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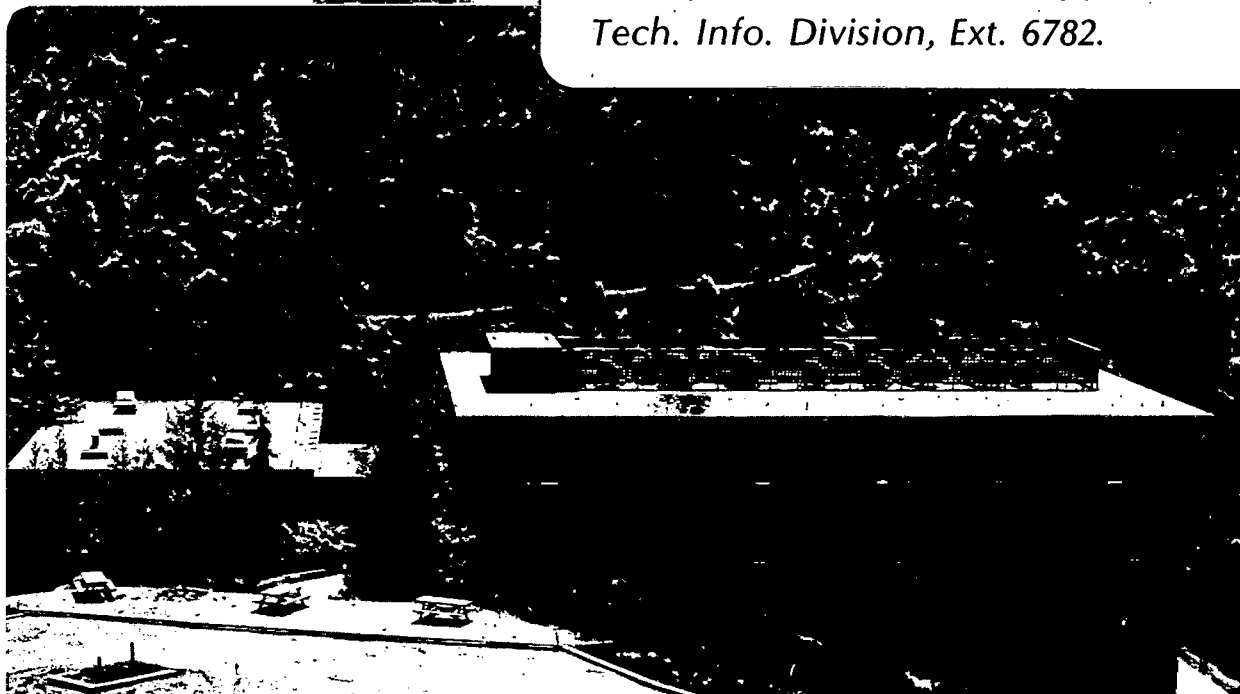
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AND RELATED PROPERTIES

Kenneth S. Pitzer

July 1982

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Relativistic Calculations of Dissociation
Energies and Related Properties

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Abstract

Methods of calculation of potential energy curves or surfaces, including dissociation energies, bond distances, and vibration frequencies, are discussed as well as recently obtained results for several molecules. The ab initio relativistic methods involve the derivation of "shape-consistent" effective potentials from Dirac-Fock atomic calculations. These effective potentials are averaged and differenced with respect to spin with the differences, $P_{3/2} - P_{1/2}$, etc., yielding spin-orbit operators. The molecular calculations are then set up in a familiar manner through the SCF stage using spin-averaged effective potentials. The final stage is a configuration interaction calculation including the spin-orbit terms as well as the electron repulsion terms.

Calculations which have been made for several low-lying excited states as well as the ground state for Au_2 , TlH , Tl_2 , Sn_2 , and Pb_2 are reviewed. Good agreement is obtained with spectroscopic data and a number of interesting predictions are made.

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This paper is based on a lecture at the 1982 Symposium on Relativistic Quantum Mechanics which reviewed both the calculational methods and the results for the dissociation energies and related properties for a variety of molecules containing very heavy atoms. Most chemical properties depend on the curves or surfaces giving potential energy, in the Born-Oppenheimer sense, for the dissociation or rearrangement of atoms in molecules or other clusters including activated complexes and in the extreme of large clusters, crystals. The location of potential minima yield bond distances and angles while the curvature near minima together, with atomic mass factors, yield vibration frequencies.

These potential curves or surfaces for light atoms are now routinely calculated to an accuracy of chemical interest and methods for improvement of precision are regularly forthcoming. The choice (1) of basis functions and (2) of excited configurations to represent electron correlation still involve some personal judgment in procedures which are otherwise quite unambiguous and based on "first principles". The calculational cost rises, however, very rapidly as the number of basis functions increases. Hence, if the atoms have many inner-shell electrons whose orbitals are essentially unchanged in the processes of interest, it is most advantageous to avoid the inclusion of large numbers of basis functions to represent these inner-shell orbitals.

Effective potential (EP) methods have been developed which circumvent the detailed representation of these inner-shell orbitals. It has now been demonstrated [1,2] that the interatomic potential curves or surfaces can be calculated accurately by effective potential methods; the agreement between the EP results and those from all-electron calculations provides the evidence of accuracy.

Relativistic effects are significant for these interatomic potential curves only for very heavy atoms which have many inner shell electrons. Thus it is very desirable to be able to use effective potential methods for any case where relativistic effects are important. Indeed for intermediate atomic numbers effective potential methods become advantageous while relativistic effects may still be negligible.

There are a number of ab initio EP methods as well as others of a semi-empirical nature. Even among the ab initio methods there are substantial differences in the accuracy to which various properties are calculated. For example, one method yields good results for the band structure of a crystal at fixed, experimental geometry, but yields poor results for the dissociation energy of either a molecule or a crystal. Thus, one should choose an EP method which has been shown to yield accurate results for the properties of interest. For interatomic potential energies, at least, the essential features are now understood [1] and there is no significant uncertainty in the choice of an accurate EP method.

Of course, if the phenomenon of interest makes a change in an inner shell of an atom, then the basic idea of an unchanged core is no longer appropriate, and no EP method will be satisfactory. The division between core and valence shells is arbitrary, however, and one can extend the valence shell to include all orbitals appreciably affected by any phenomenon related primarily to the outer electrons of the atom. For example, chemical bonding for the lead atom relates primarily to the 6p orbitals with important contributions also from the 6s orbitals. Thus the primary effects can be described by an EP treatment with a 4-electron valence shell for Pb. However, an EP treatment with a 14-electron valence shell, including the 5d shell, will yield higher accuracy for the ground state and can describe excited states with 5d vacancies.

A complete relativistic treatment of a many electron system involves many complications which are unimportant for the phenomena of interest here. Thus nuclear size and shape and many-electron relativistic effects such as the Breit term have negligible effect on valence-level properties. Furthermore, the relativistic effects which are important produce their effect on valence electrons indirectly. These effects arise in the inner portion of the atom and influence valence electrons through core-valence interactions and orthogonality. Thus these relativistic effects are all contained in the effective potentials and the Schrödinger kinetic energy operator is fully satisfactory for valence electron motion in an EP treatment.

The Pauli approximation to the Dirac equation includes three relativistic terms commonly called the mass-velocity, Darwin, and spin-orbit (SO) terms. All three yield effects of significance for our purposes. While a full atomic solution in the Pauli approximation would probably serve reasonably well as a basis for relativistic EP, there is no difficulty in using the exact Dirac operator for the atomic calculation. Desclaux [3] has developed and made available computer codes which yield numerical solutions for atoms with the Dirac operator in the self-consistent-field (SCF) approximation. There seems to the writer to be no reason to use a less accurate or complete atomic solution when a Dirac operator solution is readily available.

Given relativistic effective potentials (REP) for the atoms of the system, there are still important problems in the solution for the motion of the valence electrons for the array of two or more atoms of interest. This is the primary subject of this paper. Excited states will be considered as well as the ground state. Further comment will also be given in the next section concerning the determination of the effective potentials. Results will be presented for a number of diatomic molecules and interesting features discussed.

Effective Potentials

There is an extensive literature on effective or pseudo potentials; much of this concerns relatively crude methods which were useful for the purpose then at hand. But it is our objective to attain essentially the accuracy of an ab initio, all-electron treatment without detailed consideration of the inner orbitals in the molecular calculation. EP methods with this objective were developed on a nonrelativistic basis by Goddard and Melius [4] and by Kahn, et al. [5] among others. Their work was, in turn, based on that of Phillips and Kleinman [6].

For each angular symmetry the radial factor for the outer orbital ψ_ℓ of the atom is transformed to a pseudo-orbital χ_ℓ by a transformation which removes the inner nodes and oscillations. Then one calculates an EP for that angular symmetry U_ℓ^{EP} by requiring that it reproduce the pseudo-orbital and the true energy eigenvalue ϵ_ℓ through the one-electron equation

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} + U_\ell^{\text{EP}} + W_\ell\right) \chi_\ell = \epsilon_\ell \chi_\ell \quad (1)$$

Here Z is the nuclear charge and W_ℓ is the potential (comprising the usual Coulomb and exchange terms) arising from the interaction of the electron in χ_ℓ with all of the other electrons of the atom. This equation can be inverted to yield

$$U_\ell^{\text{EP}} = \left[\left(\epsilon_\ell + \frac{1}{2} \nabla^2 + \frac{Z}{r} - W_\ell \right) \chi_\ell \right] / \chi_\ell \quad (2)$$

which can be solved for U_ℓ^{EP} provided all nodes have been eliminated from χ_ℓ .

The critical aspect in EP methods concerns the quantity W_ℓ which should be the same whether calculated from the true orbitals or the pseudo-orbitals. At small r , i.e., within the core region, some difference in W_ℓ is unavoidable since the elimination of the nodes in the true orbitals

necessarily yields some differences between the pseudo-orbitals and the true orbitals. However, Christiansen, et al. [1] showed that differences in W_ℓ at small r were unimportant for our purposes whereas exact equality at large r , in the valence region, was essential. If the EP are to be used for a different purpose, this criterion might be altered, but we will not discuss that possibility.

It was shown that the criterion for the pseudo-orbital was exact equality to the true orbital in the region of large r . At intermediate r the difference should be only that necessary to maintain normalization with smooth behavior and with no nodes even at small r . Explicitly for each ℓ one writes

$$\begin{aligned} \chi &= \psi, & r &\geq r_m \\ \chi &= f, & r &< r_m \end{aligned} \tag{3}$$

where r_m is a radius at which the inner and outer expressions are joined. The inner function f is chosen to have the same value and the same first, second, and third derivatives as ψ at r_m and to have no nodes and not more than two inflexions or more than three inflexions in the first derivative in the range 0 to r_m . While other criteria of smoothness could be chosen, these seem satisfactory. In our work we have used a five term power series for f with a fairly high power (at least $\ell = 2$) in the leading term. The complete pseudo-orbital must be normalized and r_m is chosen as small as possible subject to satisfaction of all other criteria.

In our calculations we used the numerical expression for ψ_ℓ as it arises from the atomic calculation. Also χ_ℓ and, eventually, U^{EP} were handled as numerical expressions. For many purposes it would be useful to express the EP as expansions in analytical functions, but we have not done so in the work reported here.

The EP comprising a series of U_{ℓ}^{EP} functions of r must be generalized for use in molecules where the potential is no longer spherical. The appropriate expression for each atom in the nonrelativistic case was given by Goddard and Melius [4].

$$U^{EP} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} U_{\ell}^{EP} |\ell m\rangle\langle \ell m| \quad (4)$$

where ℓ and m have their usual significance. The final factor is a projection operator comprising the usual angular factors in the Schrödinger atomic orbitals.

While the sum over ℓ runs, in principle, to infinity, it is found that there is no appreciable change in U_{ℓ}^{EP} with change in ℓ after ℓ exceeds by one the maximum represented in the core. Thus it is convenient to rewrite equation (4) in the form

$$U^{EP} = U_L^{EP} + \sum_{\ell=0}^L \sum_{m=-\ell}^{+\ell} [U_{\ell}^{EP} - U_L^{EP}] |\ell m\rangle\langle \ell m| \quad (5)$$

where L is a value of ℓ exceeding, usually by one, the maximum ℓ represented in the core of the atom. The complete EP is then the sum of expressions of equation (5) for the various atoms in the molecule or other cluster.

This EP procedure has been tested [1,2] by comparison with all-electron calculations for the ground state potential curves for F_2 , Cl_2 , $LiCl$, Ar_2 , Ar_2^+ , Kr_2 , Kr_2^+ , Xe_2 , and Xe_2^+ . In all cases the agreement is excellent and within the uncertainties associated with small differences in choice of basis functions or other aspects of the calculations.

Relativity introduces several changes in the solution for the atom some of which must be retained in the effective potentials. Four-component spinors replace the nonrelativistic spin orbitals. It is readily shown that the two small components are negligible for valence-shell spinors (but not for inner-shell spinors). An alternate procedure, theoretically more exact, is to make

the Foldy-Wouthuysen transformation of the Dirac spinor, but this has no significant effect on the result for a valence-shell orbital. Thus it is easier and quite adequate to simply discard the small components of the Dirac spinor and to form pseudo-orbitals from the large components. In general, however, the angular factors are now different and the quantum number j is introduced to define the relativistic angular functions. Also the radial functions for $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ are now different. Thus there will be different pseudo-orbitals and effective potentials for $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$.

With this generalization the relativistic EP for an atom becomes

$$U^{EP} = U_{L,J}^{EP} + \sum_{\ell=0}^L \sum_{j=|\ell-\frac{1}{2}|}^{\ell+\frac{1}{2}} \sum_{m=-j}^j [U_{\ell,j}^{EP} - U_{L,J}^{EP}] |\ell jm\rangle \langle \ell jm| \quad (6)$$

where the projection operators are now two-component spinors comprising the angular factors for the two large components of the Dirac spinors. Again it is found that there is no significant change of $U_{\ell,j}^{EP}$ with ℓ and j above values slightly larger than those represented in the core; hence, the sum over ℓ is terminated as in the nonrelativistic case.

The difference in $U_{\ell,j}^{EP}$ between $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ is just the spin-orbit effect. We shall rearrange equation (6) on this basis later. The justification of this form of relativistic EP is discussed in more detail by Lee, et al. [7].

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 and Hay [8] discuss this problem and attempt its resolution by consideration of electron correlation.

Molecular Calculations: Theory

The Schrödinger Hamiltonian is adequate for valence-electron motion in the outer or valence region of atoms or molecules. This is established most easily by the smallness of the small component relative to the large component in the valence-level Dirac spinors for every heavy atoms. 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 $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$, impose relativistic symmetry on the molecular wavefunctions.

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.

$$H = \sum_{\mu=1}^{n_v} h_{\mu} + \sum_{\mu>\nu} (r_{\mu\nu})^{-1} \quad (7)$$

$$h_{\mu} = -\frac{1}{2} \nabla_{\mu}^2 + \sum_{\alpha}^N (-Z_{\alpha}/r_{\alpha\mu} + U_{\alpha}^{EP}) \quad (8)$$

where the n_v valence electrons are indicated by μ or ν 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., [9] for single configuration, self-consistent-field (SCF) calculations. It was extended to multi-configuration SCF (MCSCF) calculations by Christiansen and Pitzer [10].

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 usually 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.

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 $U_{\ell j}^{EP}$ for $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ and using that averaged relativistic EP (AREP) with the nonrelativistic projection operators in

Equations (5 and 6). Specifically the AREP are

$$U_{\ell}^{\text{AREP}} = (2\ell + 1)^{-1} [(\ell + 1) U_{\ell, \ell + \frac{1}{2}}^{\text{EP}} + \ell U_{\ell, \ell - \frac{1}{2}}^{\text{EP}}] \quad (9)$$

In the particular case of s electrons 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 [11,12] easily in Λ -S coupling.

Alternatively, approximate AREP have been obtained [13] 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 $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$. 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. But this method does not yield a theoretical value for the spin-orbit effect.

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.

For most examples where relativistic effects are significant, one should include the spin-orbit effect on as sound a theoretical basis as the mass-velocity and Darwin terms. The spin orbit operator operator for use with molecular pseudo-orbitals is simply the difference in the EP for $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ multiplied by the appropriate projection operator [14,15].

$$H^{\text{SO}} = \sum_{\ell=1}^{L-1} \Delta U_{\ell}^{\text{EP}} \left\{ \frac{\ell}{2\ell+1} \sum_{-l-\frac{1}{2}}^{l+\frac{1}{2}} |l, l + \frac{1}{2}, m\rangle \langle l, l + \frac{1}{2}, m| \right. \\ \left. - \frac{\ell+1}{2\ell+1} \sum_{-l+\frac{1}{2}}^{l-\frac{1}{2}} |l, l - \frac{1}{2}, m\rangle \langle l, l - \frac{1}{2}, m| \right\} \quad (10)$$

with

$$\Delta U_{\ell} = U_{\ell, \ell + \frac{1}{2}}^{\text{EP}}(r) - U_{\ell, \ell - \frac{1}{2}}^{\text{EP}}(r). \quad (11)$$

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

$$H_{pq}^{\text{SO}}(\rho_r \rho_s) = \langle \chi_p^{\rho_r} | H^{\text{SO}} | \chi_q^{\rho_s} \rangle \quad (12)$$

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 $\rho_i = \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ or $\rho_i = \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. 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.

More specifically our calculations in the Λ -S coupling method proceed first with an SCF calculation using AREP. It can be set up with either Slater or Gaussian basis functions and carried out with exactly the same programs as are used for nonrelativistic calculations including EP.

Next one carries out a configuration interaction calculation in which the spin-orbit matrix elements are included as well as those for electron repulsion. This CI calculation must include all low-energy configurations interconnected by the SO operator. The extent to which higher-energy configurations are included in order to optimize the orbitals and to represent electron correlation remains the same problem for relativistic as for non-relativistic calculations.

In general, the SO matrix elements may be complex and they are often purely imaginary. Thus the diagonalization procedure for the CI matrix must accommodate complex elements. The iterative procedure of Davidson [16] for diagonalization was readily modified to allow for complex elements. Since

the SO operator is a one-electron operator, there are only a few complex elements in a typical case, and the time required for diagonalization is not greatly increased. The roots are, of course, real.

Molecular Calculations: Results

One of the first molecules considered was Au_2 . It was chosen because the primary bonding is based on s electrons where there is no SO effect. Also it is of great interest because the bond is known to be anomalously strong, stronger even than that in Cu_2 and much stronger than that in Ag_2 . Furthermore Au_2 is isoelectronic with the unusual doubly charged, diatomic aqueous ion Hg^{++} . Unless the bond in Hg_2^{++} is very strong, one would expect that electrostatic repulsion would cause dissociation to two Hg^+ .

The calculations on Au_2 were made by older EP methods now known to yield somewhat too short bond distances. Nevertheless, the results [11,12] agreed quite well with experiment [17,18] for various properties of the ground and the two experimentally characterized excited states as shown in Table I which also includes results for six excited states not yet observed. It was found that the 2.3 eV bond in Au_2 is weakened by about 1 eV if the calculation is made on a nonrelativistic basis. Thus the anomalously great strength of the bond in Au_2 or Hg_2^{++} is primarily a relativistic effect.

The potential curves for a large number of excited states of Au_2 were calculated and are reported [12]. For the excited states the SO effect must be included; for Au_2 this was done on a semi-empirical basis.

Tl_2 and Tl_2^+ represent particularly interesting examples. The Tl atom has a single electron in a $6p_{1/2}$ spinor. The $p_{1/2}$ spinor is $2/3 p_\pi$ and $1/3 p_\sigma$ 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 Tl_2 (B_2 , Al_2 , etc.) show σ bonding which is expected from the nonrelativistic p_σ orbitals. This state can be obtained for Tl_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 [19] for Tl_2^+ are shown in Figure 1. 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 Tl_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 Tl_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 Tl_2^+ is a known species but its exact parameters (R_e , D_e) have not been determined.

Discussion of the low-lying states of Tl_2 can best begin with consideration of the situation without the SO effect as shown in the upper curves of Figure 2. There are three Λ -S terms $^3\Sigma_g^-$, $^3\Pi_u$, and $^1\Sigma_g^+$ which correspond to π^2 , $\pi\sigma$, 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^+ . 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 for these states are shown on Figure 2; 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 [19] were made in ω - ω coupling and include only the required number of configuration for dissociation to neutral atoms. This requires two configurations for O_g^+ but a single configuration sufficed for O_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 Tl_2 molecules; one preliminary report [20] on D_e appeared very recently. The bond distance, spin multiplicity, and other characteristics assumed in that report will need revision. More accurate calculations giving more consideration to electron correlation are required before one can reinterpret the experimental data and determine whether there is agreement for D_e .

The molecule TlH is also of considerable interest and has been treated in both ω - ω coupling [21,22] and Λ -S coupling [23]. The latter calculations include a much more complete consideration of electron correlation and thereby yield a deeper potential well for the ground state; when this is considered, the various calculations are fully consistent. The calculation in Λ -S coupling will be described in some detail as an example of that method.

A 13 electron valence shell was selected for the Tl atom; thus the SCF calculation involved 14 electrons. Cartesian Slater-type functions were used with a double zeta basis for s, p, and d on Tl and s on H. A single p-function on H was added. After the SCF step, the 10 primarily d orbitals were frozen and the CI calculation included explicitly only the outer four electrons.

Our CI wavefunction for the O^+ state was generated from seven reference configurations with occupations (ignoring $1\sigma^2$), σ^2 , $\sigma\pi_x\alpha\alpha$, $\sigma\pi_x\beta\beta$, $\sigma\pi_y\alpha\alpha$, $\alpha\pi_y\beta\beta$, $\pi_x\pi_y\alpha\beta$, 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 $6s^2 6p_{\sigma} \alpha$, $6s^2 6p_x \beta$ 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 [24].

For the 0^- state the first reference configuration 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 3. 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 T&H was discussed by Ginter and Battino [25] whose potential curves for the two 0^+ states are compared in Figure 4

with our calculations. Other data and references are summarized by Huber and Herzberg [26]. Calculated and experimental spectroscopic constants are given in Table II.

The calculated potential curve for the ground state is somewhat too high at short interatomic distances. The cause is probably the absence of inter-shell 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 [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 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 $2/3 p_\pi$. 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 4 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. 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. 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 and are discussed elsewhere [23]. The situation for the 2 and $1(II)$ states at 5 to 7 bohr is interesting. A very flat minimum has been observed for the $1(II)$ state as noted in Table II. When one considers the shallowness of this minimum, the agreement of calculations with experiment is remarkable. Less certain experimental evidence indicates that the curve for the 2 state crosses that for the $1(II)$ state in this region and the calculations are also in agreement on this point.

Calculations have just been completed for Pb_2 and Sn_2 . A preliminary report has been published for Pb_2 [28]. Since the method is essentially similar to that for TlH it will not be discussed. The larger number of bonding electrons do complicate the situation. The results for Sn_2 [29] are shown on Figures 5 and 6 and those for Pb_2 on Figures 7 and 8.

For Sn_2 the SO effect is considerably smaller than the bond energy. The lowest configuration $\sigma_g^2 \pi_u^2 ({}^3\Sigma_g^-)$ without SO) is split with the 0_g^+ component lower. The $\sigma_g \pi_u^3$ configuration yields ${}^3\Pi_u$ and ${}^1\Pi_u$ terms without SO and the triplet is lower in energy. It is split by SO with the 2_u state lowest, 1_u next, and 0_u^+ and 0_u^- at essentially the same energy. The configuration $\pi_u^4 ({}^1\Sigma_g^+)$ which is the lowest in C_2 , is important only at short interatomic distances where it yields an avoided crossing in the 0_g^+ states. The potential curves without SO are also shown as dashed lines.

For Pb_2 the SO effect is much larger and has a more drastic effect on the potential curves shown in Figures 7 and 8. Again the calculations without SO are shown as dashed curves. Although most of the aspects for Pb_2 are expected from Sn_2 with an increase in the SO splitting, a few points deserve

special comment. The π_u^4 configuration yields a marked shoulder on the repulsive portion of the ground 0_g^+ curve. While the 2_u curve is lower than 1_u at the distance of the minima, 2_u dissociates to higher energy atoms than 1_u ; hence the curves cross at about 3.3 \AA .

The calculated dissociation energies, 0.88 eV for Pb_2 and 1.86 eV for Sn_2 , agree well with the experimental mass spectrometric data [30,31] after recalculation to correct the partition function to present values of R_e , ω_e , and electronic multiplicity [32].

Several excited states are known for Pb_2 and the agreement between calculation and experiment is good [28]. Less is known about excited states for Sn_2 , but there is no disagreement.

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Table I. Au₂ Spectroscopic Constants

State		R_e (Å)	D_e (eV)	ω_e (cm ⁻¹)	T_e (eV)
X O _g ⁺	Calc.	2.37	2.27	165	0
	Expt. ^a	2.47	2.31 ^b	191	0
A O _u ⁺	Calc.	2.51	.79	121	2.61
	Expt. ^a	2.57	1.00	142	2.44
B O _u ⁺	Calc.	2.50	1.38	146	3.55
	Expt. ^a	2.51	1.78	180	3.18
1 _u	Calc.	2.44	.76	138	2.64
2 _u	Calc.	2.43	.94	143	2.57
0 _g ⁻	Calc.	2.44	.85	140	2.66
1 _g	Calc.	2.44	.84	140	2.67
2 _g	Calc.	2.61	.35	110	3.16
3 _g	Calc.	2.61	.41	112	3.10

^a from Ref. 17.

^b from Ref. 18.

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

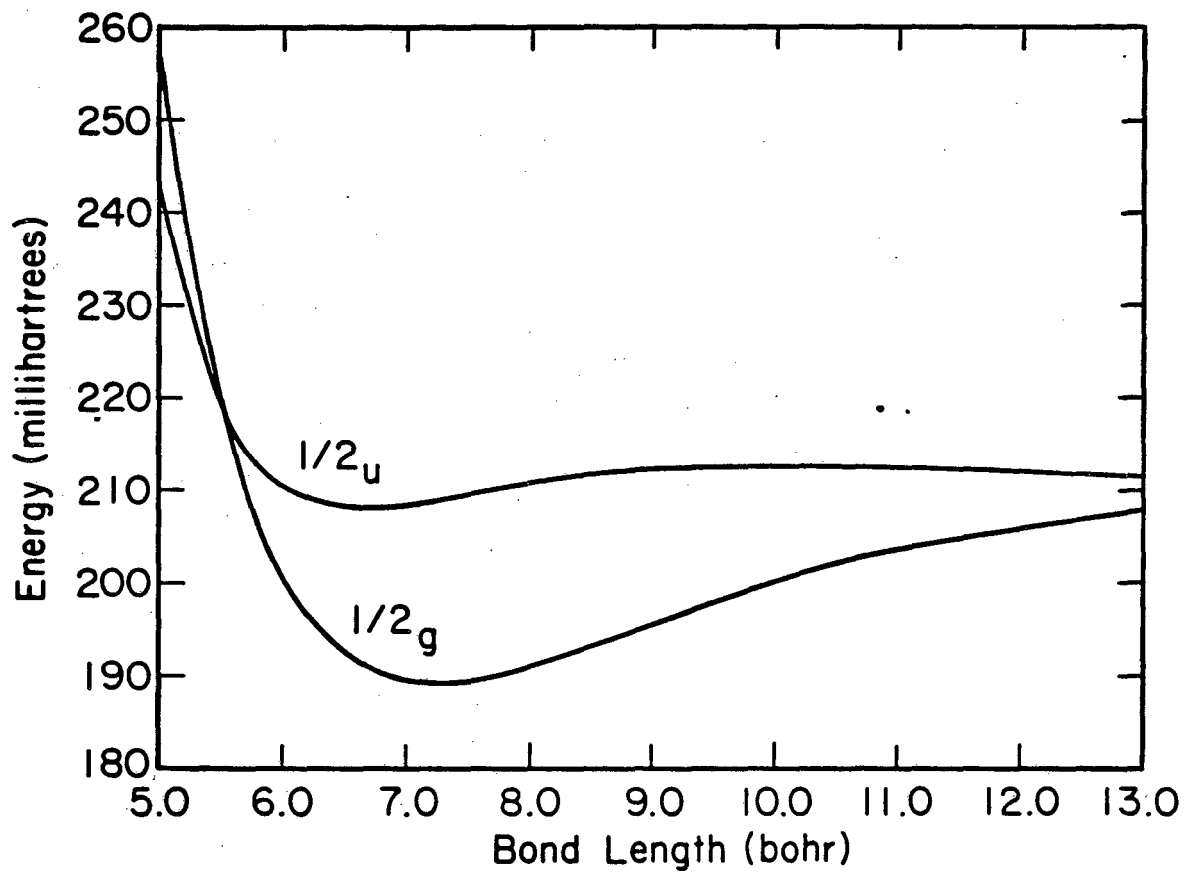


Figure 1. Potential curves for the lowest $(1/2)_g$ and $(1/2)_u$ states of Tl_2^+ .

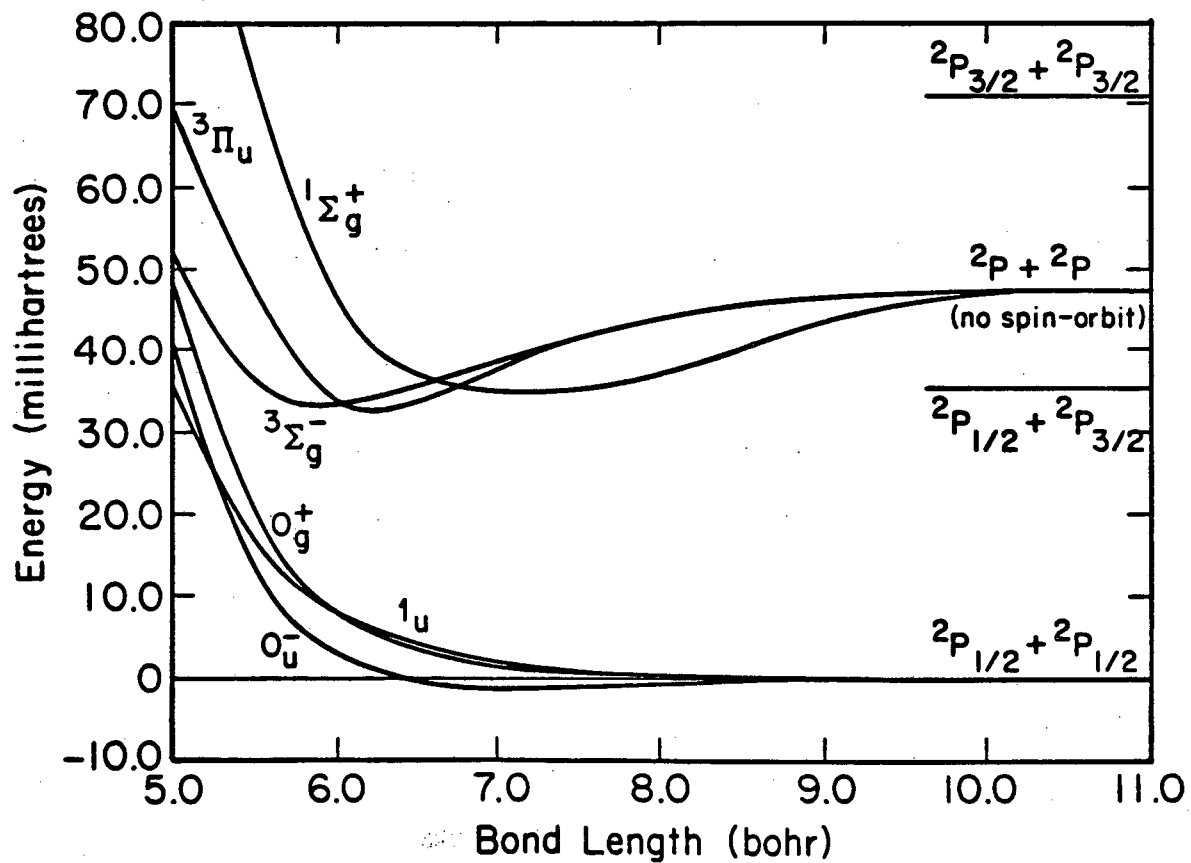


Figure 2. Potential curves for the 0_g^+ , 0_u^- , and 1_u states of Tl_2 with $3\Sigma_g^-$, $3\Pi_u$, and $1\Sigma_g^+$ curves (computed without spin-orbit coupling) for comparison.

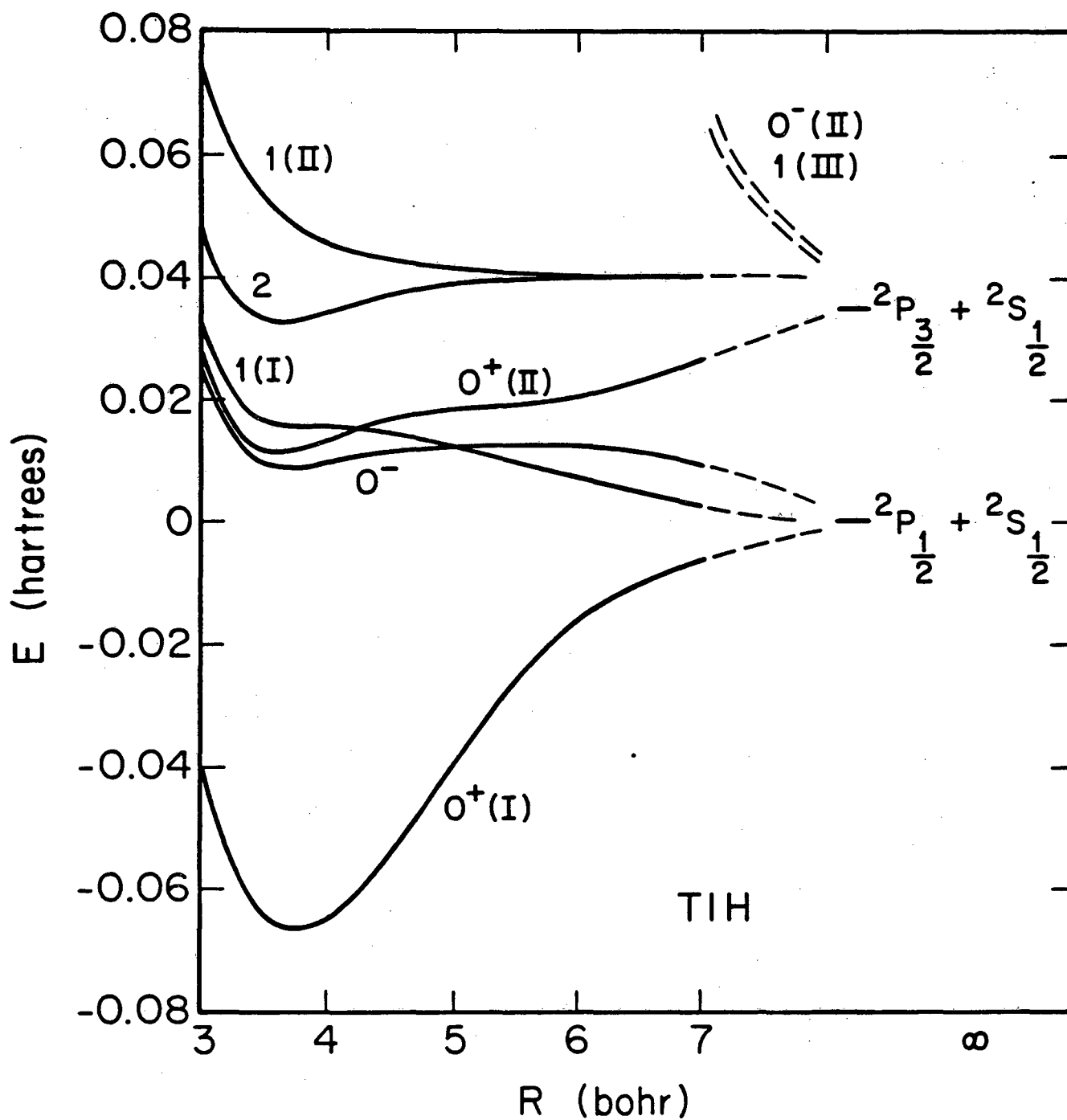


Figure 3. Computed bonding curves for the two lowest 0^+ and 1 states and the lowest 0^- and 2 states of TlH. The dashed curves at large R are estimates.

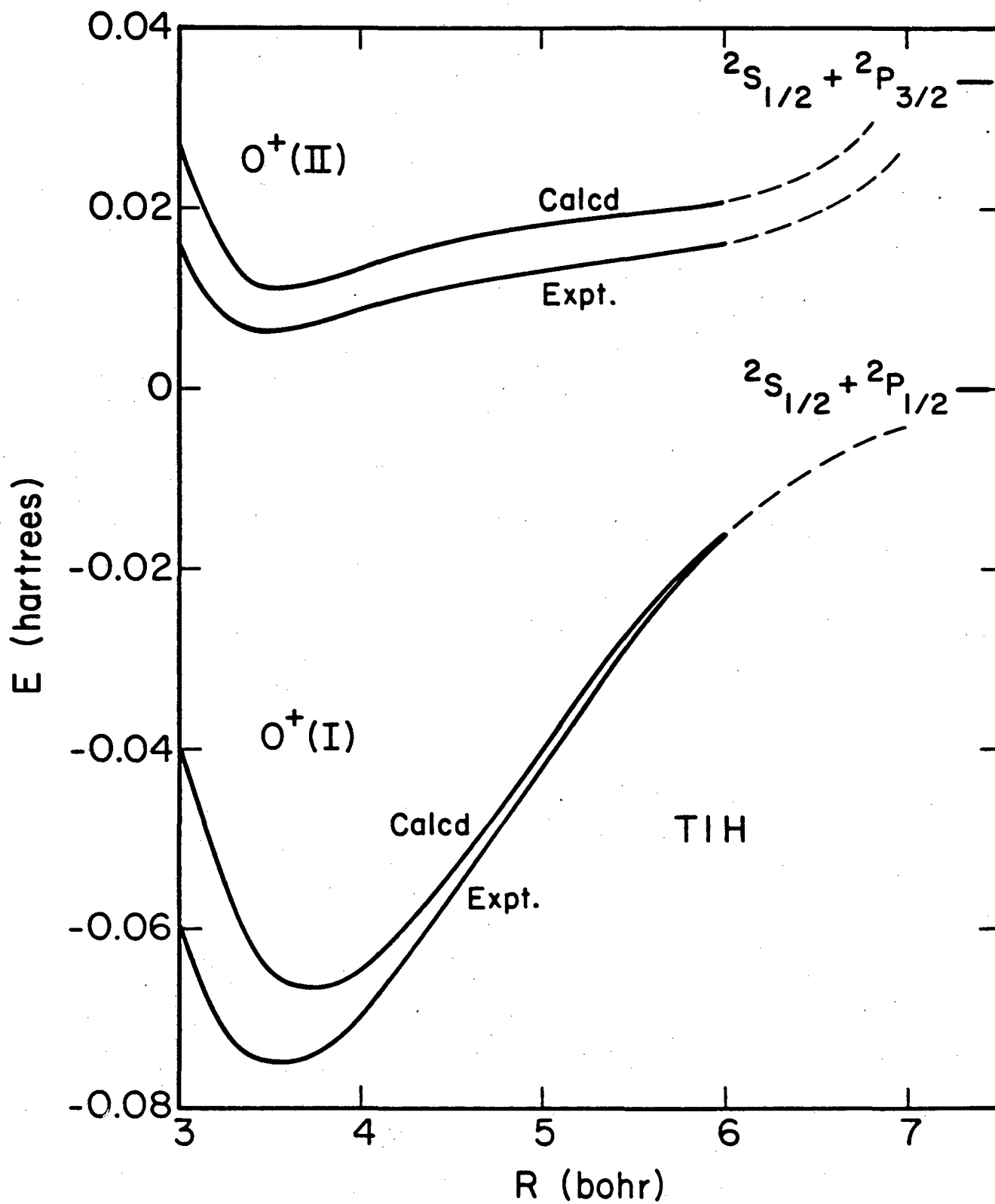


Figure 4. A comparison of the experimental and calculated potential curves for the two lowest O^+ states of TlH.

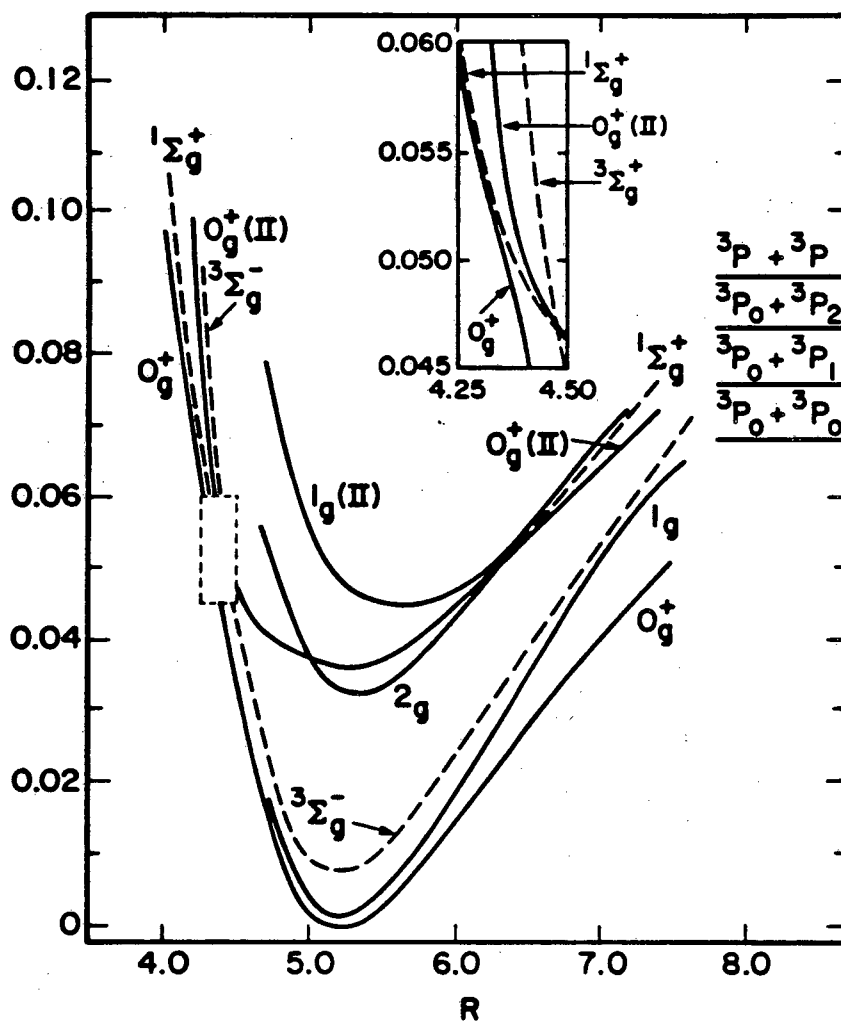


Figure 5. Potential curves for the g states of Sn_2 . The dashed curves are computed without the spin-orbit term. The energies are in hartrees and the distances in bohr. The inset shows the region of avoided crossing near 4.4 bohr.

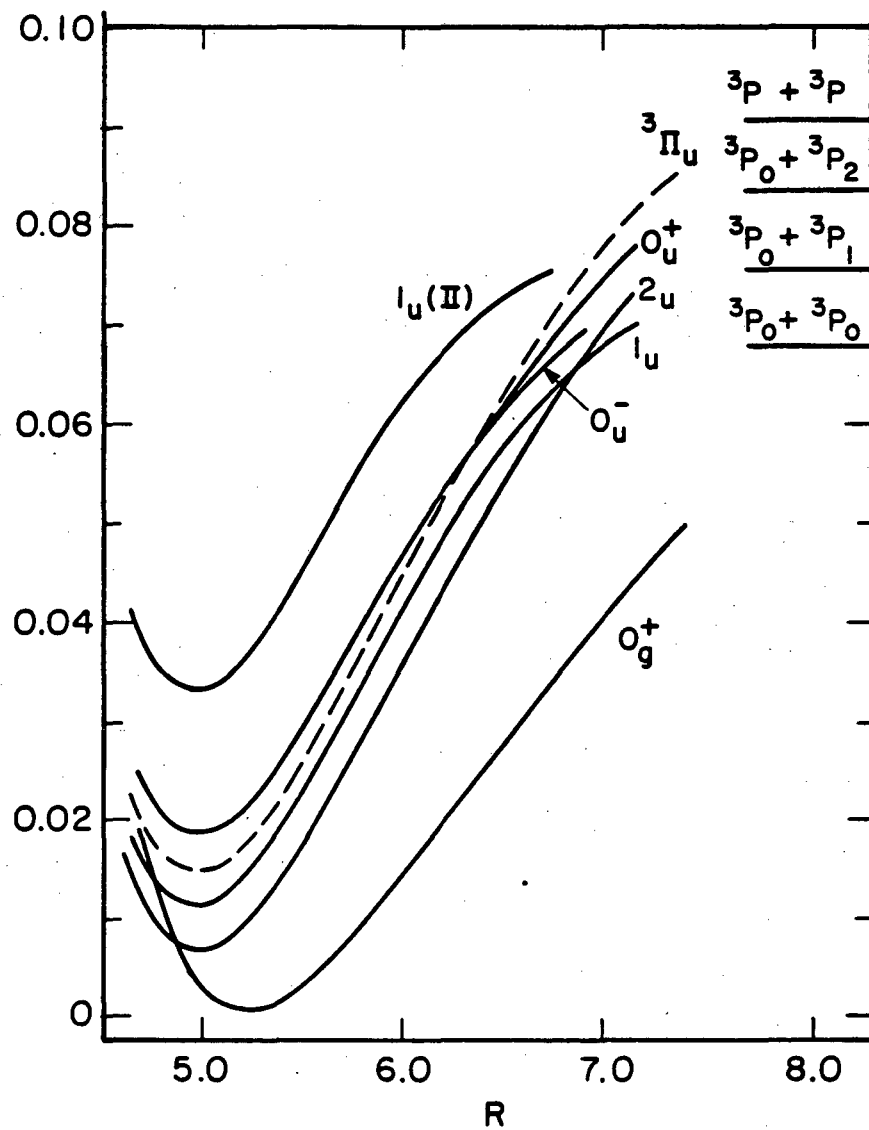


Figure 6. Potential curves for the u states and the ground 0^+ state of Sn_2 . Details are the same^g as for Figure 5.

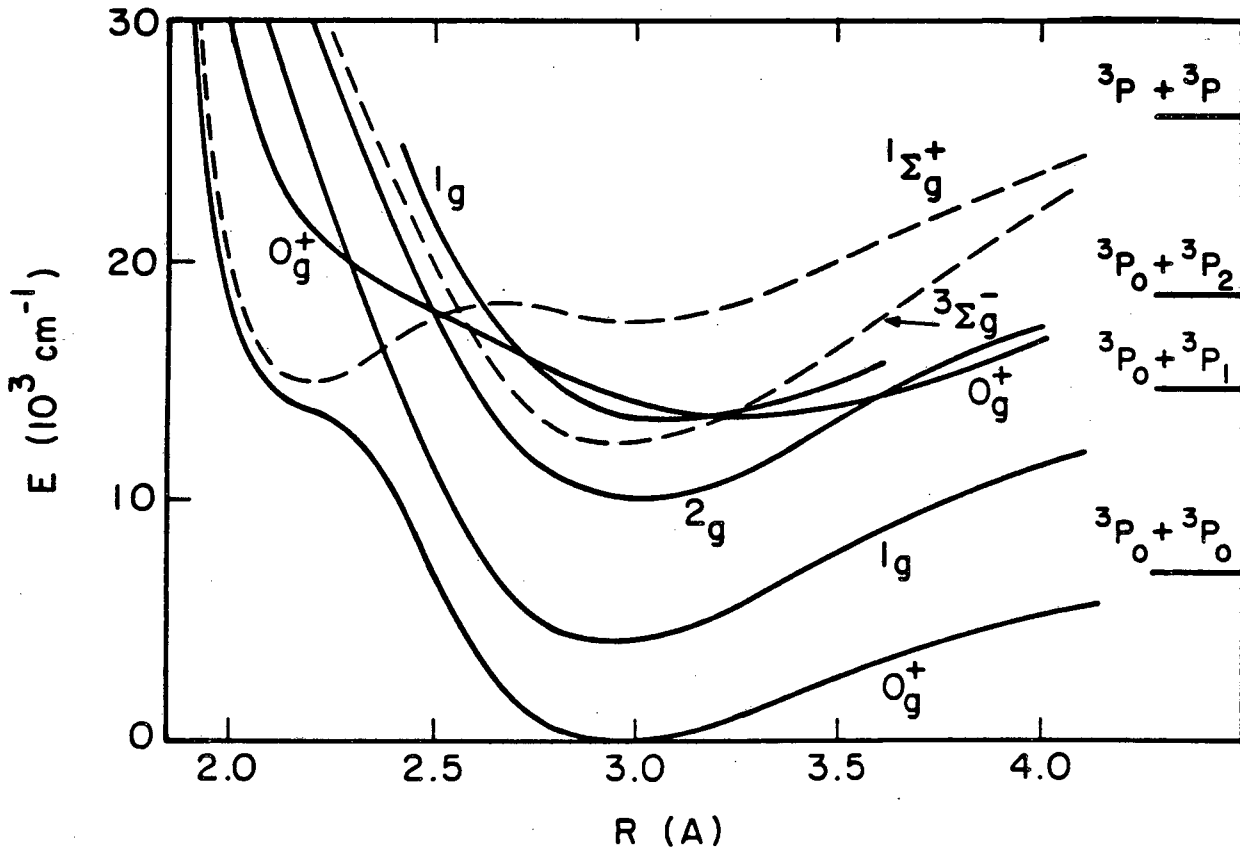


Figure 7. Calculated potential curves for g states of Pb_2 . The dashed curves are computed without the spin-orbit term.

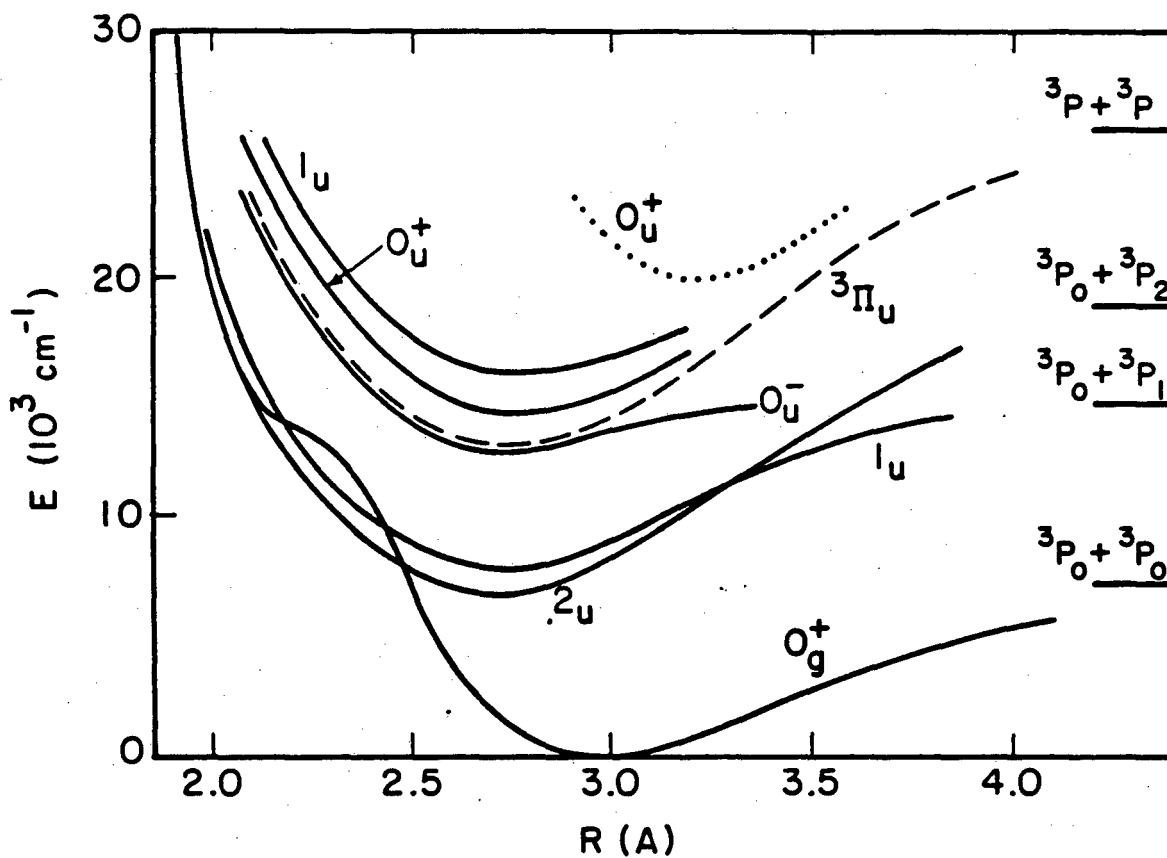


Figure 8. Calculated potential curves for u states and the ground 0_g^+ state of Pb_2 . An estimated curve at the experimental T_e is also given for the upper 0_u^+ state.

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