the experimental dissociation energy. Although similar calculations[14] for the light alkali metal dimers frequently obtain 90% or more of the bond energy, we believe that the combination of a somewhat

poorer basis set and the smaller energy difference between the Tl 6s and 6p spinors (compared to that between the alkali metal valence s and p electrons) could easily explain the differences. It is the large s-p separation which allows us to treat correlation in TlH as though there were only two valence electrons. In this respect Cs_2 would have been an easier test if the calculation of correlation energy in heavy-atom molecules had been our only objective. However, the Cs_2 bond involves primarily 6s spinors with no spin-orbit effect. Since the inclusion of spin-orbit effects was also an important aim, TlH seemed a more appropriate example.

The general picture of the valence molecular spinors for TlH obtained in this research supercedes that reported earlier from less accurate calculations.[1] There are surprisingly large differences in some aspects as well as good agreement in others. Where there are differences, the present results yield a much simpler picture.[1] The present values were taken from our five-configuration MCSCF calculations for R = 3.75 a.u.. The 6s spinor on thallium remains essentially unchanged in the molecule, the hydrogen and the thallium 6p participation remaining very small. In contrast, this spinor attained a bonding nature with nearly 30% population on hydrogen in the earlier calculations.[1] Since in our present calculations we found little difference between our single configuration and five configuration spinors, we expect that the above differences are primarily the result of the improved EPs used in the present work. In the principal bonding spinor (from our five configuration calculations) the $6p_{1/2}$ to $6p_{3/2}$ population ratio is approximately 0.6_6 - compared to 0.65 reported by Pyykkö and Desclaux[18] from one-center calculations and about 0.5 from the earlier EP results.[1] However, in our present calculations this ratio shows a marked radial dependence relative to the Tl origin, varying from about 0.5 at the Tl nucleus to about 3.5 at infinity. (The ratio for a non-relativistic sigma orbital is 2.0). In the region near the H nucleus, the ratio is such that the Tl p contribution to the spinor is more than three-quarters sigma. Since the contribution

from the hydrogen is almost exclusively 1s the bond appears to be principally sigma in character. Finally, our results indicate some ionic character (Tl^+H^-) with about 0.3 extra electron population on the hydrogen, in close agreement with the earlier calculation. Pyper[19] has shown that in TlH there is a bonding interaction between the pi component of the $6p_{1/2}$ spinor on Tl and the 1s orbital on H analogous to that in the $^3\Pi$ state of nonrelativistic third group hydrides, BH, etc. Since this $^3\Pi$ state is only weakly bound in GaH and InH, we do not believe this is a major factor for TlH. Furthermore Pyper's analysis assumes that the bonding spinor is essentially $p_{1/2}$ in form whereas our calculations indicate that the $p_{1/2}$ and $p_{3/2}$ mixing is substantial, the signs being such that the pi component nearly disappears in the bonding region. Thus the overwhelming bonding interaction appears to be the sigma bonding as in $^1\Sigma$ BH, etc.

Conclusion

We have shown that the combination of our previously developed effective potential procedure[7] with the molecular spinor formalism of Lee *et al.*[1] and its subsequent generalization to include the important electron correlation effects provides a method which is capable of yielding near-quantitative numerical results when used to study bonding in molecules containing heavy elements.

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REFERENCES

1. Y. S. Lee, W. C. Ermler and K. S. Pitzer, J. Chem. Phys. (in press); also earlier papers in that series there cited.
2. P. Hafner and W. H. E. Schwarz, Chem. Phys. Lett. 65, 537 (1979).
3. G. Das and A. C. Wahl, J. Chem. Phys. 69, 53 (1978).
4. W. R. Wadt, P. J. Hay, and L. R. Kahn, J. Chem. Phys. 68, 1752 (1978).
5. S. N. Datta, C. S. Ewig and J. R. Van Wazer, Chem. Phys. Lett. 57, 83 (1978).
6. J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).
7. P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. 71, 4445 (1979).
8. L. R. Kahn, P. Baybutt and D. G. Truhlar, J. Chem. Phys. 65, 3826 (1976).
9. P. J. Hay, W. R. Wadt, and L. R. Kahn, J. Chem. Phys. 68, 3059 (1978).
10. G. Das, Chem. Phys. Lett. 71, 202 (1980).
11. W. C. Ermler, Y. S. Lee, K. S. Pitzer and N. W. Winter, J. Chem. Phys. 69, 976 (1978).
12. These studies are summarized by K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules (Van Nostrand Reinhold Co., New York, 1979).
13. M. L. Ginter and R. Battino, J. Chem. Phys. 42, 3222 (1965).
14. H. F. Schaefer III, The Electronic Structure of Atoms and Molecules (Addison-Wesley, Reading, MA, 1972).
15. J. P. Desclaux, Comput. Phys. Commun. 9, 31 (1975).
16. P. J. Hay, personal communication.
17. G. Das and A. C. Wahl, Argonne National Laboratory Report No. ANL-7955 (1972).

18. P. Pyykkö and J. P. Desclaux, Chem. Phys. Lett. 42, 545 (1976).

19. N. C. Pyper, Chem. Phys. Lett., submitted.

Table I. Potential Curves for TlH (all values are in a.u.)

R	Single Conf.[a]	Two Conf.[a]	Five Conf. MCSCF[a]
3.0		-.0275	-.0377
3.25	-.0273	-.0434	-.0532
3.5	-.0332	-.0510	-.0600
3.75	-.0336	-.0532	-.0614
4.0	-.0303	-.0519	-.0593
4.5	-.0175	-.0434	-.0493
5.0		-.0321	-.0366
6.0		-.0125	-.0138
8.0		-.0010	-.0010
10.0		0.0001	0.0001

[a]Energies relative to the value obtained at R = 15.0 for the two and five configuration wavefunctions.

Table II. Spectroscopic Constants for TlH

	Present MCSCF	Present Single Conf.	Single Conf.[a]	Single Conf.[b]	Exp[c]
R_e (Å)	1.96	1.93	1.84	1.87	1.87
D_e (eV)	1.66	0.93	1.55	--	1.97
ω_e (cm^{-1})	1330	1450	1450	1500	1391

[a] 13 electron calculations employing Phillips-Kleinman type relativistic EPs from Ref. 1.

[b] One-center Dirac-Fock, Ref. 18.

[c] Reference 12.

Figure Caption

Figure 1. Dissociation curves for single configuration (SC), double configuration (DC), and five configuration (MCSCF) calculations for the ground state of TlH. The minimum in the experimental curve is also indicated (+).

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