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Phillip A. Christiansen, K. Balasubramanian, and Kenneth S. Pitzer

December 1981

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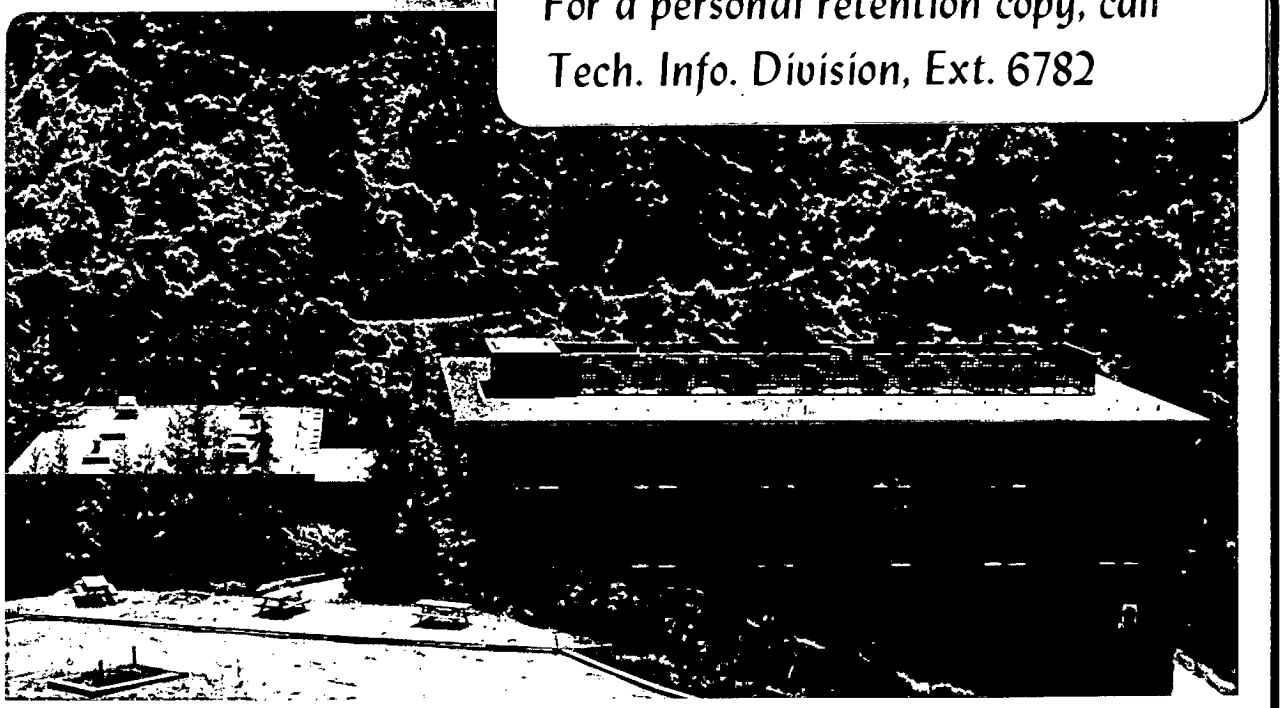

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Relativistic, ab Initio, Molecular Structure Calculations Including Configuration Interaction with Application to Six States of T&H

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ABSTRACT

A system for the inclusion of spin-orbit coupling along with moderate scale CI in calculations for molecules containing very heavy elements is demonstrated. In this effective potential procedure rigorous ab initio spin-orbit integrals are computed and added to the conventional integral set after the SCF and integral transformation steps of the calculation. This avoids the use of complex coefficients in the integral transformation and yet includes spin-orbit corrections on an equal footing with electron correlation. The diagonalization of the resulting complex CI plus SO matrix requires only about twice the time of a real CI diagonalization. Our present calculations on the two lowest 0^+ and 1 states and the lowest 0^- and 2 states of T&H indicate that this procedure allows adequate flexibility in the electronic coupling, resulting in bonding curves which are in good agreement with the experimentally established curves. The results also help to understand and to confirm previously conjectural interpretations of other spectral data.

Introduction

In a series of papers,[1-9] ab initio, relativistic core potentials (REP) have been defined and applied to the calculation of the electronic structure of molecules which include one or more very heavy atoms. The exact method of defining the effective potentials (EP) and calculating them from atomic Hartree Fock (HF) or Dirac Fock (DF) results required considerable investigation,[10] but a set of essential principles was established and a detailed procedure was found which reproduces accurately the results from all-electron calculations[10,11] for molecules such as Cl_2, Kr_2, Kr_2^+, Xe_2, and Xe_2^+. All-electron relativistic calculations have not been[12] available for molecules containing very heavy atoms, but this analysis of pertinent principles confirmed by these examples gives us confidence in the validity of the method for even heavier atoms.

The spin-orbit (SO) effect is large for most very heavy atoms. Gold is an exception where the only valence electron is in an s orbital, and Au_2 was treated[3,4] by methods not generally applicable to molecules containing such heavy atoms. Where valence-level p or d electrons are present, the SO energy is of a magnitude comparable to that of valence-level electron repulsion integrals and the SO matrix elements should be included on an equal basis. One method is to set up the molecular wavefunction in terms of relativistic spinors, i.e., in ω-ω (type c) coupling. Actually two-component spinors suffice; the two small components of four-components Dirac spinors are negligible for valence orbitals in an effective potential treatment. Such calculations in ω-ω coupling were made, first on a single configuration basis,[5] and then on a multiconfiguration (MCSCF) basis.[7,8] The results[7,8] for TlH, Tl_2^+, and Tl_2 on these bases appear to be reliable and as accurate as can be expected where only a few configurations are included. Thus the bond distances are quite

well determined but the calculated dissociation energies are at best semiquantitative.

While it would be possible to develop high-order configuration interaction (CI) methods in terms of two-component spinors, an alternate procedure has been devised which is much easier to implement and is probably more desirable in other respects. This is based upon an *ab initio* spin-orbit operator proposed by Ermler, *et al.*,[13] which is defined in terms of the difference between the REP for $j = \ell + 1/2$ and $j = \ell - 1/2$. This paper constitutes the first application of the new procedure.

Many of the relativistic, molecular calculations which have been reported,[14-19] including the first results from this laboratory,[2-4] were obtained by procedures which omit the SO effect until the final step. The wavefunction is set up in Λ-S (type a) coupling as it would be for a nonrelativistic calculation. The appropriate EP are the averaged REP (AREP), i.e., the weighted average REP for $j = \ell + 1/2$ and $j = \ell - 1/2$. Alternatively, some workers use atomic calculations in the Pauli approximation but with the SO terms deleted and thus obtain approximate AREP directly. Familiar calculational procedures are then available to obtain molecular potential curves, with extensive CI, for the Λ-S states without SO. If the SO effect is small, as it is for atoms of intermediate atomic number and may be in some other cases, it suffices to add the SO effect as a perturbation. A semi-empirical method is commonly used for the SO contribution; each coefficient is evaluated from atomic spectral data.

While some results obtained by the semi-empirical method are probably quite accurate, that method becomes much more doubtful when the orbitals contributing large SO terms are intimately involved in bonding. Furthermore, we wished to maintain fully the *ab initio* basis of our method.

With the recognition[13] that an ab initio SO operator can be derived from differences in the REP for $j = \ell + 1/2$ and $j = \ell - 1/2$, it became possible to assemble a complete calculational program which begins with molecular orbitals in Λ-S coupling and which includes electron correlation via a high-order CI step. Indeed the SO terms are introduced at the CI step on an equal basis with the electron repulsion terms.

Method

The REP are obtained from DF orbitals for the atoms by methods already well described. These REP are averaged and differenced with respect to spin as follows

$$U_\ell^{AREP} = (2\ell+1)^{-1} \left[\ell\, U^{REP}_{\ell,\ell-1/2} + (\ell+1)\, U^{REP}_{\ell,\ell+1/2}\right] \tag{1}$$

$$\Delta U_\ell^{REP} = U^{REP}_{\ell,\ell+1/2} - U^{REP}_{\ell,\ell-1/2}. \tag{2}$$

The complete effective potential without SO is

$$U^{AREP} = U_L^{AREP} + \sum_{\ell=0}^{L-1} \sum_{m=-\ell}^{\ell} (U_\ell^{AREP} - U_L^{AREP}) \,|\ell m\rangle\langle \ell m| \tag{3}$$

with the final factor the usual projection operator. The potentials cease to depend appreciably on the angular quantum number as soon as it exceeds that represented in the core of the atom; thus L can be chosen on that basis. This EP is introduced into the Hamiltonian and applied to the wavefunction in a now-familiar manner.

The wavefunction can be set up in Slater or Gaussian basis functions with real or complex angular factors. For linear molecules such as we consider in this paper, there would be considerable advantage in the use of the complex angular factors which are eigenfunctions of angular momentum. Nevertheless, we chose to use real, cartesian Slater-type

functions with a view toward future calculations for nonlinear molecules (in which cartesian Gaussian functions would be used).

The spin-orbit operator is just the difference between the complete, relativistic EP and the AREP. As shown in detail in reference 13, this may be simplified to

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

$$\left. - \frac{\ell+1}{2\ell+1} \sum_{-\ell+1/2}^{\ell-1/2} |\ell,\ell-1/2,m\rangle\langle\ell,\ell-1/2,m| \right] \qquad (4)$$

where the projection operators are now based on two-component relativistic spinors $|\ell,j,m\rangle$. The ΔU_{ℓ}^{REP} was defined in equation (2). The SO matrix elements for an atomic spin-orbital basis set will have the form

$$H_{pq}^{SO}(\rho_r\rho_s) = \langle\chi_p\rho_r|H^{SO}|\chi_q\rho_s\rangle \qquad (5)$$

where the χ are spacial basis functions and the Pauli spinors ρ define the α and β spins such that

$$\rho_i = \alpha = \binom{1}{0}, \quad \rho_i = \beta = \binom{0}{1}.$$

In this system the molecular calculation starts in the usual way with a choice of basis functions and the evaluation of the various integrals including those involving the AREP and the SO. An SCF calculation in Λ-S coupling is carried out and the resulting molecular orbitals may then be used to define the occupied and virtual space for a subsequent integral transformation and CI calculation. If, following the integral transformation, the spin-orbit integrals, equation (5), are added into the normal CI matrix, and the matrix diagonalized, one is able to avoid

he difficulties involved in a complex two-electron transformation while treating the spin-orbit corrections on an equivalent level with electron correlation. Within this general plan, the CI matrix may be formulated in either Λ-S or ω-ω coupling by making the proper spatial and spin combinations. However, for convenience and because the final wavefunction is probably intermediate in coupling, in the present work we have defined the CI matrix in terms of primitive determinants formed directly from the molecular orbital basis. Within such a crude formalism particular care must be taken in selecting determinants to ensure that the full range of coupling, from Λ-S to ω-ω is accounted for.

Given the integrals obtained from the transformation step, one can evaluate the elements of the CI matrix in the usual manner. One should note that, since this integral set does not include the spin-orbit integrals, many of the determinants will not couple to the dominant configuration. At this stage the matrix could be written out as block diagonal, the different blocks contributing to states, which in Λ-S coupling, do not mix due to space or spin symmetry differences. The spin-orbit integrals are now added to the matrix. In general the SO integral matrix may be complex leading to complex elements in the CI matrix. However, in the EP formalism the SO operator is a strictly one-electron operator. Therefore the number of such integrals will be small. Furthermore since a one electron operator can only couple determinants which differ by single promotions, the number of complex CI matrix elements will also be relatively small. This fact can be taken advantage of in the diagonalization algorithm.

Using conventional techniques (Givens or Jacobi) to diagonalize a complex hermitian matrix is a nontrivial task both in terms of developing computer codes and in actual computational time relative to a real symmetric

matrix. However, for very large matrices iterative techniques are typically employed. For algorithms such as the Nesbet procedure,[20] or Davidson procedure[21] or the method of optimal relaxation (MOR),[22] the required modifications in code to allow for complex elements are trivial. Furthermore due to the small number of such elements, the time required for diagonalization is only about a factor of two longer than that required for a comparable real matrix. (If one were to take advantage of the fact that for many cases the matrix elements are not complex but either real or imaginary, this factor could be reduced even further.)

The algorithm employed in the present work is a modification of the Davidson procedure. This scheme has the advantage that it is relatively stable even if the initial guess for the vector is poor. Furthermore since the CI matrix is defined in terms of primitive determinants, in the initial stages of the diagonalization the Nesbet or MOR procedures may tend to mix symmetries and thereby prolong the iterative process, whereas the Davidson technique will preserve the symmetry of the starting vector to within round-off error.

Calculations and Results

The effective potentials used in the present work are identical to those employed in references 7 and 8. Thus on thallium we treated explicitly the outer 13 electrons (10d, 2s and 1p), the frozen core comprising the remainder. The basis set for hydrogen was composed of two 1s Slater type orbitals (STO) and a single set of 2p STO for polarization. The exponents were taken from the AlH calculations of Cade and Huo.[23] For thallium we optimized a (2s, 2p, 2d) STO basis set using the ground state of the isolated atom. The optimization was carried out in L-S coupling using the spin-averaged potentials. The values of the n quantum numbers for the s, p, and d basis functions were

respectively 6, 6 and 5. This is a substantially better basis than was used in the previous Tl_2[13] and TlH[12] calculations where the maximum n value was 4. In subsequent molecular SCF calculations we found that using a triple zeta basis insignificantly altered the shape of the bonding curve for the ground state.

All calculations were carried out using real STO. Although this complicates the CI diagonalization by forcing some of the SO integrals to be imaginary, as stated earlier these problems cannot be easily avoided in polyatomic calculations. Also most available SCF and integral transformation programs are not compatible with complex basis functions.

Using the SO averaged EPs and the above basis set, molecular single configuration SCF calculations were carried out for the singlet sigma ground state of TlH. We then generated SO integrals and transformed the atomic orbital (AO) basis set integrals (including SO) into MO form. Since our previous MCSCF calculations suggested that the thallium d shell was largely unaffected by bond formation, that shell was frozen at the integral transformation stage of the calculation. Thus the CI calculation included explicitly only the outer three electrons of thallium and the 1s hydrogen electron.

Our CI wavefunction for the 0^+ state was generated from seven references with occupations (ignoring $1\sigma^2$), σ^2, $\sigma\pi_x\alpha\alpha$, $\sigma\pi_x\beta\beta$, $\sigma\pi_y\alpha\alpha$, $\sigma\pi_y\beta\beta$, $\pi_x\pi_y\alpha\beta$, and $\pi_x\pi_y\beta\alpha$. All normal single and double promotions were allowed from the first five references. The sixth and seventh were allowed only limited single and double promotions. This results in a total of approximately 1700 determinants. These seven references are required to allow the wavefunction the flexibility of intermediate coupling. The wavefunction formed in this manner will not give a fully balanced description

of the separated atoms relative to the molecule; hence, we have not attempted to compute a bond energy from this wavefunction alone. However, we have computed the energy for the separated atoms for comparison. For thallium we used a CI wavefunction generated using all single and double promotions from the three references $6s^2 6p_\sigma \alpha$, $6s^2 6p_x \beta$ and $6s^2 6p_y \beta$. For the $^2P_{1/2}$ state we obtained the total energy -50.6827 a.u. The $^2P_{3/2}$ state was higher in energy by .0339 a.u. or .92 eV, which is in reasonable agreement with the experimental splitting of .97 eV.[24]

For the 0^- state the first reference listed above (for the 0^+ state) is eliminated and certain sign relationships between the other terms are reversed. Also a $\sigma\sigma'\alpha\beta$ reference must be added for proper dissociation. Similar methods yield the appropriate references for the 1 and 2 states. From a Λ-S coupling basis the $^1\Sigma^+$ state relates to the lowest 0^+ state and the $^3\Pi$ term is split to yield the second 0^+ state and the lowest 0^-, 1, and 2 states. The $^1\Pi$ term yields the second 1 state while the highly repulsive $^3\Sigma^+$ term yields the second 0^- and third 1 states.

The calculated energies, relative to ground-state atoms, are listed in Table I and plotted in figure 1. Included are results for the first excited states of 0^+ and 1 symmetry. These states are related to the $^3\Pi$ and $^1\Pi$ terms and should be reasonably well described by the basis of these calculations.

The experimental evidence for TℓH was discussed by Ginter and Battino[25] whose potential curves for the two 0^+ states are compared in figure 2 with our calculations. Other data and references are summarized by Huber and Herzberg.[26] Calculated and experimental spectroscopic constants are given in Table II. As noted by Ginter and Battino there is some

uncertainty in the absolute energy scale, i.e., in the relationship of the atomic energies to the molecular curves in the measured region. The close agreement of our calculated curve for $0^+(I)$ with the experimental curve in the range 4.5 to 6 bohr supports the present interrelationship of atomic and molecular energies.

Our calculated potential curve for the ground state is somewhat too high at short interatomic distances. We believe that the cause is the absence of intershell correlation involving thallium d-shell electrons together with valence-shell electrons. Expansion of the CI to include all d-shell excitations of this type would exceed the capacity of our present program. Also, to properly include these effects, one would have to expand the basis by the addition of f orbitals. The very recent nonrelativistic calculations of McLean[27] for AgH with very extensive CI lend support to this view. He finds about 0.2 bohr shortening of R_e from that for an MCSCF calculation to the values for any of a number of calculations with high order CI including these intershell correlation terms. McLean also reports similar but less extensive results for AuH. It is clear that our wavefunction for T&H is somewhat deficient at these short interatomic distances but further work will be required to remedy this situation. For distances greater than about 4.5 bohr, where d-electron effects on the potential curve should be negligible, the agreement is excellent and confirms our general procedures.

The wavefunctions for the two 0^+ states, as expected, are dominated by singlet sigma and triplet pi character. As noted in our earlier work,[7] in the bonding region the molecular ground state is essentially singlet sigma. However, at very large distances the triplet pi slightly dominates. The reverse is true for the excited state; at shorter distances the wavefunction is heavily dominated by triplet pi character, with the singlet

sigma slightly dominating at very large distances. This interchange of sigma and pi character is apparently responsible for the peculiar behavior of the excited state around 5 to 7 bohr. Figure 2 shows the striking agreement of the shapes of the calculated and experimental curves for this 0^+(II) state.

With this substantial confirmation of our calculations for the two 0^+ states where the experimental evidence is unambiguous, it is interesting to consider our predictions for the 0^-, 1, and 2 states in relationship to the minimal experimental data for these states for TlH and in comparison with the data for InH where the spin-orbit splitting is much smaller but still significant. First, we note that the inner well at about 3.5 bohr in the 0^+(II), 0^-, 1(I), and 2 states appears to be at least partially the result of an avoided crossing which has been previously observed for the lowest $^3\Pi$ state of BH.[28] In the region outside the inner well the wavefunction is dominated by configurations which correspond roughly to the s^2p isolated thallium atom. However, in the region of the inner well, there is considerable sp^2 character, thereby allowing substantial sigma bonding of H with the s orbital on thallium. As noted above, this unusual shape of the excited 0^+ state agrees very well with the experimentally known potential.[25]

The inner portion of the potential curves for the 0^-, 0^+(II), 1(I), and 2 states are all very similar, hence their relationship to the $^3\Pi$ state in Λ-S coupling is pertinent. This is confirmed by an examination of the wavefunctions which are dominantly $^3\Pi$ in the range 3.0 to 3.5 bohr. The spin-orbit energies simply shift the absolute energies in this region, and the pattern is similar to that found for InH where the order is the same and the spacings also increase in the same sequence $(0^+-0^-)<(1-0^+)<(2-1)$. But the very large spin-orbit separation of the atomic energies for Tl has

a profound effect at larger R. The curve for the 1(I) state has no significant minimum; this agrees with the failure to observe discrete spectra for this state in TlH (in contrast to InH where it is observed).

Selection rules make direct observation of the 0^- state difficult, and it has not been measured for any of the molecules GaH, InH, or TlH, although there are reasonable estimates[26] for the first two. We predict a low but significant hump in the 0^- potential near 5 bohr. The relative shapes of the 0^- and 1(I) curves in the vicinity of 6 bohr can be understood from the details of the wavefunctions. At long distance the Tl atom must approach a $s^2p_{1/2}$ configuration where the $p_{1/2}$ spinor is 1/3 p_σ and 2/3 p_π. For the 1 state the s orbital on H can immediately have a bonding interaction with the p_σ on Tl whereas this is not possible for the 0^- state. Thus the initial interaction of the atoms is more repulsive in the 0^- state than in the 1 state.

There are several spectral lines observed by Larsson and Neuhaus[29] for TlH and TlD which have been interpreted as arising from transitions from the ground state to the 2 and 1(II) states. They conclude that their "explanations are largely conjectural" and that further experiments are needed. There is little doubt that these lines lie close to the dissociation limit to $^2P_{3/2}$ and $^2S_{1/2}$ atoms; indeed this interpretation is the basis for the interrelationship of atomic and molecular energies presently accepted by various authors.[26] Larsson and Neuhaus find for the 1(II) state the remarkably low and anharmonic sequence of vibrational spacings of 98 and 56 cm^{-1} with ω_e = 140 cm^{-1} and an R_e value about 2.9 Å or 5.5 bohr. Our calculated curve for the 1(II) state shows a nearly flat region from 5 to 7 bohr; a cubic equation through the four points in this region yields the results given in Table II, $\omega_e \cong 200$ cm^{-1} and $R_e \cong 3.1$ Å. Thus the agreement is remarkably good for such a sensitive feature in an excited state.

Larsson and Neuhaus also assign a few lines to transitions $2 \leftarrow 0^+(I)$ appearing in violation of selection rules because of a perturbation with the 1(II) state. Indeed our calculations yield a crossing of the 2 and 1(II) curves at 7 bohr. However, the curves are so flat that a very small shift in their relative energy would cause a large change in the R-value of the crossing.

In their second paper Larsson and Neuhaus also propose a crossing between the curves for, in their terms, the $^1\Pi$ and $^3\Pi_1$ states. This is unacceptable since both of these states have the same symmetry in type c coupling, i.e., they are the 1(I) and 1(II) states.

Our calculations indicate low potential maxima at large distances for the 2 and 1(II) states. The exact heights of these maxima are rather uncertain, however, because the electron correlation included in our atomic calculations is not exactly equivalent to that in the molecular calculations at large R-values. The calculations of Blint and Goddard for BH also show maxima at long distances for both the $^3\Pi$ and $^1\Pi$ states which lends some support for the existence of similar maxima in T&H.

Thus our calculated results are fully consistent with the experimental measurements, if allowance is made for uncertainties in accuracy, and tend to confirm some previously speculative aspects of interpretation while suggesting revision of other aspects.

Conclusion

We have demonstrated a method by which spin-orbit and electron-correlation effects are simultaneously introduced into the wavefunction for molecules containing very heavy atoms. This is the first calculation of this type that we are aware of. As opposed to most earlier calculations in which the spin-orbit corrections were added semi-empirically, in the

present work we have employed the rigorously defined (within the effective potential approximation) spin-orbit operator of ref. 13. Our work demonstrates that the use of imaginary matrix elements (as may be required in future polyatomic calculations) introduces only minor complications into the configuration interaction calculation.

Acknowledgments

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Table I. Potential Energy Curves for Several Low Lying States of T&H

R	$0^+(I)$	0^-	1(I)	$0^+(II)$	2	1(II)
3.0	-.0398	+.0250	+.0330	+.0272	+.0477	+.0736
3.25	-.0564	-	-	.0155	-	-
3.5	-.0645	.0093	.0166	.0115	.0327	.0526
3.75	-.0667	.0089	.0154	.0116	.0329	.0482
4.0	-.0648	.0100	.0153	.0133	.0344	.0457
4.5	-.0541	-	-	.0167	-	-
5.0	-.0398	.0127	.0115	.0183	.0385	.0410
5.5	-.0257	-	-	.0195	-	.0401
6.0	-.0137	.0126	.0070	.0214	.0394	.0399
7.0	-	-	.0048	-	.0402	.0402
∞	0.0	0.0	0.0	.0339	.0339	.0339

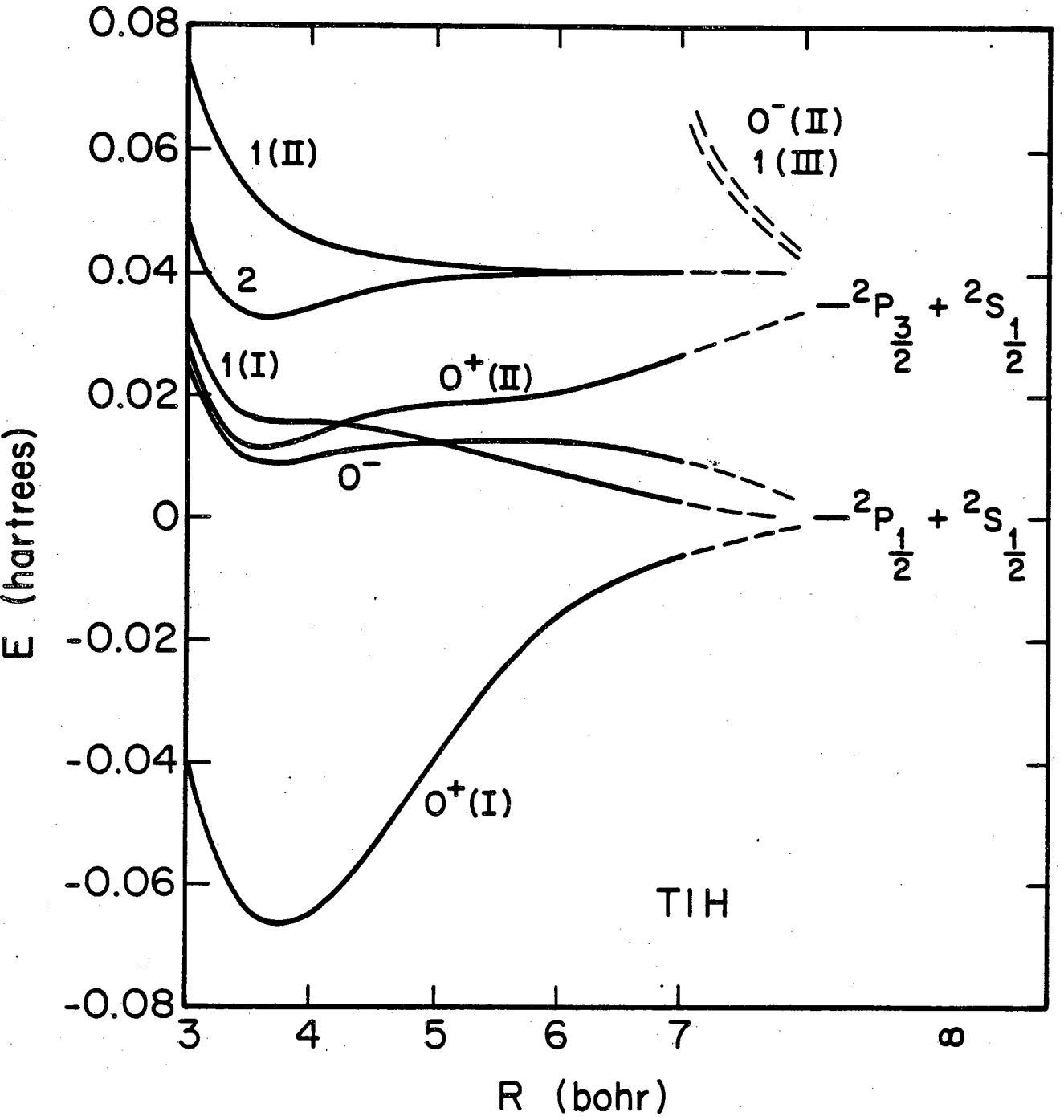
Table II. Spectroscopic Constants for Some Low Lying Bound States of TℓH

State	R_e(Å)	D_e(eV)	ω_e(cm^{-1})	T_e(cm^{-1})
0^+(I) Theory	1.99	1.81	1300	0
0^+(I) Experiment	1.87	1.97	1391	0
0^- Theory	1.95	0.24	795	16600
0^+(II) Theory	1.91	0.61	~1000	17100
0^+(II) Experiment	1.91	0.74	~760	17723
2 Theory	1.90	0.035	740	21800
1(II) Theory	3.1	-	~200	23400
1(II) Experiment	2.9	-	~140	24180

FIGURE CAPTIONS

Figure 1. Computed bonding curves for the two lowest 0^+ and 1 states and the lowest 0^- and 2 states of T&H. The dashed curves at large R are estimates.

Figure 2. A comparison of the experimental and calculated potential curves for the two lowest 0^+ states of T&H.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E (hartrees)
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6
7
∞
R (bohr)
1(II)
2
1(I)
O⁻(II)
1(III)
O⁺(II)
O⁻
O⁺(I)
$^2P_{\frac{3}{2}} + {}^2S_{\frac{1}{2}}$
$^2P_{\frac{1}{2}} + {}^2S_{\frac{1}{2}}$
TlH

Figure 1

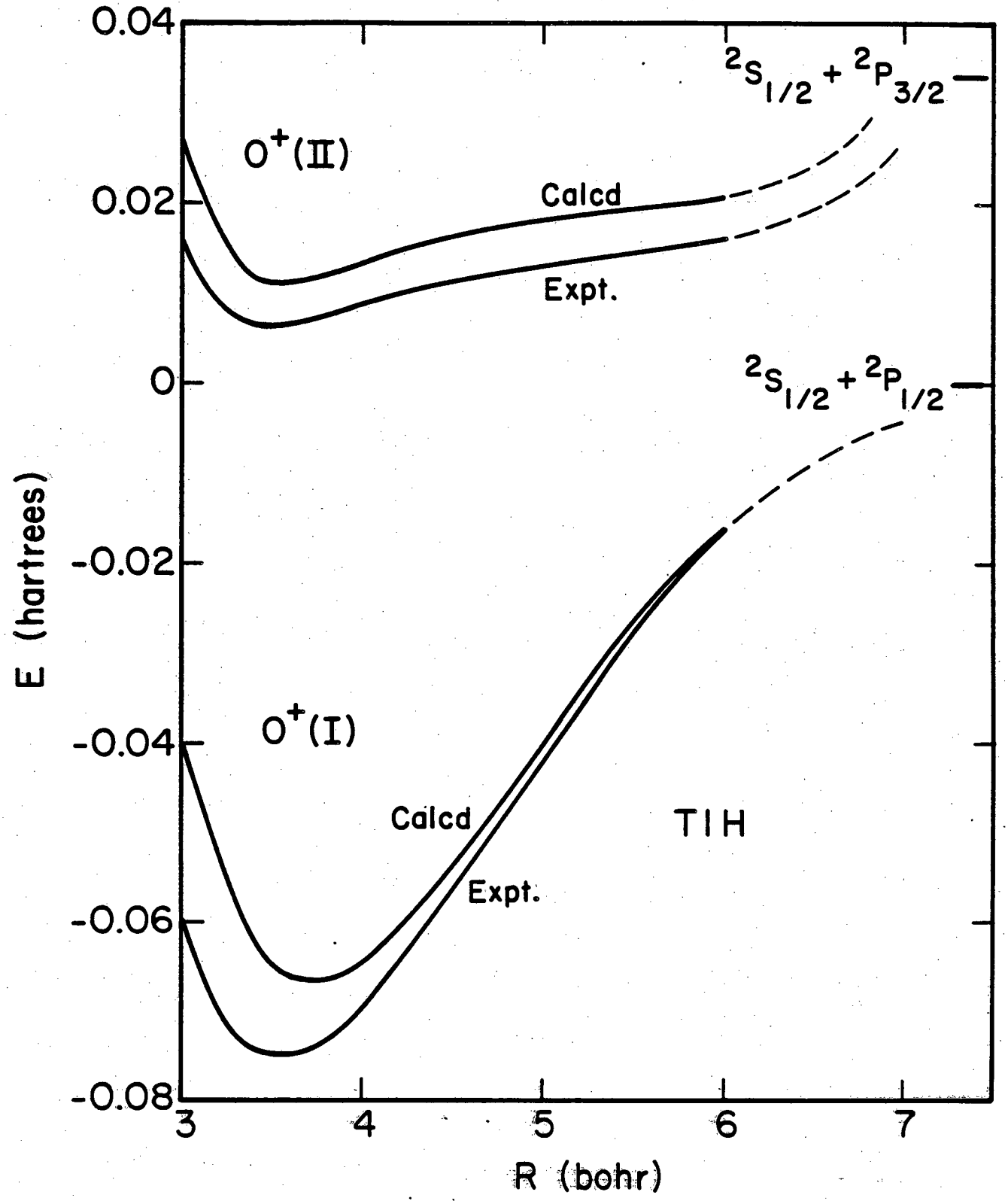
0.04
0.02
0
-0.02
-0.04
-0.06
-0.08
E (hartrees)
3
4
5
6
7
R (bohr)
$^2S_{1/2} + ^2P_{3/2}$
$^2S_{1/2} + ^2P_{1/2}$
$O^+(II)$
$O^+(I)$
Calcd
Expt.
Calcd
Expt.
TlH

Figure 2

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