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DISCLAIMER

Correlation Diagram for He + He → Be*

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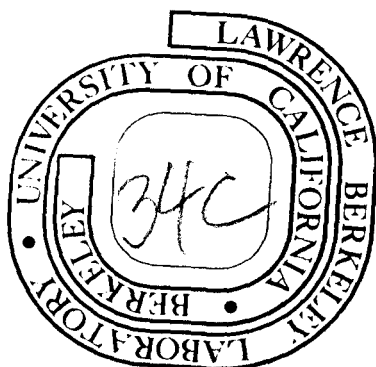
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ABSTRACT

An electronic correlation diagram has been calculated

a priori for the model system He + He → Be. The suitability

of different types of basis sets and of the Hartree-Fock

approximation is discussed. The relation of this diagram

to experimental inner shell collision chemistry is discussed

briefly.

INTRODUCTION

Electronic correlation diagrams have played an important

role in the development of chemical physics over the past four

decades. Among the most important contributions have been:

a) Mulliken's correlation[1] of diatomic molecular orbitals with

those of the separated atom and united atom limits; b) Walsh's

diagrams[2] for the prediction of the shapes of polyatomic mole-

cules; and c) the rules of Woodward and Hoffmann[3] for "allowed"

and "forbidden" chemical reactions.

Particularly relevant to the present research is the

importance of diatomic correlation diagrams to the interpretation

of inner shell ionization phenomena.[4] The use of the electron

promotion mechanism of molecular orbital theory to describe such

phenomena was suggested by Fano and Lichten[5] in their analysis

of Ar^+ - Ar collisions at Ar^+ energies from 12 to 150 keV. More

recently, a clear review of the theory of electronic excitation

in heavy-particle collisions has been given by Smith, Lorents,

and Olson.[6] Among the many applications[4] of inner shell collision

chemistry, one of the most intriguing concerns the possibility

of identifying superheavy elements from the "molecular orbital"

X-rays arising at very short internuclear separations.[7]

Thus the need for quantitatively correct diatomic correlation

diagrams has become increasingly clear in recent years. Among the

numerous ab initio calculations along these lines, the most reli-

able and interesting appear to be those of Mulliken,[8] Briggs and

Hayns,[9] and Barat and Sidis.[10] One of the most difficult

problems involved in such theoretical studies is the choice

of a finite basis set. While it is clear that a united atom

basis is appropriate at $R = 0$, and a separated atom basis is

appropriate at $R = \infty$, the intermediate range is more difficult

to deal with. Mulliken[8] obtained an $N + N \rightarrow N_2$ correlation

diagram (orbital energy vs. internuclear separation) in the

most straightforward manner; namely by optimizing basis func-

tions (orbital exponents ζ in $r^n e^{-\zeta r}$) at each internuclear

separation. While this is certainly the most reliable method,

it is quite time consuming and tends to blur the qualitative

distinction between united atom (UA) and separated atom (SA)

limits. Briggs and Hayns,[9] on the other hand, used both UA

and SA basis sets for $N + N \rightarrow N_2$. In the intermediate region

($R = 0.1$ to 0.6 bohrs) they attempted to judiciously combine

appropriate elements of the two bases. A similar approach has

been taken by Sidis and Barat[10] for the $Ar^+ + Ar$ system.

The present paper is devoted to the study of a simpler

system, $He + He \rightarrow Be$. However, this very simplicity allows a

more detailed exploration of the relation between UA and SA

basis sets as a function of internuclear separation. In addition,

by considering the lowest electron configuration for both the

UA and SA limits, either diabatic or adiabatic processes[6] may

be discussed. The diabatic representation (in which potential

curves cross) is more useful at higher energies, while an adiabatic

representation (avoided crossings of potential curves) is more

appropriate to lower energy processes.

ELECTRONIC STRUCTURE CONSIDERATIONS

For the process He + He → Be, the ground state wave

function at large internuclear separations is dominated by

the electron configuration $1\sigma_g^2\ 1\sigma_u^2$, corresponding to the

Hartree-Fock description of two separated He atoms. At

very short internuclear separations, however, the wave function

resembles the $1s^2\ 2s^2$ configuration of the Be atom. For the

point group $D_{\infty h}$ this configuration becomes $1\sigma_g^2\ 2\sigma_g^2$. Thus it

is clear that there must be an avoided crossing of these two

electron configurations at some intermediate internuclear

separation. It is worth noting that for very small R the

$1\sigma_g^2\ 1\sigma_u^2$ configuration becomes the $1s^2\ 2p\sigma^2$ configuration of

the Be atom. This configuration represents a linear combina-

tion of two excited singlet state wave functions for Be.

$$1s^2\ 2p\sigma^2 = (\tfrac{2}{3})^{1/2}\ {}^1D_g - (\tfrac{1}{3})^{1/2}\ {}^1S_g \qquad (1)$$

In an analogous way, the $1\sigma_g^2\ 2\sigma_g^2$ configuration at large separa-

tions is a linear combination of separated atom and ion wave functions:

$$1\sigma_g^2\ 2\sigma_g^2 =$$

$$(\tfrac{2}{16})^{1/2} \left[\text{He}^=\ ^1S\ (1s^2\ 2s^2) + \text{He}^{+2} \right]$$

$$+ (\tfrac{2}{16})^{1/2} \left[\text{He}\ ^1S\ (1s^2) + \text{He}\ ^1S\ (2s^2) \right]$$

$$+ (\tfrac{4}{16})^{1/2} \left[\text{He}^+\ ^2S\ (1s) + \text{He}^-\ ^2S\ (1s\ 2s^2) \right]$$

$$+ (\tfrac{4}{16})^{1/2} \left[\text{He}^-\ ^2S\ (1s^2\ 2s) + \text{He}^+\ ^2S\ (2s) \right]$$

$$- (\tfrac{3}{16})^{1/2} \left[\text{He}\ ^3S\ (1s\ 2s) + \text{He}\ ^3S\ (1s\ 2s) \right]$$

$$- (\tfrac{1}{16})^{1/2} \left[\text{He}\ ^1S\ (1s\ 2s) + \text{He}\ ^1S\ (1s\ 2s) \right] \qquad (2)$$

Even for as simple a system as He + He → Be, a rather extended basis set must be used to describe all the possibilities outlined above. For the Be atom, we have adopted the (9s)

primitive gaussian basis set of Van Duijneveldt,[11] contracted[12] to (5s). In addition we optimized a primitive gaussian (4p) set via SCF calculations of the lowest ^3P ($1s^2$ 2s 2p) state of beryllium. The final atomic SCF energy obtained with this basis was -14.5102 hartrees, to be compared with Dunning's near Hartree-Fock result,[13] -14.5115 hartrees. This (4p) set was contracted to (2p), and the entire Be basis is summarized in Table I.

For the He atom, we need an adequate description of both the 1s and 2s orbitals. The 1s basis was derived from the (6s) primitive basis of Van Duijneveldt.[11] To describe the 2s orbital, three additional uncontracted primitive gaussians were added. These basis functions were chosen by the "even-tempered" criterion of Ruedenberg, Raffenetti, and Bardo.[14] Specifically, we noted that the exponent ratio of the two most diffuse functions in Van Duijneveldt's He basis was:

$$\frac{0.2082}{0.6643} = 0.3134 = x \tag{3}$$

By adopting this same ratio, the three diffuse functions were generated: 0.2082 x, 0.2082 x^2, and 0.2082 x^3. Finally, an SCF calculation was performed on the ^3S(1s 2s) state of He to yield suitable contraction coefficients. The He(9s/5s) basis so obtained is seen in Table I. This basis yielded an SCF energy of -2.1729 hartrees for the ^3S(1s 2s) state of He. For comparison we note the rather good agreement with the exact result of Pekeris,[15] -2.1752 hartrees.

In the discussion that follows, the Be atom basis is termed the united atom or UA basis. When the helium basis is centered on both He nuclei, this is designated the separated atom or SA basis. For the $1\sigma_g^2 \, 1\sigma_u^2$ configuration, the SA basis becomes approximately linearly dependent at very small internuclear separations. For the $1\sigma_g^2 \, 2\sigma_g^2$ configuration, however, there is no such problem, since only the σ_g functions need be included in the basis set. The σ_u functions in this case are simply discarded. The three center (He − Be − He) basis set, the union of the UA and SA bases, is referred to as the merged basis set in the present work. It is clear that this merged basis will be appropriate at all internuclear separations at which it is not linearly dependent.

The present study, then, centers about several different calculations as a function of R:

A. $1\sigma_g^2 \, 1\sigma_u^2$ configuration. United atom basis set.

B. $1\sigma_g^2 \, 1\sigma_u^2$ configuration. Separated atoms basis set.

C. $1\sigma_g^2 \, 1\sigma_u^2$ configuration. Merged basis set.

D. $1\sigma_g^2 \, 2\sigma_g^2$ configuration. United atom basis set.

E. $1\sigma_g^2 \, 2\sigma_g^2$ configuration. Separated atoms basis set.

F. $1\sigma_g^2 \, 2\sigma_g^2$ configuration. Merged basis set.

G. $1\sigma^2 \, 2\sigma^2$ configuration. Merged basis set.

In the last calculation (G), we have constrained neither the individuals orbitals nor the four-electron wave function to have g or u (inversion) symmetry. Thus calculation G must always yield a total energy less than or equal to the lower of

energies C and F. Note that, unlike earlier workers,[9,10] we have not attempted to combine subsets of the UA and SA basis sets to yield a basis appropriate to the intermediate region.

RESULTS AND DISCUSSION

To present the broad picture first, we will initially describe the results obtained with the merged basis set. Figures 1 and 2 summarize these results.

Figure 1 illustrates the orbital energies obtained in calculations C and F. An interesting point seen there is that the $1\sigma_g$ orbital energy depends on the configuration employed, $1\sigma_g^2 1\sigma_u^2$ or $1\sigma_g^2 2\sigma_g^2$. Although such details are never included in Mulliken-type diagrams,[1,5] it is clear that inner shell ionization potentials will be different for different electronic states. Note also that the $1\sigma_u$ and $2\sigma_g$ orbital energies cross at R $\sim$ 0.75 bohrs. In a model theory,[5] of course, the crossing of these two orbital energies would correspond to the crossing of the two lowest $^1\Sigma_g^+$ electronic configuration energies.

In fact, the energies of the $1\sigma_g^2 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g^2$ configurations become degenerate at R $\sim$ 0.56 bohrs, as seen in Table II. This result is consistent with the earlier Matsumoto, Bender, and Davidson[16] He-He calculations, designed to test the experimentally derived potential of Amdur and Jordan.[17] Also demonstrated in Table II is that the $1\sigma^2 2\sigma^2$ energy, where no inversion (g or u) symmetry has been imposed, is identical (to four decimal places) to the lower of the $1\sigma_g^2 1\sigma_u^2$ or $1\sigma_g^2 2\sigma_g^2$ energies. Thus the $^1\Sigma_g^+$ symmetry is not "broken".

Figure 2 shows the adiabatic $1\sigma^2 \, 2\sigma^2$ total and orbital

energies. The total energy (potential energy curve) shows

no indication of an avoided crossing, since the $1\sigma_g^2 \, 1\sigma_u^2$ and

$1\sigma_g^2 \, 2\sigma_g^2$ curves have similar slopes at R = 0.56 bohrs. However,

as expected, the 1σ and 2σ orbital energies do change abruptly

at this point. These same changes can of course be seen by

inspection of Figure 1 at internuclear separation 0.56 bohrs.

Given the results obtained with our merged basis set, we

can now look at the strengths and weaknesses of the UA and SA

subsets. Such an analysis is seen in Table III for the $1\sigma_g^2 \, 2\sigma_g^2$

configuration. We consider this configuration first since there is

no linear dependence problem. As must be the case, of course,

the merged basis set always gives the lowest energy. However,

for the united atom (R = 0.0), the He atom basis functions

lower the energy by only 0.0002 hartrees. At the other end

of the range illustrated in Table III, R = 2.0 bohrs, the

merged basis energy is only 0.0438 hartrees below the SA basis

energy. <u>Both</u> the UA and SA basis sets are inadequate near the

avoided crossing (R = 0.56 bohrs). At R = 0.5, for example,

the merged basis result is more than 0.3 hartrees = 8.2 eV

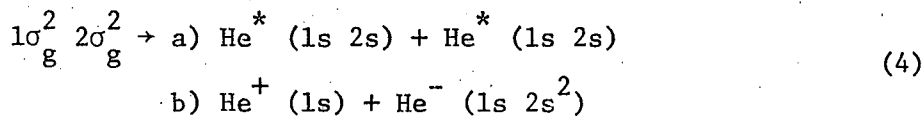lower than either the SA or UA results.

Analogous results for the $1\sigma_g^2 \, 1\sigma_u^2$ configuration are given

in Table IV. Note that converged SCF wave functions were ob-

tained with the merged basis set for bond distances as small as

0.1 bohr radius. There it is seen that the UA basis is quite

reasonable, yielding an energy only 0.0347 hartrees above the

merged result. At large R the SA basis is a significantly better approximation for $1\sigma_g^2 \, 1\sigma_u^2$ than it was for the $1\sigma_g^2 \, 2\sigma_g^2$ configuration. For example, for R = 2.0 bohrs, the SA result lies only 0.0038 hartrees above the merged basis energy. Again we see that neither the SA nor UA basis is adequate near the point of avoided crossing. The discrepancies with the merged basis results are comparable to the earlier discussed $1\sigma_g^2 \, 2\sigma_g^2$ case. Since the problem of linear dependence is nonexistant in the region of the avoided crossing, it would appear that the use of a (UA + SA), or merged, basis is to be recommended. In a natural way, then, this procedure eliminates the arbitrariness inherent in the "hybrid" basis sets used for this range of R by earlier workers.[9,10]

CONCLUDING REMARKS

In one sense, our choice of He + He for this theoretical

study is less than optimal, since there is   considerably more

experimental interest in heavier systems in which one partner

is charged, e.g., Ar^+ - Ar. However, He-He collisions can

create one or two K-shell vacancies,[18,19] and these may be

interpreted via the Fano-Lichten promotion mechanism. In this

picture, the He atoms approach (on the ground state potential

curves) with two electrons in the $1\sigma_u$ orbital, pass through

the crossing point (for the $1\sigma_g^2 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g^2$ configurations),

and separate with two electrons promoted to the $2\sigma_g$ orbital,

corresponding to the first excited $^1\Sigma_g^+$ potential. Since this

first excited $^1\Sigma_g^+$ state correlates adiabatically with

^1S_g He $(1s^2)$ + ^1S_g He $(1s\,2s)$, a single K-shell vacancy will be

created. On the other hand, if the partners separate diabatically

$$1\sigma_g^2 \, 2\sigma_g^2 \rightarrow \text{ a) He}^*\,(1s\,2s) + \text{He}^*\,(1s\,2s) \qquad\qquad (4)$$
$$\text{b) He}^+\,(1s) + \text{He}^-\,(1s\,2s^2)$$

two K-shell vacancies may be created.

As we have noted, the $1\sigma_u$ and $2\sigma_g$ orbital energies cross

at a separation of 0.75 bohrs, while the $1\sigma_g^2 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g^2$

configurations (or quasi-diabatic[20] potential curves) cross

at R = 0.56 bohrs. In this sense the promotion model is

verified qualitatively but not quantitatively. The crossing

of the diabatic curves occurs at an energy of 69.3 eV relative
to two infinitely separated ground state helium atoms. This
energy is, of course, sufficient for the creation of one or
two K-shell vacancies. However, this energy is not sufficient
to doubly ionize a single He atom (79.0 eV is required[21]), to
produce [see Eq. (2)] the neutral dissociation limit
[He ^{1}S ($1s^2$) + He ^{1}S ($2s^2$)], or the ionic limit involving
He$^+$ ^{2}S (2s).

ACKNOWLEDGMENTS

REFERENCES

1. R. S. Mulliken, Rev. Mod. Phys. $\underline{4}$, 1 (1932).

2. A. D. Walsh, J. Chem. Soc. (London) $\underline{1953}$, 2260; and
    several following papers.

3. R. B. Woodward and R. Hoffmann, The Conservation of
    Orbital Symmetry (Verlag Chemie, Weinheim/Bergstr.,
    1970).

4. Proceedings of the International Conference on Inner
    Shell Ionization Phenomena, Atlanta, Georgia, 1972,
    edited by R. W. Fink, S. T. Manson, J. M. Palms, and
    P. V. Rao (U.S. AEC, Oak Ridge, Tenn., 1973).

5. U. Fano and W. Lichten, Phys. Rev. Letters $\underline{14}$, 627
    (1965); see also M. Barat and W. Lichten, Phys. Rev.
    A6, 211 (1972).

6. F. T. Smith, D. C. Lorents, and R. E. Olson, page
    1175 of reference 4.

7. W. E. Meyerhof, T. K. Saylor, S. M. Lazarus, W. A. Little,
    B. B. Triplett, and L. F. Chase, Phys. Rev. Letters $\underline{30}$,
    1279 (1973).

8. R. S. Mulliken, Chem. Phys. Letters $\underline{14}$, 137 (1972).

9. J. S. Briggs and M. R. Hayns, J. Phys. B $\underline{6}$, 514 (1973).

10. M. Barat, D. Dhuicq, R. Francois, and V. Sidis, J. Phys.
    B $\underline{6}$, 2072 (1973); V. Sidis and M. Barat, VIII ICPEAC,
    editors B. C. Cobic and M. V. Kurepa (Institute of Physics,
    Beograd, Yugoslavia, 1973).

11. F. B. Van Duijneveldt, IBM Report RJ 945 (IBM Research Laboratory, San Jose, California, December, 1971).

12. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results (Addison-Wesley, Reading, Mass., 1972).

13. T. H. Dunning, unpublished calculations on the lowest ^3P state of Be using a (4s 3p) basis set of Slater functions.

14. K. Ruedenberg, R. C. Raffenetti, and R. D. Bardo, pages 164-169 of Energy, Structure, and Reactivity, edited by D. S. Smith and W. B. McRae (Wiley, New York, 1973).

15. C. L. Pekeris, Phys. Rev. 134, A638 (1964).

16. G. H. Matsumoto, C. F. Bender, and E. R. Davidson, J. Chem. Phys. 46, 402 (1967).

17. I. Amdur and J. Jordon, Adv. Chem. Phys. 10, 29 (1966).

18. G. Gerber, R. Morgenstern, and A. Niehaus, J. Phys. B 6, 493 (1973).

19. M. Barat, D. Dhuicq, R. Francois, C. Lesech, and R. McCarroll, J. Phys. B 6, 1206 (1973).

20. V. Sidis and H. Lefebvre-Brion, J. Phys. B 4, 1040 (1971).

21. C. E. Moore, Atomic Energy Tables, Nat. Bur. Std. (U.S.) Circ. No. 467 (1949).

Table I. Basis set of contracted gaussian functions for He + He $\rightarrow$ Be.

Be Atom E $(1s^2\ 2s\ 2p)$ ^3P = -14.5102 hartrees

Type	Exponent α	Contraction Coefficient
1s	2732.0	0.001916
1s	410.3	0.014720
1s	93.67	0.074290
1s	26.59	0.275402
1s	8.630	0.720340
1s	3.056	1.0
1s	1.132	1.0
1s	0.1817	1.0
1s	0.05917	1.0
2p	3.202	0.052912
2p	0.6923	0.267659
2p	0.2016	0.792085
2p	0.06331	1.0

Table I. (Continued)

He Atom E (1s 2s) ^{3}S = -2.1729 hartrees

Type	Exponent α	Contraction Coefficient
1s	233.1	0.003311
1s	35.02	0.025461
1s	7.956	0.120438
1s	2.203	0.400907
1s	0.6643	0.571980
1s	0.2082	1.0
1s	0.06528	1.0
1s	0.02029	1.0
1s	0.006414	1.0

Table II. Comparison of total SCF energies (in hartrees) near the point

of avoided crossing of the two lowest $^1\Sigma^+$ states for the process

He + He $\rightarrow$ Be. The merged basis set was used in all calculations.

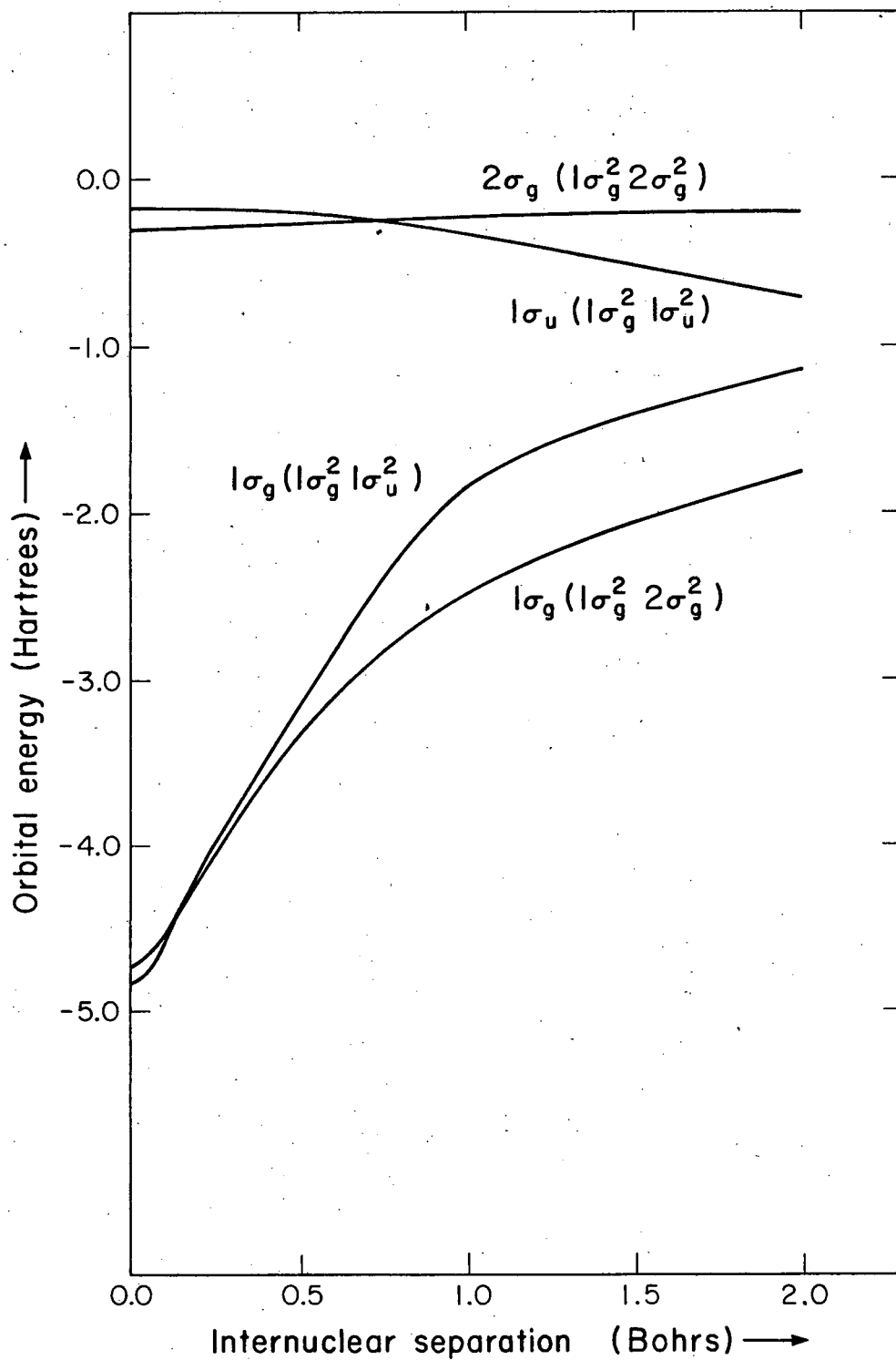| R (bohrs)	$1\sigma_g^2 \, 1\sigma_u^2$	$1\sigma_g^2 \, 2\sigma_g^2$	$1\sigma^2 \, 2\sigma^2$
0.70	−3.9513	−3.8145	−3.9513
0.60	−3.4456	−3.4093	−3.4456
0.56	−3.1741	−3.1736	−3.1741
0.55	−3.0980	−3.1059	−3.1059
0.50	−2.6546	−2.7030	−2.7030
0.40	−1.3036	−1.4224	−1.4224

Table III. SCF energies (in hartrees) of the $1\sigma_g^2\ 2\sigma_g^2$ configuration

for He + He → Be. Bond distances are in bohrs.

Basis Set R (He-He)	United Atom	Separated Atoms	Merged Basis
0.0	-14.5723	-12.6704	-14.5725
0.0625	49.6741	51.4120	49.6682
0.125	18.2344	19.6198	18.1712
0.25	3.5469	4.2297	3.3151
0.5	- 2.3342	- 2.3817	- 2.7030
1.0	- 3.6193	- 4.1922	- 4.2513
2.0	- 2.9402	- 4.0335	- 4.0773

Table IV. SCF total energies (in hartrees) of the $1\sigma_g^2\, 1\sigma_u^2$ configuration

for He + He → Be.   Bond distances are in bohrs.

Basis Set R (He-He)	United Atom	Separated Atoms'	Merged Basis
0.0	-14.2821		
0.1	26.2578	27.8061	26.2231
0.25	3.7476	4.4588	3.5189
0.5	- 2.2723	- 2.3050	- 2.6546
0.75	- 3.5661	- 4.0075	- 4.1407
1.0	- 3.9170	- 4.7168	- 4.7667
2.0	- 3.8327	- 5.5915	- 5.5953

FIGURE CAPTIONS

Figure 1. Orbital energies as a function of internuclear

separation for He-He. Note that SCF calculations

on the $1\sigma_g^2\ 1\sigma_u^2$ and $1\sigma_g^2\ 2\sigma_g^2$ configurations yield

different $1\sigma_g$ orbital energies.

Figure 2. Adiabatic total energies and orbital energies for

He + He → Be. Note the avoided crossing at R = 0.56

bohrs. To lessen confusion, the total energy has

not been plotted in that region.

Fig. 1

XBL 745-3036

Fig. 23

XBL 745-3037