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INTRODUCTION

One of the primary objectives of quantum chemical theory is the calculation of the energy of arrays of atoms (molecules, activated complexes, etc.) as a function of their geometrical arrangement. One seeks to make these calculations from first principles (i.e., without empirical adjustments) but approximations are necessary. The first approximation is implicit in the statement of the problem - that of Born and Oppenheimer in treating electronic motion separately with fixed nuclei. For elements of low atomic number, the nonrelativistic Schrödinger Hamiltonian is commonly assumed. One of our principal interests concerns the difference between results calculated on the basis of the Dirac, relativistic Hamiltonian from those calculated nonrelativistically. Before proceeding to that topic, however, it is desirable to review further the other approximations in the usual nonrelativistic treatments. Most serious are the approximations in the expression of the wavefunction: (1) the basis functions and (2) the terms for electron correlation (usually via configuration interaction (CI)). For atoms of small atomic number, all electrons are treated explicitly, but even for atoms of intermediate atomic number (e.g., chlorine) the calculational burden associated with inner-shell electrons has become substantial. Since these inner-shell orbitals are practically unaffected in molecule formation, it is useful to attempt to simplify the calculation by some process averaging the net effect of core electrons on valence electrons. Under given computer limitations this allows the use of more extended basis functions or more complete CI for the valence electrons.

As one turns ones attention to atoms of very high atomic number, the problem of inner-shell electrons becomes more severe and their removal from the detailed calculations is essential for most work with current computers. Also, relativistic effects are now very significant and the calculations must be based on the Dirac equation. These two aspects will be the primary topics of this paper.

Additional points to be noted include (1) the size and shape of the nucleus and (2) many particle relativistic effects. While these are important for some purposes, their effect on valence electrons is very small and will be ignored.

The general method for the removal of inner-shell electrons from the detailed calculations is a frozen core, effective potential approximation. Pertinent theory related to such an approximation will be considered on both nonrelativistic and relativistic bases. But the eventual verification is comparison with accurate all-electron calculations. Such comparisons will be made for nonrelativistic examples. All-electron, relativistic calculations on appropriate molecules with very heavy atoms are needed as standards of comparison but are not yet available.

EFFECTIVE POTENTIALS

There are several ways of formulating a frozen-core, effective potential (EP) approximation.[1] The basic criterion of merit is agreement with all-electron calculations for the properties of primary interest. The widely used Phillips-Kleinman[2] method was designed to yield accurate orbital energies. The initial emphasis was band energies for crystals. In effect the Phillips-Kleinman method transfers the orbital energy for core orbitals to the valence-electron orbital energy; hence, molecular or crystal orbitals in E.P. calculations yield relatively accurate orbital energies at the fixed, experimental geometry. But it has been found that the Phillips-Kleinman procedure is not satisfactory for calculation of dissociation energies or for determination of the potential minima which determine bond distances if there is more than one valence electron in the atom. Christiansen, et al.,[3] explained the cause of this difficulty and proposed a greatly improved alternative for the purposes of bond-distance and dissociation-energy calculations.

As shown in detail by Christiansen, et al., the basic requirement is that the valence pseudo-orbital from which the EP is derived, must be exactly the true atomic valence orbital in the outer or valence portion of the atom. In the core region the oscillations of the true atomic orbital are eliminated by a smoothing process, the details of which may be varied somewhat, but the total electron population in the core region must be the same for the pseudo-orbital as for the true atomic orbital. The Phillips-Kleinman method transfers some electron population from the valence to the core region; this is the cause of the difficulties with that procedure.

The particular improved procedure for definition of a valence pseudo-orbital used in this laboratory involves adoption of the exact atomic orbital outside a radius r_{match}. Inside r_{match} the pseudo-orbital is chosen to be a five-term polynomial in r with a leading power $\ell + 2$. At r_{match}, the amplitude and first three derivatives must agree. Also the total pseudo-orbital must be normalized, have no more than two inflexions nor more than three inflexions in the first derivative. One chooses the smallest r_{match} at which all of these conditions can be fulfilled. For a particular angular symmetry, the EP is derived from the radial factor χ_v of a valence pseudo-orbital by the expression

$$U_v^{EP}(r) = [(\epsilon_v + 1/2\ \nabla^2 + Z/r - W^{PS}_{val})\chi_v]/\chi_v \qquad (1)$$

where ϵ_v is the atomic orbital energy and W^{PS}_{val} is the potential (comprising the usual coulomb and exchange terms) arising from the interaction of an electron in χ_v with all other valence electrons in their pseudo-orbitals.

The general form of effective potential expression of Phillips and Kleinman[2] and of Kahn and Goddard[4] is retained. On the non-relativistic basis it is

$$U^{EP} = U^{EP}_L(r) + \sum_{\ell=0}^{L} \sum_{m=-\ell}^{\ell} [U^{EP}_\ell(r) - U^{EP}_L(r)] |\ell m\rangle\langle \ell m| \qquad (2)$$

where L is an angular quantum number larger than the ℓ values represented in the core, $U^{EP}_\ell(r)$ is the effective potential for angular symmetry ℓ in the atom of interest and the final factor is the projection operator for angular symmetry ℓ, m. Lee, et al.,[5] showed that the substitution of the Dirac Hamiltonian for the Schrödinger Hamiltonian led in a straightforward manner to the relativistic EP

$$U^{EP} = U^{EP}_{LJ}(r) + \sum_{\ell=0}^{L} \sum_{j=|\ell-1/2|}^{\ell+1/2} \sum_{m=-j}^{j} [U^{EP}_{\ell j} \quad U^{EP}_{LJ}] |\ell j m\rangle\langle \ell j m| \qquad (3)$$

Now the $U^{EP}_{\ell j}(r)$ are obtained from relativistic pseudo-orbitals and are different for $j = \ell - 1/2$ and $j = \ell + 1/2$. This difference with j for a given ℓ is just the spin-orbit effect. Again L, J are angular quantum numbers exceeding those represented in the core; it is found that there is no significant change of $U_{\ell j}^{EP}(r)$ for values of ℓ and j higher than this. The projection operators are now two-component angular bases that are eigenfunctions of the Pauli approximation to the Dirac Hamiltonian.

In addition to the spin-orbit effect, the relativistic EP will differ from the nonrelativistic EP numerically. In the Pauli approximation these differences are ascribed to the mass-velocity and the Darwin terms. But in our calculations we use the full Dirac operator rather than the Pauli approximation.

The EP can be expressed numerically or by expansions in appropriate mathematical functions. Since they are ordinarily derived from orbitals expressed numerically, we have found it convenient also to express the EP numerically.

Of course, one does not ordinarily have exact atomic orbitals as an input to the generation of effective potentials. Usually the orbitals from numerical Hartree-Fock (HF) or Dirac-Fock (DF) calculations are used. In addition to ground state atomic calculations, one must have results for appropriate excited states in which other orbitals of interest are occupied. If the energies calculated for these excited states agree reasonably well with the experimental values, one presumes that the various orbitals, pseudo-orbitals, and effective potentials will be quite accurate. This has been the case for the atoms of greatest interest in our recent work, e.g., gold, thallium, and lead.

But there are cases where the HF or DF calculations are in serious error with respect to the energy differences between various low-energy atomic states. This is well-known for the elements of the first transition series. For example, for nickel the $3d^8 4s^2 (^3F)$ and $3d^9 4s (^3D)$ states actually differ in energy by only 0.03 eV whereas HF calculations place the ^3D state higher by 1.28 eV. The error for the $3d^{10} (^1S)$ state is even larger. Also these errors are increased somewhat for relativistic DF calculations. Martin[6] discusses this problem and attempts its resolution by consideration of electron correlation. For the molecule Ni_2, fairly accurate calculations[7] can be made by considering only the $3d^9 4s$ state and suppressing the $3d^8 4s^2$ state of the atom. Such molecular calculations are hazardous, however, and it is desirable to obtain atomic calculations which accurately reproduce all of the important atomic states as a basis for the generation of the effective potentials.

The Christiansen effective potentials have been employed in comparison with all-electron (AE) calculations for F_2, $C\ell_2$, and $LiC\ell$ in the original paper[3] proposing that method and more recently[8] for the ground states of Ar_2, Kr_2, and Xe_2 and for the $^2\Sigma_u^+$ states of Ar_2^+, Kr_2^+, and Xe_2^+. In the first series the AE calculations are by Hay, et al;[9] in the latter by Wadt.[10] The basis sets and the extent of CI were chosen in each case to be effectively identical for the AE and the EP treatments. In all cases the AE and EP potential curves are essentially identical; this is true, not only at radii from the potential minima outward, but also at distances well up the repulsive curves where the frozen-core, EP approximation would be expected to be poorest. Figure 1 shows this comparison for the ground state of Ar_2 and the $^2\Sigma_u^+$ state of Ar_2^+. Thus for a variety of molecules the comparison of nonrelativistic EP and AE calculations confirms the accuracy of the EP results with the procedures described above. It is highly desirable that accurate, relativistic, AE calculations be completed for a few molecules where relativistic effects are substantial. Such standards can then be used to check relativistic EP calculations.

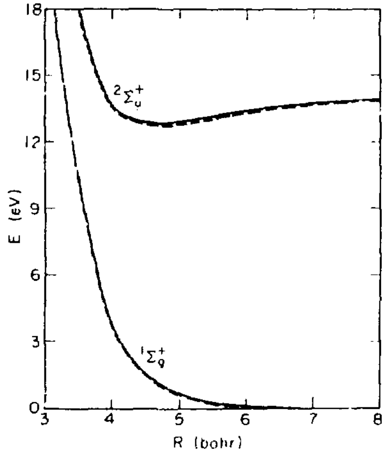

Figure 1. Comparison of AE (dashed) and EP (solid) dissociation curves for Ar_2 and Ar_2^+ from POL-CI calculations.

HAMILTONIAN FOR VALENCE-ELECTRON MOTION

The Schrödinger Hamiltonian is adequate for valence-electron motion in the outer or valence region of atoms or molecules. This is established[5] most easily by the smallness of the small component relative to the large component in the valence-level Dirac spinors for every heavy atoms. Thus it is an adequate approximation to simply ignore the small component and adopt the large component as the pseudo-orbital in the outer region of the atom. An alternate procedure, theoretically more exact, is to make the Foldy-Wouthuysen transformation of the DF orbital, but it has no significant effect on the result. Relativistic effects are important, in heavy atoms, on the motion of electrons near the nucleus - even of valence electrons of low angular momentum which do approach the nucleus. But *all of these effects are incorporated in the effective potentials:* both the indirect effects of core electrons and the direct effects on valence electron motion near the nucleus. Thus the use of the nonrelativistic Hamiltonian is adequate for molecular calculations but the relativistic properties of the EP, i.e., the difference for $j = \ell + 1/2$ and $j = \ell - 1/2$, impose relativistic symmetry on the molecular wavefunctions.

MOLECULAR CALCULATIONS: THEORY

Given the EP and the adequacy of the nonrelativistic Hamiltonian for valence electron motion, the form of the Hamiltonian for molecular problems is the same for the relativistic or nonrelativistic basis.

$$H = \sum_{\mu=1}^{n_v} h_\mu + \sum_{\mu>\nu} (r_{\mu\nu})^{-1} \qquad (4)$$

$$h_\mu = -1/2\, \nabla_\mu^2 + \sum_\alpha^N (-Z_\alpha/r_{\alpha\mu} + U_\alpha^{EP}) \qquad (5)$$

where the n_v valence electrons are indicated by μ or and the N nuclei by α. The effective charge Z_α is defined consistently with the EP for that atom. But, as noted above, the angular symmetries of the projection operators in U_α^{EP} differ in the relativistic and nonrelativistic cases and this must be recognized in the formulation of the wavefunction. Two general approaches are possible in the relativistic case and they will be discussed serially.

ω-ω Coupling

The most straightforward procedure for a relativistic problem is to formulate the molecular wavefunction as linear combinations of relativistic atomic spinors. For valence electrons the small components of the four-component Dirac spinors may be neglected, leaving two-component spinors. The matrix elements of the EP on the same atom are very simple since the projection operators involve the angular factors of these same two-component spinors. The radial factors can be expressed in either Slater or Gaussian basis functions. This procedure is given in detail (for Slater basis functions and linear molecules) by Lee, et al.,[12] for single configuration, self-consistent-field (SCF) calculations. It was extended to multiconfiguration SCF (MCSCF) calculations by Christiansen and Pitzer.[13]

For linear molecules this method is reasonably satisfactory since a relatively small basis of Slater functions is adequate and the various matrix elements are calculated without particular difficulty. For most cases, however, a single configuration is inadequate - even more inadequate than for the nonrelativistic examples with light atoms. The reason is that the ground atomic states of even the heaviest atoms of interest are in intermediate coupling rather than very close to j-j coupling. In other words the valence-level, electron-repulsion integrals are of the same magnitude as the spin-orbit (SO) terms. In ω-ω coupling the SO terms are included in the single configuration treatment. But it is not a good approximation to regard the electron-repulsion terms as a small perturbation; hence an appropriate MCSCF calculation is required. To properly account for electron correlation a large configuration interaction (CI) calculation is required, and this has not yet been accomplished in ω-ω coupling.

Molecules containing the thallium atom were chosen as examples for early treatment since that atom has only one 6p electron, but its SO interaction is large. Calculations were made for TℓH[13,14] and for several low-energy states of $T\ell_2^+$ and $T\ell_2$.[15]

There are serious limitations to the method starting in ω-ω coupling. Programs for CI calculations have not been prepared. Extensions from linear to nonlinear molecules will require new programs of considerable complexity. Also, one has been trained to think about molecules in Λ-S rather than ω-ω coupling, and it is easier, conceptually, to add SO terms to a calculation initiated in Λ-S coupling than to add electron repulsion terms to the ω-ω treatment. Thus we turn now to the alternate approach.

Λ-S Coupling

If one eliminates, for the moment, the spin-orbit term, the relativistic EP have the same symmetry as the nonrelativistic EP (but the numerical values of the EP still differ). This can be accomplished by taking the appropriate weighted average of $U^{EP}_{\ell j}$ for $j = \ell + 1/2$ and $j = \ell - 1/2$ and using that averaged relativistic EP (AREP) with the nonrelativistic projection operators in Equation (2). Specifically the AREP are

$$U^{AREP}_{\ell} = (2\ell + 1)^{-1} \; [(\ell + 1) \; U^{EP}_{\ell, \ell + 1/2} + \ell \; U^{EP}_{\ell, \ell - 1/2}] \qquad (6)$$

In the particular case of s elections there is no SO effect and no averaging is involved. Thus molecules such as Au_2, where the bonding involves primarily s orbitals, can be treated[16,17] easily in Λ-S coupling.

Alternatively, approximate AREP have been obtained[18] by the use of atomic calculations in which the mass-velocity and Darwin terms in the Pauli approximation are added to the nonrelativistic Hamiltonian. Since the SO terms is not included, the orbitals remain the same for $j = \ell + 1/2$ and $j = \ell - 1/2$. While this method is less accurate than the averaging of results from DF atomic calculations, the difference does not appear to be significant in work published to this time.

Given the AREP, the molecular calculation is set up with a wavefunction expressed in spin-orbitals and can be completed at the SCF, MCSCF, or CI level by the same methods used in nonrelativistic calculations. Either Slater or Gaussian basis functions can be used and programs are available for nonlinear as well as linear structures.

But for accurate results in most cases the SO term must be included at the MCSCF or CI level (or as a perturbation if it is small). In most work presently available this SO term is introduced empirically[18,19] with an operator related to the experimental SO splitting in the spectra. In many cases this appears to be a good approximation. Nevertheless, one prefers a nonempirical method with a sound theoretical basis and this was recently developed by Ermler, et al.[20] The spin orbit operator for use with molecular pseudo-orbitals is simply the difference in the EP for $j = \ell + 1/2$ and $j = \ell - 1/2$ multiplied by the appropriate projection operator.

$$H^{SO} = \sum_{\ell=1}^{L-1} \Delta U_{\ell}^{EP} \Big(\frac{\ell}{2\ell+1} \sum_{-\ell-1/2}^{\ell+1/2} |\ell,\ell+1/2,m\rangle\langle\ell,\ell+1/2,m|$$

$$- \frac{\ell+1}{2\ell+1} \sum_{-\ell+1/2}^{\ell-1/2} |\ell,\ell-1/2,m\rangle\langle\ell,\ell-1/2,m| \Big) \tag{7}$$

with

$$\Delta U_{\ell} = U^{EP}_{\ell,\ell+1/2}(r) - U^{EP}_{\ell,\ell-1/2}(r). \tag{8}$$

The matrix elements of H^{SO} with respect to the atomic spin-orbital basis set will have the form

$$H^{SO}_{pq}(\rho_r\rho_s) = \langle\chi_p\rho_r|H^{SO}|\chi_q\rho_s\rangle \tag{9}$$

where χ_p and χ_q are spacial basis functions and the Pauli spinors ρ_i define the α and β spins of the electrons such that $\rho_i = \alpha = \binom{1}{0}$ or $\rho_i = \beta = \binom{0}{1}$. The matrix elements of H^{SO} between various Λ-S states for a given molecule can then be obtained as a sum of these terms with appropriate expansion coefficients.

If real spin-orbitals are chosen for the basis, some of the SO matrix elements may be imaginary. This introduces some complications in CI procedures, but the roots are still real. Calculations following this procedure are in progress in this laboratory for TℓH, $T\ell_2$ and Pb_2; enough results have been obtained to establish the effectiveness of the method with relatively large CI.

It appears to be relatively straightforward to extend these methods to nonlinear molecules using existing programs for all but the SO terms and this is also in progress in this laboratory.

MOLECULAR CALCULATIONS: RESULTS

In view of the fact that the bonding electron in the gold atom is an s electron without SO effect, Au_2 was chosen for early study.[16,17] The bond in this molecule is anomalously strong, stronger than in either Cu_2 or Ag_2. It is found that this bond is stronger by about one electron volt on the real, relativistic basis than on a nonrelativistic basis. It is also of interest to note that Hg_2^{++} is isoelectronic with Au_2 and the stability of this anomalous dimeric, doubly charged ion can be ascribed to this [illegible] eV relativistic strengthening of the bond. Numerous excited states were calculated for Au_2. Good agreement was obtained for all experimentally known quantities, for both ground and excited states, although the calculated bond distances are somewhat too short. These Au_2 calculations were made with Phillips-Kleinman EP which are now known to yield bond distances that are too short. It would be desirable to repeat the Au_2 calculations with more reliable EP.

$T\ell_2$ and $T\ell_2^+$ represent particularly interesting examples. The $T\ell$ atom has a single electron in a $6p_{1/2}$ spinor. The $p_{1/2}$ spinor is 2/3 p_π and 1/3 p_σ and if one combines these to form a diatomic molecular spinor it is either σ bonding and π antibonding (if of g symmetry) or σ antibonding and π bonding (if of u symmetry). The lighter analogs of $T\ell_2$(B_2, $A\ell_2$, etc.) show σ bonding which is expected from the nonrelativistic p_σ orbitals. This state can be obtained for $T\ell_2$ but it requires promotion of the $6p_{1/2}$ electrons to p_σ orbitals which are 2/3 $p_{3/2}$ + 1/3 $p_{1/2}$ and this requires almost 2/3 eV per electron. Of course, one expects partial rather than full promotion.

The results[15] for $T\ell_2^+$ are shown in Figure 2. These are single configuration calculations in ω-ω coupling. Since there is a single bonding electron, the correlation correction for the change in energy on dissociation should be small. We see that the $(1/2)_g$ state of $T\ell_2^+$ is significantly bound with D_e = 0.58 eV and R_e = 3.84 Å. There is substantial promotion from $p_{1/2}$ toward p_σ spinors in this state. For the $(1/2)_u$ state of $T\ell_2^+$ there is only a very shallow potential minimum, but it does lie at a short bond distance (3.50 Å) as would be expected for a π bond. At longer distances the σ antibonding effect yields a broad maximum in the energy curve for the $(1/2)_u$ state. Experimentally $T\ell_2^+$ is a known species but its exact parameters (R_e, D_e) have not been determined.

Discussion of the low-lying states of $T\ell_2$ can best begin with consideration of the situation without the SO effect as shown in the upper curves[15] of Figure 3. There are three Λ-S terms $^3\Sigma_g^-$, $^3\Pi_u$, and $^1\Sigma_g^+$ which correspond to π^2, $\sigma\pi$, and σ^2 bonding, respectively. The potential minima lie at about the same level. When the spin-orbit effect is included, the energy of the dissociated atoms drops far below the minima of the curves without SO. The $^3\Sigma_g^-$ term splits into 0_g^+ and 1_g states while the $^3\Pi_u$ splits into 0_u^-, 0_u^+, 1_u, and 2_u states. The $^1\Sigma_g^+$ is a single state now called 0_g^+.

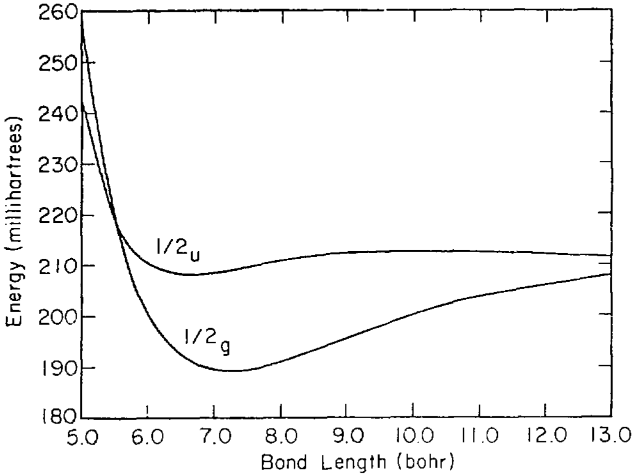

Figure 2. Potential curves for the lowest $(1/2)_g$ and $(1/2)_u$ states of $\mathrm{T}\ell_2^+$.

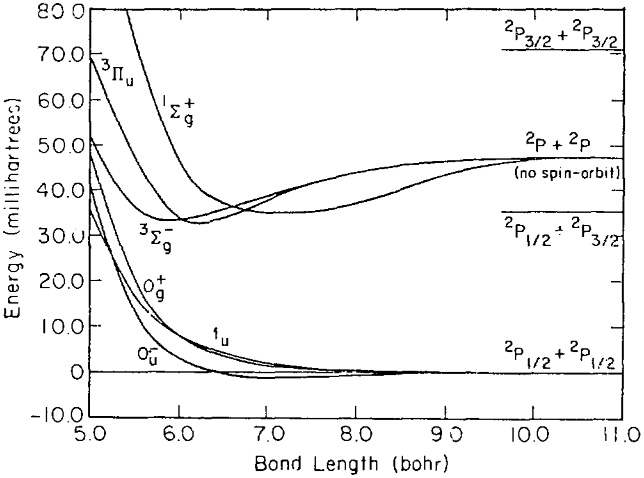

Figure 3. Potential curves for the 0_g^+, 0_u^-, and 1_u states of $\mathrm{T}\ell_2$ with ${}^3\Sigma_g^-$, ${}^3\Pi_u$, and ${}^1\Sigma_g^+$ curves (computed without spin-orbit coupling) for comparison.

Among these states in ω-ω coupling only 0_g^+, 0_u^-, and 1_u dissociate to yield two ground state atoms ($^2P_{1/2}$). The potential curves[15] for these states are shown on Figure 3; none is strongly bound but, with more adequate CI, all would doubtless show significant potential minima. The 0_u^- state is lowest in our calculations but the differences are small. These calculations (made in ω-ω coupling) include only the required number of configuration for dissociation to neutral atoms. This requires two configurations for 0_g^+ but a single configuration sufficed for 0_u^- and 1_u. Thus electron correlation for the two bonding electrons is not well-described in these calculations and the true potential curves will be somewhat lower at bond distances. There is very little experimental evidence for $T\ell_2$ molecules; one preliminary report[21] appeared very recently. The bond distance, spin multiplicity, and other characteristics assumed in that report will need revision. It is not now clear whether revised interpretation of these experiments will yield agreement with accurate calculations giving more consideration to electron correlation.

The calculations[13] made in ω-ω coupling for $T\ell H$ yielded the results in Table 1.

Table 1. Spectroscopic Parameters for $T\ell H$ in the Ground State Calculated by the ω-ω Coupling Method

	Calculated		
	SCF	MCSCF	Experimental
R_e (A)	1.93	1.96	1.87
D_e (eV)	0.93	1.66	1.97
ω_e (cm^{-1})	1450	1330	1391

In view both of basis set inadequacies and the small number of configurations (5) in the MCSCF treatment, the agreement is good.

RESULTS OF CI-SO CALCULATIONS IN Λ-S COUPLING

This supplement, written after completion of the preceding sections, reports results of CI calculations for several states of TℓH which were made by the Λ-S coupling procedure described above. The REP were the same as used previously[13,15] for Tℓ with 10d 2s 1p valence electrons. After the SCF calculation with 14 valence electrons in TℓH, the 10 primarily d orbitals were frozen and the CI calculation included explicitly only the outer three electrons of thallium and the 1s electron of hydrogen.

Our CI wavefunction for the 0^+ state was generated from seven reference configurations 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, the bond energy was not computed from this wavefunction alone. Instead, the energy for the separated atoms was computed for comparison. For thallium a CI wavefunction was generated using all single and double promotions from the three references $6s^2 6p_0\alpha$, $6s^2 6p_x\beta$ and $6s^2 6p_y\beta$. For the $^2P_{1/2}$ state the total energy was −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.[22]

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 was added. 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 shown in figure 4. 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[23] whose potential curves for the two 0^+ states are compared in figure 5 with our calculations. Other data and references are

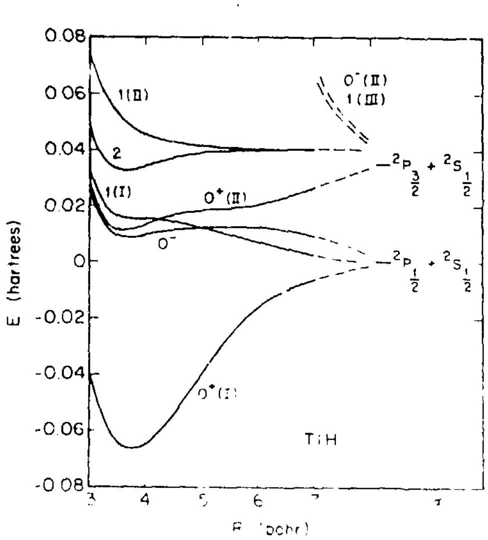

Figure 4. Computed bonding curves for the two lowest 0^+ and 1 states and the lowest 0^- and 2 states of TiH. The dashed curves at large R are estimates.

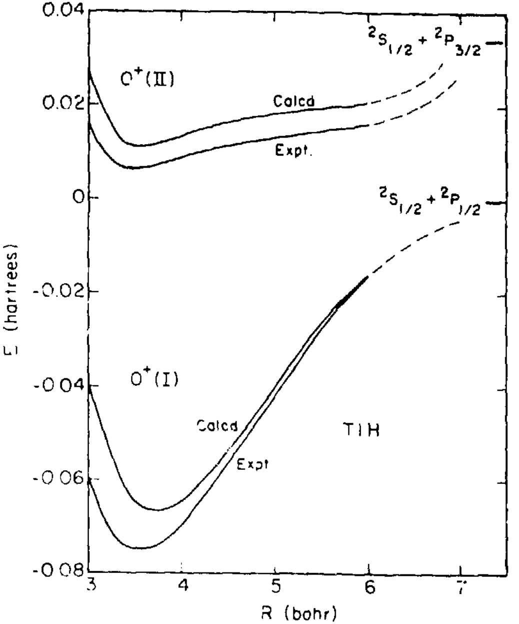

Figure 5. A comparison of the experimental and calculated potential curves for the two lowest 0^+ states of TiH.

summarized by Huber and Herzberg.[24] Calculated and experimental spectroscopic constants are given in Table II.

Table II. Spectroscopic Constants for Some Low Lying Bound States of TℓH Calculated with CI by the Λ-S Coupling Method

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	-	795	16600
0^+(II) Theory	1.91	0.61	1000	17100
0^+(II) Experiment	1.91	0.74	760	17723
2 Theory	1.90	-	740	21800
1(II) Theory	3.1	-	200	23400
1(II) Experiment	2.9	-	140	24180

The calculated potential curve for the ground state is somewhat too high at short interatomic distances. The cause is probably 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 the 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[25] 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 TℓH 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.

The wavefunctions for the two 0^+ states, as expected, are dominated by singlet sigma and triplet pi character. In the bonding region the molecular ground state is essentially singlet sigma. However, at very large distances the triplet pi slightly dominates since the Tℓ atom is 2/3 p_π. 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 5 shows the striking agreement of the shapes of the calculated and experimental curves for this 0^+(II) state.

With this substantial confirmation of these calculations for the two 0^+ states where the experimental evidence is unambiguous, it is interesting to consider the 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, one notes 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.[26] 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.[23]

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. 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[27] for $T\ell H$ and $T\ell D$ 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. 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 $\omega_e = 140$ cm^{-1} and an R_e value about 2.9 Å or 5.5 bohr. The 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, $\omega_e \doteq 200$ cm^{-1} and $R_e \doteq 3.1$ 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.

Thus these calculated results are fully consistent with the experimental measurements, if allowance is made for uncertainties in accuracy, and indicate the potential of this method to calculate rather complex features in molecular potential surfaces.

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