

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVISTIC EFFECTS. IV. POTENTIAL ENERGY CURVES FOR THE GROUND AND SEVERAL EXCITED STATES OF AU2

### Permalink

<https://escholarship.org/uc/item/1h27m3r6>

### Author

Ermler, Walter C

### Publication Date

1978-08-01

*A*  
*RCO*  
*OSTI*  
*CSL*

AB INITIO EFFECTIVE CORE POTENTIALS INCLUDING RELATIVE EFFECTS. IV. POTENTIAL ENERGY CURVES FOR THE GROUND AND SEVERAL EXCITED STATES OF  $Au_2$

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

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

August 1978

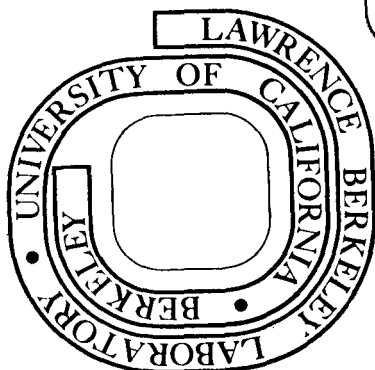
OCT 6 1978

LIBRARY AND  
DOCUMENTS SECTION

Prepared for the U. S. Department of Energy  
under Contract W-7405-ENG-48

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782*



*LBL-8057  
c. j.*

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Ab Initio Effective Core Potentials Including Relativistic Effects. IV. Potential Energy Curves for the Ground and Several Excited States of Au<sub>2</sub>

Walter C. Ermler,<sup>a)</sup> Yoon S. Lee, and Kenneth S. Pitzer

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

Abstract

The ground and excited states of Au<sub>2</sub> are studied using ab initio averaged relativistic effective core potentials (AREP) and MCSCF-CI procedures. Spin-orbit effects are included in the excited states derived from  $^2S_{1/2} + ^2D_{3/2}$  and  $^2S_{1/2} + ^2D_{5/2}$  atomic states using an empirical procedure. The ground state dissociation energy is calculated to be 2.27 eV as compared to the experimental value of 2.31 eV. The calculated energies for the two spectroscopically allowed  $O_g^+$  to  $O_u^+$  transitions and other molecular parameters also agree reasonably with experiment.

a) Present Address: Department of Chemistry and  
Chemical Engineering  
Stevens Institute of Technology  
Hoboken, N.J. 07030

## I. Introduction

There were several reasons for the choice of diatomic gold for an early study in relativistic molecular quantum mechanics. The dissociation energy is anomalously large, larger even than for  $\text{Cu}_2$  whereas  $\text{Ag}_2$  has a much smaller dissociation energy. Also  $\text{Au}_2$  is isoelectronic with the mercurous ion  $\text{Hg}_2^{++}$  which is unique in its stability as a dimeric dipositive species. Also our present theoretical methods appeared to be adequate at this point for the treatment of a molecule where the primary bond was based on  $s$  orbitals as is explained below.

All-valence-electron calculations on the ground and several excited states of  $\text{Au}_2$  are presented here as the fourth paper in a series dealing with the use of ab initio effective core potentials (EP). Paper I<sup>1</sup> describes the formal procedure for deriving the EP's and reports results for the Xe and Au atoms, Paper II<sup>2</sup> presents SCF calculations on the ground, positive ion, and  $6s\sigma_g$  Rydberg states of  $\text{Xe}_2$ , and Paper III<sup>3</sup> contains the first calculations using these methods on the ground state of  $\text{Au}_2$  employing relativistic basis functions in which the results include the effects of spin-orbit coupling directly by the use of an EP defined in terms of two-component spinors. In addition comparisons with other forms of EP's, both relativistic and non-relativistic, are discussed in Paper III.

The  $\text{Au}_2$  molecule was chosen as a test system because, as discussed in Paper I, it may be logically treated as a 22-valence electron system with the ground state predominantly being a  $6s-6s \sigma_g$  bonding state and the low-lying excited states coming from the  $5d^9 6s^2$  configuration leading to twelve states (in standard LS coupling notation)  $1\Sigma_g^+$ ,  $1\Sigma_u^+$ ,  $3\Sigma_g^+$ ,  $3\Sigma_u^+$ ,  $1\Pi_g$ ,  $1\Pi_u$ ,  $3\Pi_g$ ,  $3\Pi_u$ ,  $1\Delta_g$ ,  $1\Delta_u$ ,  $3\Delta_g$ , and  $3\Delta_u$ . The  $2D_{5/2}$  and  $2D_{3/2}$  states of Au are 1.136 and 2.558 eV above the ground  $2S$  state whereas the next levels ( $2P_{1/2}$  and  $2P_{3/2}$ ) are at 4.632 and 5.105 eV.<sup>4</sup> Hence the treatment of the  $2D$  valence states should constitute a reasonably "clean" set in the sense of not being strongly perturbed by other low-lying states of the same symmetry. The availability of experimental results for the ground and some of the excited states allows us to make some comparisons with various spectroscopic constants.

Because the spin-orbit splitting of the  $2D_{5/2}$  and  $2D_{3/2}$  levels of Au is so great (1.522 eV), the description of excited electronic states of  $\text{Au}_2$  in terms of  $\omega-\omega$  coupling would appear to be most appropriate. The twelve LS symmetries above are combined using an empirical model<sup>6</sup> based on the atomic spin-orbit splitting to yield states of  $0_g^+$ ,  $0_u^+$ ,  $0_g^-$ ,  $0_u^-$ ,  $1_g$ ,  $1_u$ ,  $2_g$ ,  $2_u$ ,  $3_g$ , and  $3_u$  symmetry in Hund's coupling case c ( $\omega-\omega$ ) notation. The observed molecular electronic states may then be compared directly with calculated results.

The following two sections describe the form of the wavefunctions used in this study and the methods of introducing

spin-orbit effects. The resulting potential energy curves are discussed in the last section. Some comments regarding analogous calculations on  $\text{Ag}_2$  and  $\text{Cu}_2$  are also included.

## II. Calculations

The wavefunctions for the twelve LS-coupling symmetries arising from the interaction of  $^2S + ^2S$  and  $^2S + ^2D$  atomic states were computed using a model of the Au atom whereby the 68 core electrons were replaced by an averaged relativistic effective core potential (AREP), as described in Paper III, and the 11 valence electrons ( $\dots 5d^{10} 6s$ ) were described by a valence basis set of two 2s, two 2p, two 3d, and one 4f Slater-type functions (STF). The AREP was represented as a numerical function including angular symmetries up to  $\ell=4$  (g-type) as the "residual potential" (see Paper III).

The (2s 2p 2d 1f) STF set (see Paper III) was determined by first fitting the s, p, and d-type pseudo-orbitals as two-term expansions then fully optimizing the exponents in atomic calculations for various LS-states in the field of the AREP. The 4f-type STF was optimized in ground-state SCF calculations on  $\text{Au}_2$  near  $R_e$  and resulted in an energy lowering of about 0.003 a.u.

To insure that the molecular wavefunctions for the ground state of  $\text{Au}_2$  was sufficiently flexible to allow for the proper dissociation to two  $^2S$  Au atoms, it was necessary to include the two configurations allowed from the combination of the 6s electrons;  $6s\sigma_g^2$  and  $6s\sigma_u^2$ . MCSCF calculations were carried

out incorporating these two configurations at 16 internuclear separations and are reported in Table I together with the analogous SCF (single-configuration) and CI (see below) results.

The molecular integrals for each of the 16 internuclear distances shown in Table I, including the matrix elements involving the AREP (see Paper III) were transformed over the MCSCF orbitals for the ground state and used in first-order<sup>7</sup> CI calculations designed as follows. The MCSCF orbitals were placed in three classes, the first corresponding to those derived from the 5d shell of Au, viz.  $5d\sigma_g$ ,  $5d\sigma_u$ ,  $5d\pi_u$ ,  $5d\pi_g$ ,  $5d\delta_g$ , and  $5d\delta_u$ . These orbitals were restricted to be fully occupied in the MCSCF calculations but their respective linear coefficients were optimized for each internuclear separation. The second class consists of the  $6s\sigma_g$  and  $6s\sigma_u$  orbitals that were optimized with respect to configuration mixing at each internuclear separation. The  $6s\sigma_g$  orbital is dominant near  $R_e$  but the two configurations have equal coefficients as dissociation is approached. The third class is made up of the remaining orbitals that can be constructed from the basis set. This class is usually termed the "external" or "virtual" class of orbitals whereas the first two are termed the "valence" space. The inclusion of only the 5d and 6s/<sup>shells</sup> in the valence space may be rationalized on the grounds that the  $^2P$  states of Au lie about 2 eV higher than  $^2D$  states, as mentioned above.

To construct a list of configurations for the CI calculations, excitations are defined in terms of the distribution of the 22 valence electrons among the orbitals in the three



classes. Table II shows how the configurations were defined for the twelve LS-symmetries desired and the number of configurations for each electron distribution for  $^1\Sigma_g^+$  symmetry. The final electron distribution in Table II corresponds to the double excitations of the two 6s electrons and would serve to comprise a complete CI for the two electron (frozen 5d) system. The importance of including these "bond doubles" as well as the successive improvement of the ground state wavefunction of  $\text{Au}_2$  as more electron distributions are included is shown in Fig. 1. The 6s valence (VCI) 6s first-order (FOCI) binding energies ( $E(R = 4.75) - E(R = 20.0) \approx D_e = 0.91 \text{ eV}$ ) are the same since only the two MCSCF configurations are allowed. The additional 10 single excitations, which would allow for orbital relaxation effects,<sup>7</sup> yield no contribution because the two valence configurations were optimized in the MCSCF procedure. The curve for the complete VCI (distributions 1, 3, and 4) is slightly lower (0.1 eV) than the 6s VCI due to some effects coming from inclusion of 5d(Class I) excitations into the 6s orbitals (Class II). The addition of the 5d FOCI configurations (distributions 5, 6, and 7) causes a significant increase in binding energy due to the effects of relaxation and polarization of the orbitals arising from the 5d shells of the Au atoms. Finally it is seen in Fig. 1 that the "bond doubles" (distribution 8) results in an additional increase in the binding energy of about 0.3 eV to yield a  $D_e$  value of 2.27 eV. This change shows the importance of including this class of configurations, or conversely, the degree of reliability of the first-order method (distributions 1-7) in describing the ground state

of  $\text{Au}_2$ . It should also be pointed out that the inclusion of configurations that correspond to excitations of one or more electrons from the 5d-shells with one electron residing in the external space result in the inclusion of 0.3 eV of atomic correlation energy (lower two curves of Fig. 1). This effect is due to atomic excitations and should be nearly constant for all internuclear distances. The upper two curves have dissociation limits that are precisely the sum of two  $^2\text{S}$  atomic SCF energies.

### III. Spin-Orbit Interaction

In order to obtain the states corresponding to Hund's coupling case c ( $\omega$ - $\omega$  coupling), the calculated LS states from  $^2\text{S} + ^2\text{D}$  atomic asymptote were corrected with an empirical model<sup>6</sup> based on the experimental atomic spin-orbit splittings  $^2\text{D}_{3/2}$  and  $^2\text{D}_{5/2}$ . All the  $\omega$ - $\omega$  coupled states from  $^2\text{S} + ^2\text{D}_{3/2}$  and  $^2\text{S} + ^2\text{D}_{5/2}$  atomic asymptotes can be obtained as roots to the spin-orbit matrices given in Appendix 1 with  $\zeta = .6087$  eV. Since the contribution from the ion pair ( $\text{Au}^+ + \text{Au}^-$ ) accounts for all the bonding of the first  $^1\Sigma_u^+$  state, it was necessary to modify the spin-orbit matrix for  $0_u^+$  states that come from the mixing of  $^3\Pi_u$  and  $^1\Sigma_u^+$  states. Instead of solving the  $2 \times 2$  matrix for  $0_u^+$  states, three LS states were included in the spin-orbit matrix as shown in Appendix II. This approximation is based upon two additional assumptions. First, the spin-orbit splitting of ion pair states is zero, which is rigorously true for atomic ions. Second, the two lower lying  $^1\Sigma_u^+$  states are composed of ion pairs and  $^2\text{S}$  and  $^2\text{D}$  atoms,

which is a reasonable approximation as can be estimated from CI coefficients. Then the contributions from  $^2S + ^2D$  atoms can be calculated using CI coefficients as shown in Appendix II. This modification is not used for  $0_g^+$  states since the ion-pair contributes little to the first excited  $1_g^+$  state.

In order to obtain the experimental energy separation for the atomic limits, the energies of all the excited states are shifted by .305 eV relative to the ground state.

#### IV. Results and Discussion

The calculated potential curves for the excited states that have allowed transition moments from the ground state are shown in Fig. 2. The circle in Fig. 2 indicates the site of an avoided crossing of  $1_u$  states if a CI calculation were done in the  $\omega$ - $\omega$  coupled configurations. All other u states are shown in Fig. 3. Potential curves of calculated g states appear in Fig. 4. Vertical transition energies of these states calculated at the internuclear distance of 4.5 a.u. are given in Table III. They can be of some interest for certain applications and are useful as an additional guide for identifying the curves in Figures 2, 3, and 4.

Spectroscopic constants were calculated for states that have  $D_e$  larger than 0.3 eV and summarized in Table IV with the experimental results.

The spectroscopic information on  $Au_2$  is given by Ames and Barrow<sup>5</sup> and by Kleman, et al,<sup>8</sup> who also cite earlier work. The fact that gold has but a single isotope allowed resolution of rotational structure<sup>5</sup> and yielded the precise interatomic distances which are given in Table IV together with other spectroscopic parameters. The dissociation energy of the

ground state is obtained from mass spectrometric experiments, most recently by Kordis, et al.<sup>9</sup> Their result,  $D_0 = 52.9 \pm 0.5$  kcal/mole agrees well with earlier work including the value  $51.5 \pm 2.2$  kcal/mole from Ackerman, et al.<sup>10</sup> With correction for zero point energy one obtains  $D_e = 2.305 \pm 0.02$  eV.

The values of 1.00 eV for the A  $O_u^+$  state and 1.78 eV for the B  $O_u^+$  state are calculated from the experimental  $T_e$  values of corresponding states<sup>5</sup> using the dissociation energy of the ground state and the atomic excitation energies to  $D_{5/2}$  and  $D_{3/2}$  states, respectively. It may be noted that simple extrapolations of vibrational levels yield  $D_e$  values of 1.41 eV and 1.47 eV for the A  $O_u^+$  and B  $O_u^+$  states, respectively.

One might have expected to observe also transitions to the  $1_u$  state at 2.64 eV but this feature is evidently less intense than the X-A bands at nearly the same energy. Since the large transition dipole arising from the molecular ion-pair state falls only into the  $O_u^+$  symmetry, the lower intensity for the transition to the  $1_u$  state is not surprising.

The agreement of calculated and experimental dissociation energies for the ground state is fortuitously good; that for  $R_e$  and  $\omega_e$  reasonable. Although there is as much as  $0.1 \text{ \AA}$  difference in calculated and experimental  $R_e$  values, it is interesting to note that the calculations reproduce the correct order with A  $O_u^+$  longest and B  $O_u^+$  intermediate. The total energies of excitation to the A and B states are also fitted quite well. Indeed the entire pattern of agreement with experimental values is remarkable and probably somewhat

fortuitous. All important aspects of the lower energy states of  $\text{Au}_2$  appear to be appropriately taken into account by the relativistic E.P. methods adopted.

It is also recognized that most states coming from the  $^2\text{S} + ^2\text{D}_{3/2}$  asymptote and some repulsive states from the  $^2\text{S} + ^2\text{D}_{5/2}$  could be changed through the configuration mixing in  $\omega$ - $\omega$  coupling case since the energy of the  $^2\text{D}_{5/2} + ^2\text{D}_{5/2}$  atomic asymptote is lower than that of  $^2\text{S} + ^2\text{D}_{3/2}$ . However, there are no  $\text{O}_u^+$  or  $\text{O}_g^-$  states arising from  $^2\text{D}_{5/2} + ^2\text{D}_{5/2}$ ; hence the calculated curves for these symmetries are unaffected. This last point is important for the B  $\text{O}_u^+$  state.

Calculations were also initiated for  $\text{Cu}_2$  and  $\text{Ag}_2$  following the same general system. While the results for the ground states give qualitatively correct sequences of  $R_e$  values and  $D_e$  values, several difficulties arose which made the results unsatisfactory on a quantitative basis. The same problems became even more serious for excited states.

For copper the most serious difficulty is the failure of SCF atomic calculations to reproduce, even approximately, the relative energies of the  $^2\text{S}$  and  $^2\text{D}$  states. Similar difficulties are known to arise for nickel. We understand that very extensive CI calculations<sup>11</sup> are required to remedy this situation and such extensive atomic CI would be beyond the scope of our present pattern.

For silver the problem arises from the fact that the  $^2\text{P}$  excited state is somewhat lower than the  $^2\text{D}$  state for the atom. Thus excitations involving both d and p orbitals must be

included in an adequate treatment. Furthermore, the methods used here for spin-orbit effects in  $\text{Au}_2$  would be inadequate for  $\text{Ag}_2$ . In view of the more extensive efforts required to properly deal with  $\text{Cu}_2$  and  $\text{Ag}_2$ , it seemed better to present just the results for  $\text{Au}_2$  at this time.

## ACKNOWLEDGEMENT

Most of the calculations were carried out with the IBM San Jose ALCHEMY programs of M. Yoshimine, A. D. McLean, B. Lin, and P. S. Bagus, extended by the present authors to include averaged relativistic core potentials. We thank A. D. McLean and B. Lin for their help, and the IBM Corporation for their support of this work under a Joint Study Agreement with the Lawrence Berkeley Laboratory.

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

## References

1. Y. S. Lee, W. C. Ermler, and K. S. Pitzer, J. Chem. Phys. 67, 586 (1977).
2. W. C. Ermler, Y. S. Lee, K. S. Pitzer and N. W. Winter, J. Chem. Phys. (in press).
3. Y. S. Lee, W. C. Ermler, K. S. Pitzer, and A. D. McLean, J. Chem. Phys. (to be submitted).
4. C. E. Moore, Natl. Bur. Stand. Arc. 467, Vol. III (1958).
5. L. L. Ames and R. F. Barrow, Trans. Faraday Soc., 63, 39 (1967).
6. See J. S. Cohen and B. Schneider, J. Chem. Phys. 61, 3230 (1974).
7. See H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules: A survey of Rigorous Quantum Mechanical Results," Addison-Wesley, Reading, MA, 1972.
8. B. Kleman, S. Lindqvist, and L. E. Selin, Arkiv Fysik., 8, 505 (1954).
9. J. Kordis, K. A. Gingerich, and R. J. Seyse, J. Chem. Phys., 61, 5114 (1974).
10. M. Ackerman, F. E. Stafford, and J. Drowart, J. Chem. Phys., 33, 1284 (1960).
11. W. A. Goddard III, private communication.



Appendix I. Spin-Orbit Matrices for  $d^9s^2 + d^{10}s$  Molecules

$$\Omega = 3: \quad [E({}^3\Delta) + \zeta]$$

$$\Omega = 2: \quad \begin{bmatrix} E({}^3\Delta) & & \\ \zeta/\sqrt{2} & E({}^3\Pi) + \zeta/2 & \\ \zeta & -\zeta/\sqrt{2} & E({}^1\Delta) \end{bmatrix}$$

$$\Omega = 1: \quad \begin{bmatrix} E({}^3\Delta) - \zeta & & & \\ \zeta/\sqrt{2} & E({}^3\Pi) & & \\ 0 & \sqrt{3}\zeta/2 & E({}^3\Sigma^+) & \\ \zeta/\sqrt{2} & \zeta/2 & -\sqrt{3}\zeta/2 & E({}^1\Pi) \end{bmatrix}$$

$$\Omega = 0^-: \quad \begin{bmatrix} E({}^3\Pi) - \zeta/2 & \\ \sqrt{6} \zeta/2 & E({}^3\Sigma^+) \end{bmatrix}$$

$$\Omega = 0^+: \quad \begin{bmatrix} E({}^3\Pi) - \zeta/2 & \\ \sqrt{6} \zeta/2 & E({}^1\Sigma^+) \end{bmatrix}$$

## Appendix II

In an attempt to account for ion pair character let

$$\beta^2 = (C_{II}^2 + C_{III}^2) / (C_I^2 + C_{II}^2 + C_{III}^2),$$

where the C's are mixing coefficients corresponding to the respective (dominant) configurations in the first  ${}^1\Sigma_u^+$  wave function,

$$\left. \begin{array}{l} \text{I} \quad (s\sigma_g)(s\sigma_u), \quad - \text{ion pair configuration} \\ \text{II} \quad (d\sigma_u)(s\sigma_g)(s\sigma_u)^2, \\ \text{III} \quad (d\sigma_g)(s\sigma_g)^2(s\sigma_u). \end{array} \right\} \text{}^2S + \text{}^2D \text{ configurations}$$

The energies of the  $O_u^+$  states are roots of

$$\begin{bmatrix} E({}^3\Pi_u) - \zeta/2 & & & \\ \beta(\sqrt{6}/2)\zeta & E_1({}^1\Sigma_u^+) & & \\ (1-\beta)(\sqrt{6}/2)\zeta & 0 & E_2({}^1\Sigma_u^+) & \end{bmatrix}$$

Table I. Ground State Au<sub>2</sub> Valence Energies (a.u.)

R	E(SCF)	E(MCSCF)	E(CI)
3.0	-70.272820	-70.291183	-70.387333
3.5	.618155	.632900	.719504
4.0	.738262	.751744	.825669
4.25	.759430	.773288	.841041
4.5	.767895	.782712	.844318
4.75	.769278	.785526	.841337
5.0	.766328	.784477	.835026
5.25	.760811	.781305	.827011
5.5	.754218	.777429	.818684
5.75	.746473	.773001	.809870
6.0	.739423	.769366	.802415
7.0	.712174	.758443	.779374
8.0	.690422	.753765	.768405
9.0	.673762	.751926	.764050
10.0	.661266	.751150	.762353
20.0	.621691	.750536	.761078

Table II. Electron Distributions for CI Calculations  
for 22-Valence Electron Au<sub>2</sub>

Electron Distribution	I	II	III	No. $1\Sigma_g^+$	Description
1	20	2	0	2	6s Valence CI(VCI)
2	20	1	1	10	6s First-order (FO CI)
3	19	3	0	2	5d VCI
4	18	4	0	6	5d VCI
5	19	2	1	88	5d FO CI
6	18	3	1	296	5d FO CI
7	17	4	1	402	5d FO CI
8	20	0	2	56	6s "Bond Doubles"
Total				862	

Table III. Vertical transition energies<sup>a</sup> (in eF) of selected excited states of Au<sub>2</sub> calculated at R = 4.50 a.u.

States	Vertical transition energies (eV)	States	Vertical transition energies (eV)
0 <sub>g</sub> <sup>+</sup>	0.0	0 <sub>u</sub> <sup>+</sup>	2.6529
	3.4550		3.6157
	5.6131		6.0626
0 <sub>g</sub> <sup>-</sup>	2.5616	0 <sub>u</sub> <sup>-</sup>	2.4482
	5.5161		3.0125
1 <sub>g</sub>	2.5710	1 <sub>u</sub>	5.7679
	3.9543		2.4482
	5.2359		2.6602
	5.7027		3.6495
2 <sub>g</sub>	3.2056	2 <sub>u</sub>	5.0216
	3.9443		5.8219
	5.1911		2.4688
3 <sub>g</sub>	3.1508	3 <sub>u</sub>	3.6563
			5.0316
			3.6002

<sup>a</sup> The energy scale shown in the figures can be obtained by adding the energy of the ground 0<sub>g</sub><sup>+</sup> state (-2.265 eV).

Table IV. Au<sub>2</sub> Spectroscopic Constants

State		$R_e$ (Å)	$D_e$ (eV)	$\omega_e$ (cm <sup>-1</sup> )	$T_e$ (eV)
X O <sub>g</sub> <sup>+</sup>	Calc.	2.37	2.27	165	0
	Expt. <sup>a</sup>	2.47	2.31 <sup>b</sup>	191	0
A O <sub>u</sub> <sup>+</sup>	Calc.	2.51	.79	121	2.61
	Expt. <sup>a</sup>	2.57	1.00	142	2.44
B O <sub>u</sub> <sup>+</sup>	Calc.	2.50	1.38	146	3.55
	Expt. <sup>a</sup>	2.51	1.78	180	3.18
1 <sub>u</sub>	Calc.	2.44	.76	138	2.64
2 <sub>u</sub>	Calc.	2.43	.94	143	2.57
O <sub>g</sub> <sup>-</sup>	Calc.	2.44	.85	140	2.66
1 <sub>g</sub>	Calc.	2.44	.84	140	2.67
2 <sub>g</sub>	Calc.	2.61	.35	110	3.16
3 <sub>g</sub>	Calc.	2.61	.41	112	3.10

<sup>a</sup> from Ref. 5.

<sup>b</sup> from Ref. 9.

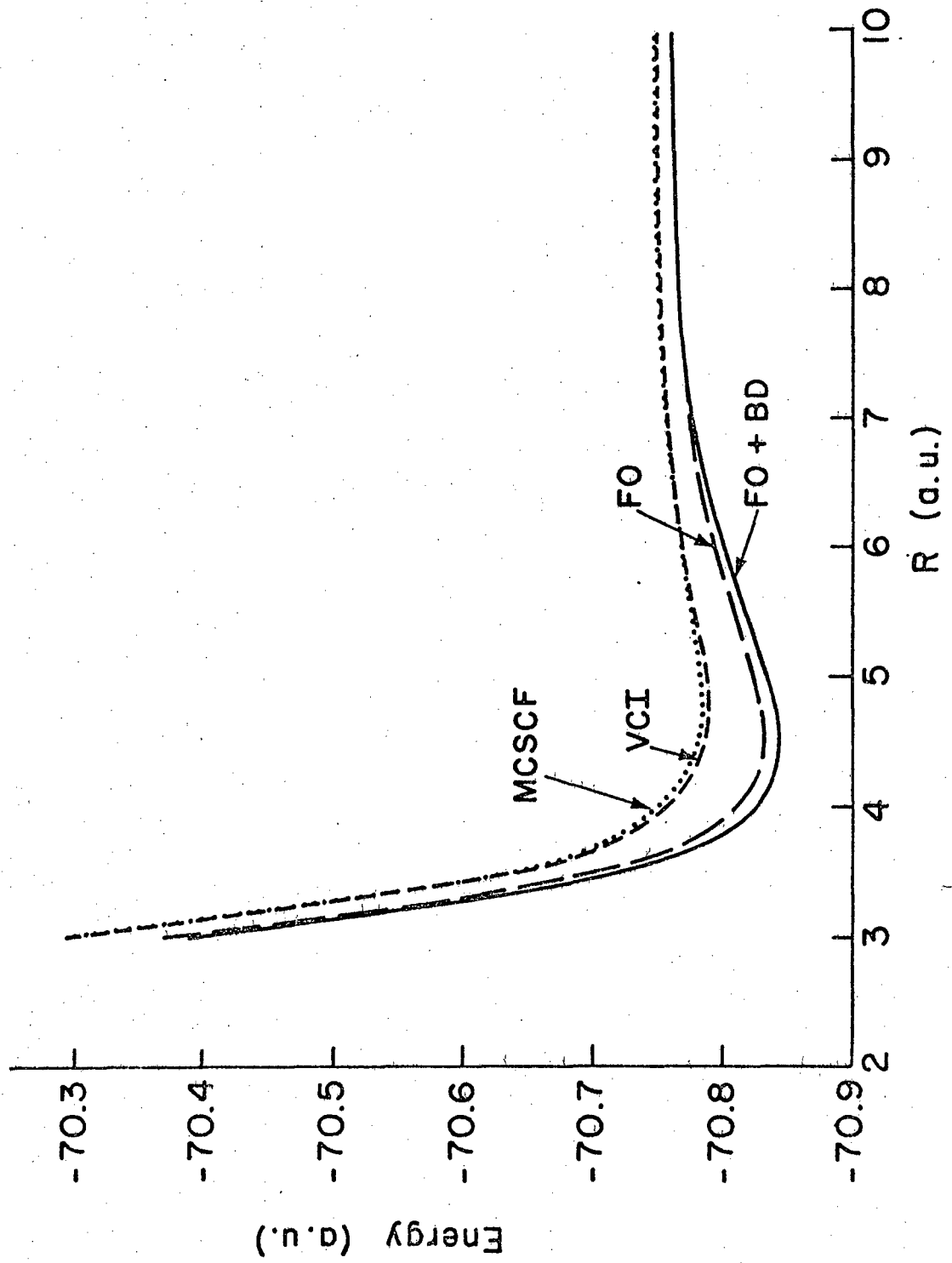
## Figure Captions

Fig. 1. Potential curves of  $0_g^+$  of  $Au_2$  calculated with the various levels of configuration interactions (CI).

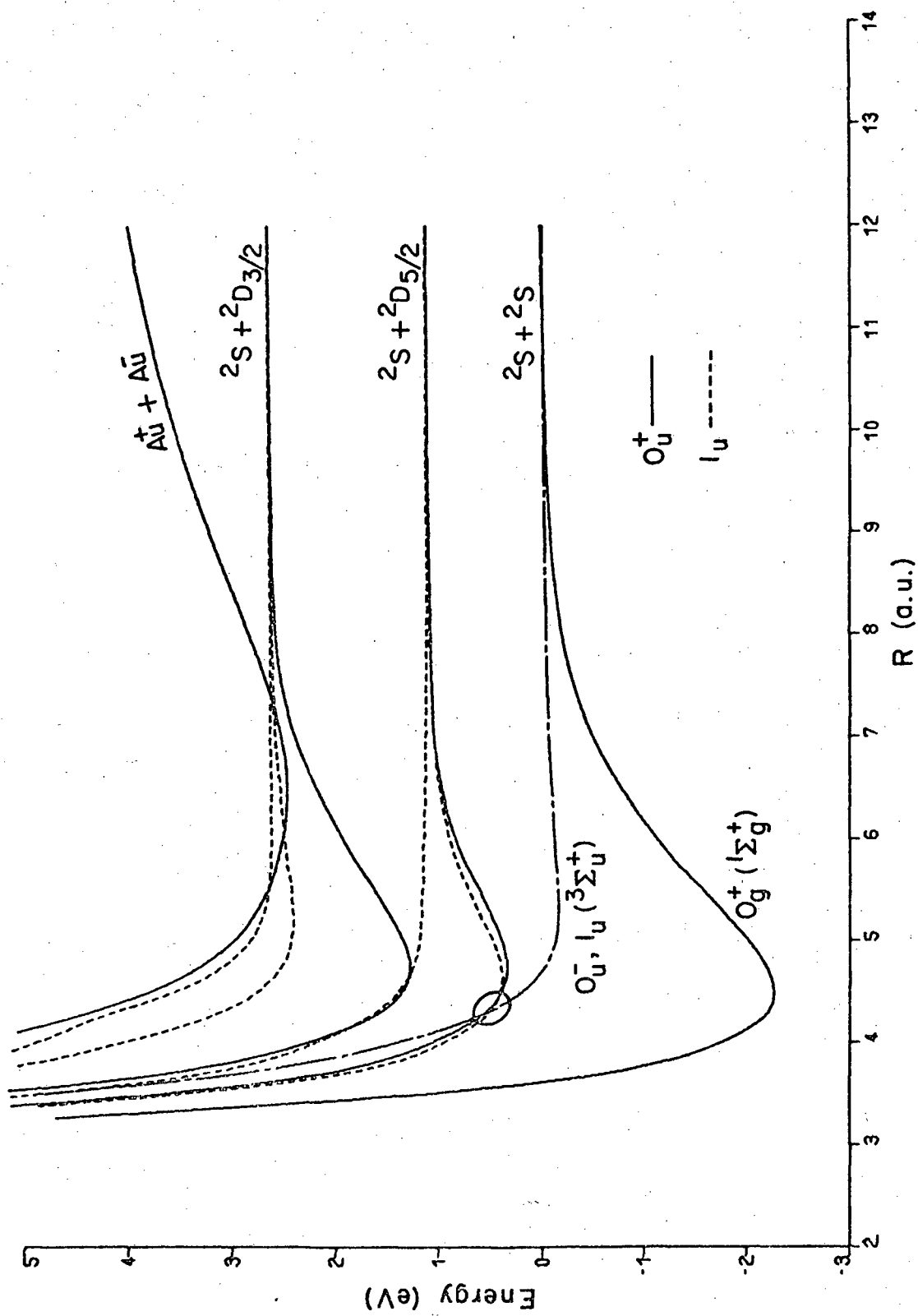
Fig. 2. Molecular states of  $Au_2$  derived from the  $^2S + ^2S$  atomic asymptote and the spectroscopically allowed excited states from  $^2S + ^2D$  asymptote. Spin-orbit effects and ion-pair mixing are included in the calculation.

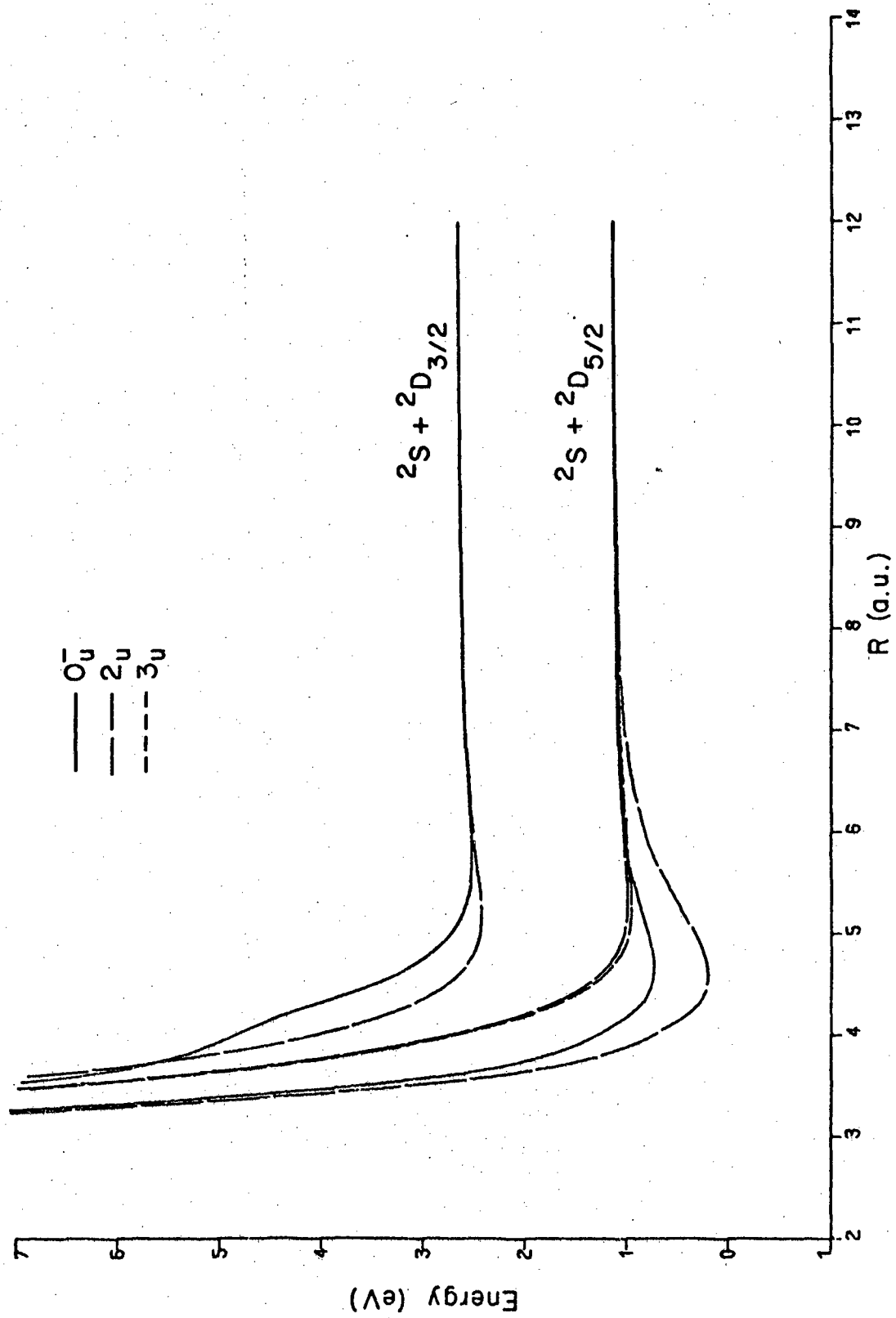
Fig. 3.  $0_u^-$ ,  $2_u$  and  $3_u$  states of  $Au_2$  derived from  $^2S + ^2D$  atoms.

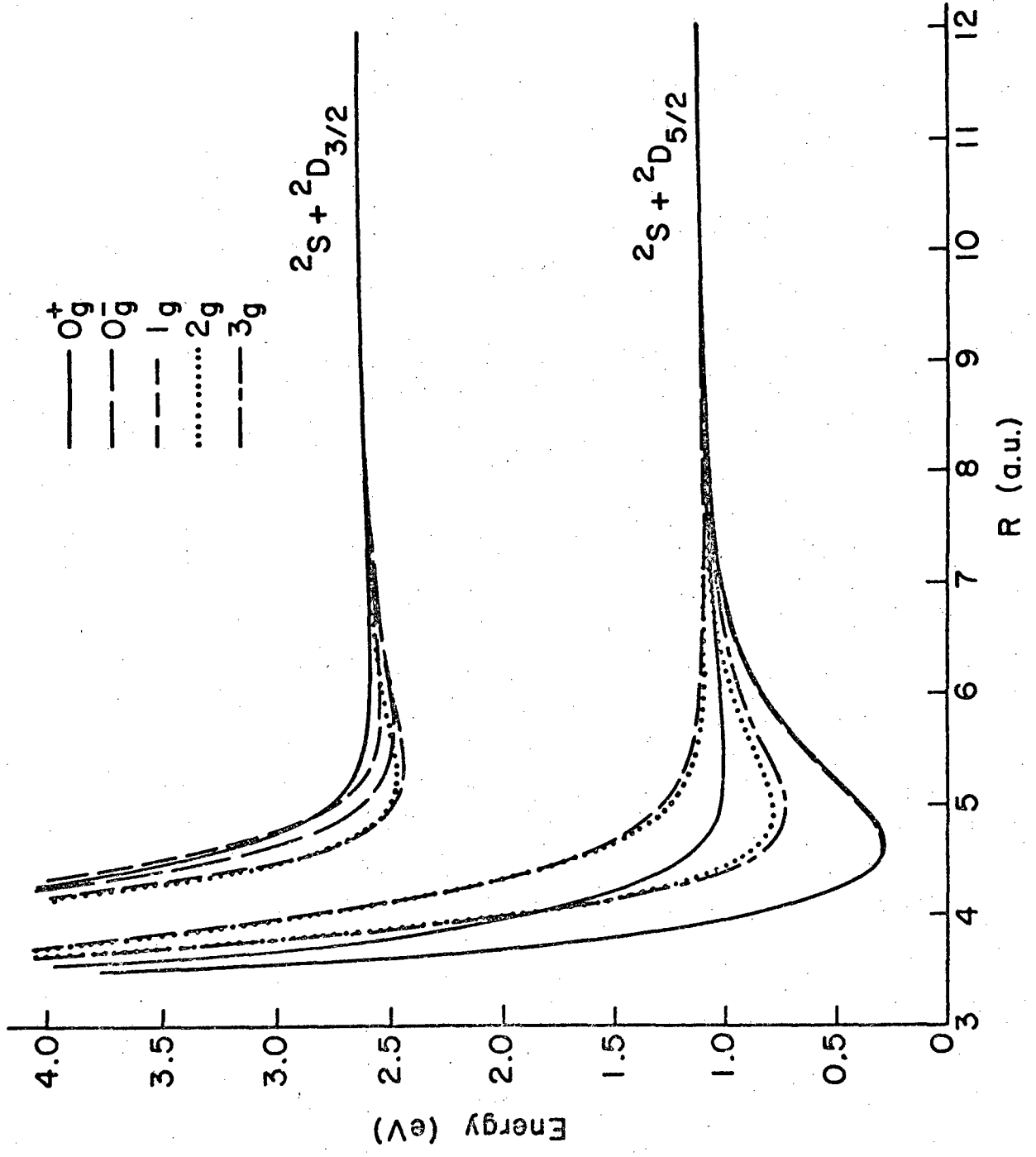
Fig. 4.  $0_g^+$ ,  $0_g^-$ ,  $1_g$ ,  $2_g$  and  $3_g$  states of  $Au_2$  derived from  $^2S + ^2D$  atoms.











This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720