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Henry F. Schaefer III

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ELECTRON CORRELATION IN THE LOWEST $^1\Sigma^+$ STATE OF BERYLLIUM OXIDE

Henry F. Schaefer III

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

December 1970

ABSTRACT

Ab initio first-order wave functions, which include electron correlation, are reported for the lowest $^1\Sigma^+$ state of BeO. A contracted Slater function basis of better than double zeta plus polarization accuracy was used, resulting in 157 configurations, constructed from 569 distinct Slater determinants. Practical convergence in form of the molecular orbitals was obtained using the iterative natural orbital procedure. Considerable emphasis is placed on obtaining the correct dissociation behavior, in the present case to a two configuration ($1s^2 2s^2$ and $1s^2 2p^2$) wave function for ^1S Be plus a slightly better than Hartree-Fock wave function for the ^1D state of oxygen. The calculated dissociation energy is 6.58 eV, compared to the Hartree-Fock value, 4.13 eV, and the spectroscopic value recommended by Gaydon 6.69 ± 0.4 eV. The other spectroscopic constants represent a substantial improvement over the Hartree-Fock values and are all within 10% of experiment. The dominant configurations in the wave function are presented, and it is seen that, contrary to the suggestion of previous workers, the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2$ is not particularly important near the equilibrium internuclear separation. The natural orbital occupation numbers complete our picture of the electronic structure of $^1\Sigma^+$ BeO.

INTRODUCTION

For none of the alkaline earth oxides BeO, MgO, and CaO, has the electronic ground state been determined experimentally.[1,2] From symmetry considerations[3] and the known positions[4] of the electronic states of the isoelectronic molecule C_2, it has been concluded[1] that the ground states of these molecules might be $^1\Sigma^+$, $^3\Pi$, or $^3\Sigma^-$. Recent experimental work[5] seems to imply that the ground state of CaO is not $^1\Sigma^+$.

Thus it is not surprising that single configuration self-consistent-field calculations have been carried out on BeO,[6-9] MgO,[9,10] and CaO.[9,11] Perhaps the most interesting of the above theoretical studies[6-11] was that of Huo, Freed, and Klemperer.[8] They carried out near Hartree-Fock calculations on the $^1\Sigma^+$, $^3\Pi$, and $^1\Pi$ states of BeO, and found the $^1\Pi$ state to lie below the $^1\Sigma^+$. The fact that the $^1\Pi$ state is known to lie 9406 cm^{-1} above the $^1\Sigma^+$ state demonstrates clearly that electron correlation[12] determines the ordering of the low-lying states of BeO. The calculations on MgO by Richards, et al.[10] and on CaO by Carlson, et al.[11] also imply that the Hartree-Fock approximation is inherently inadequate for the prediction of the electronic ground states.

In light of recently developed methods[14-16] for the computation of electronic wave functions for diatomic molecules, it now seems feasible to attempt to predict the order of the low-lying states of BeO from ab initio calculations including electron correlation. In the present paper we report a first-step in this direction, a theoretical potential energy curve for the lowest $^1\Sigma^+$ state of BeO.

BASIS SET

The basis set used in the present work yields total energies slightly below the "double-zeta plus polarization functions" set described by Nesbet.[17] The oxygen atom basis has been given in an earlier paper[16] on O_2 and consists of a set of 5s, 3p, and 1d Slater type orbitals (STO's) contracted[18] to 4s, 2p, and 1d functions. For beryllium the Bagus-Gilbert set[19] of five s type STO's (optimized in a Hartree-Fock calculation for ^1S Be) was similarly contracted to four s following Dunning's rules.[18] Two 2p STO's were taken from an optimized SCF calculation by Dunning[20] on the $1s^2 2s2p$ ^3P excited state of Be. $d\sigma$ and $d\pi$ STO's with exponent 1.8 (chosen by inspection of earlier optimized SCF calculations[8,9] on BeO) completed the basis set. Table I shows the Be atom basis.

The above contracted basis yields an SCF energy of -74.72919 hartrees for the ^1D state of oxygen, while the Hartree-Fock energy is -74.72925.[19] For the ^1S state of Be our basis reproduces the Hartree-Fock energy -14.57302 hartrees.[19] An indication of the usefulness of our basis set in the BeO molecule is given by comparison of our SCF energies with the near Hartree-Fock results of Yoshimine.[9] At 2.5 bohrs separation the present basis set yields an SCF energy of -89.44461 hartrees, versus the more accurate value -89.45299 hartrees, which has been estimated[9] to lie no more than 0.0005 hartrees above the true Hartree-Fock energy. The 0.00838 hartrees missing in our basis is probably due both to the lack of additional polarization (d and f) functions and to the inflexibility of our sp basis.

THEORETICAL APPROACH

There is a growing body of evidence[16,21,22] that a particular type of configuration interaction (CI) wave function, here called the first-order wave function, may provide a reasonable description of molecular structure and molecular formation. This type of wave function was first used for the prediction of atomic electron affinities[23] and hyperfine structure[24] but has wider validity since it attempts to include only the structure sensitive part of the correlation energy. Many of the types of correlation effects included in the first-order wave function were discussed earlier by Silverstone and Sinomoglu.[25] The first molecular calculations involving some of these configurations were carried out by Das and Wahl[26] using their multiconfiguration SCF approach.[27]

In general the first-order wave function is the optimum linear combination of all possible configurations in which no more than a single electron occupies any orbital other than an SCF orbital or an orbital nearly degenerate with[28] one or more of the SCF orbitals. In practice our atomic calculations include only configuration of the above type which differ by one or two orbitals from the SCF reference configuration. In molecules we have imposed[16,21,22] the further "chemical" restriction that inner shell orbitals remain doubly-occupied in all configurations.

The configurations used in the present BeO calculations are shown in Table II. They are of three distinct types

a) Single excitations

b) Excitations of the type $X_i X_j \rightarrow X_k X_\ell$ where X is one of the orbitals $3\sigma, 4\sigma, 5\sigma, 6\sigma, 1\pi, 2\pi$. Note that although the 5σ, 6σ, and 2π orbitals of not occupied in the $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$ SCF configuration, they play a crucial role in our wave function.

c) Excitations of the type $X_i X_j \rightarrow X_k Y_\ell$ where Y_ℓ is not a valence orbital, i.e. Y_ℓ is one of the higher ($7\sigma, 8\sigma, \ldots$ or $3\pi, 4\pi, \ldots$) orbitals in our basis.

PROPER DISSOCIATION OF $^1\Sigma^+$ BeO

The Wigner-Witmer rules[3] state that the lowest $^1\Sigma^+$ state of BeO cannot dissociate to ground state Be and O atoms, but rather to ground state Be plus the first excited state (^1D) of oxygen. Any acceptable theory of molecular formation must reproduce this known behavior. Despite the fact that Be is a closed-shell atom, BeO does not dissociate properly in the Hartree-Fock approximation. While the sum of the Hartree-Fock atom energies is -89.30227,[19] a R = 5.5 bohrs the molecular Hartree-Fock energy[9] is -89.26894. The reason for this improper dissociation behavior is that the Hartree-Fock configuration for $^1\Sigma^+$ BeO

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4 \quad ,$$

can describe the ^1S state of Be but cannot describe the ^1D state of O, since a linear combination of two determinants represents the $M_L = 0$ component of the ^1D LS eigenfunction for the $1s^2 2s^2 2p^4$ orbital occupancy. The second configuration required for dissociation to Hartree-Fock atoms is

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 1\pi^2 \quad .$$

The atomic wave functions for ^1S Be and ^1D O, consistent with the molecular wave function described in the previous section, go somewhat beyond the Hartree-Fock approximation. For Be the configuration included are $1s^2 2s^2$,

$1s2s^23s$, $1s2s^24s$, $1s^22s3s$, $1s^22s4s$, $1s^22p^2$, and $1s^22p3p$. Upon applying the Bender-Davidson iterative natural orbital procedure[29,30] to this Be wave function, all but the $1s^22s^2$ and $1s^22p^2$ configurations are annihilated (i.e. their coefficients in the CI expansion go to zero) and an energy of -14.61359 hartrees is obtained. This energy can be compared to the two configuration SCF result of Clementi and Veillard[28] -14.61545 hartrees, obtained with a larger basis set. For ^1D oxygen the configurations included were $1s^22s^22p^4$, $1s2s^23s2p^4$, $1s2s^24s2p^4$, $1s^22s3s2p^4$, $1s^22s4s2p^4$, and $1s^22s^22p^33p$ were included and the computed energy was -74.72936, only 0.00011 hartrees below the Hartree-Fock energy.[19] Thus we see that our BeO wave function should dissociate to a two configuration SCF wave function for beryllium plus a wave function only slightly better than Hartree-Fock for ^1D oxygen.

Using the 153 configurations given in Table II the calculated BeO energy at 6 bohrs separation was -89.33523 hartrees, or 0.00772 hartree above the sum of the atomic energies -84.34295. The reason for this apparent slight maximum in our potential curve is that configurations arising from two additional orbital occupancies must be included to obtain the correction dissociation.

At large separation the 4σ, 6σ, and 2π natural orbitals are essentially the 2s, $2p\sigma$, and $2p\pi$ Be atom orbitals. Thus the four electron molecular "subconfigurations" $2\sigma^24\sigma^2$, $2\sigma^26\sigma^2$, and $2\sigma^22\pi^2$ are required to describe the Be atom $1s^22s^2$ and $1s^22p^2$ configurations. However, as pointed out above, the eight electron functions $1\sigma^23\sigma^21\pi^4$ and $1\sigma^23\sigma^25\sigma^21\pi^2$ are needed to describe the ^1D O SCF configuration. It follows that in order to describe the dissociation of $^1\Sigma^+$ BeO we must include all configurations which arise as products of the four and eight electron subconfigurations, i.e.,

$$\begin{matrix} 2\sigma^2\ 4\sigma^2 \\ 2\sigma^2\ 6\sigma^2 \\ 2\sigma^2\ 2\pi^2 \end{matrix} \quad \otimes \quad \begin{matrix} 1\sigma^2 3\sigma^2 1\pi^4 \\ 1\sigma^2 3\sigma^2 5\sigma^2 1\pi^2 \end{matrix}$$

Two configurations arising above,

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 5\sigma^2\ 6\sigma^2\ 1\pi^2$$

$$1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 5\sigma^2\ \ 1\pi^2\ 2\pi$$

are not included in our 153 configuration wave function. Although these two configurations are of the type that should in general be included in first-order wave functions[23] (see section above on Theoretical Approach), they were excluded because they are quadrupole excitations with respect to the SCF reference state.

After including the four additional configurations arising from these two orbital occupancies, the calculated energy at 6 bohrs was -89.34422 hartrees, or 0.00127 hartrees below the asymptotic limit. These four extra configurations were also included in our calculations at R = 4.0 bohrs. However, for smaller bond distances these quadruple excitations become unimportant[16] and were excluded since we do not intend to explicitly demonstrate the correct dissociation behavior for the other electronic states of BeO. On the basis of the present results and our O_2 experience,[16] where one quadruple excitation was required to attain correct dissociation, we conclude that unless one is willing to go to a complete first-order wave function within the chosen basis,[31] a certain amount of thought is required for each state under consideration.

COMPUTATIONAL PROCEDURE

For our basis of 14σ and 6π orbitals, 11,802 distinct nonvanishing two-electron integrals over molecular orbitals must be computed. A completely numerical procedure, described elsewhere,[14] is used to directly compute these integrals over the orthogonal molecular orbitals. Symmetry-adapted $^1\Sigma^+$ configurations were construction by diagonalization of the operator $\underset{\sim}{S}^2 - (\frac{1}{2})\,\sigma_v$ over sets of Slater determinants with $M_s = 0$.[15] The 157 configuration (4 and 6 bohrs only) wave function is constructed from 569 distinct Slater determinants.

The Bender-Davidson iterative natural orbital (INO) procedure[29,30] was used to obtain optimum or nearly optimum sets of molecular orbitals. For O_2 the use of symmetry orbitals provided rapid and consistent convergence of the INO procedure.[16] However, for BeO there is less symmetry and use of Hartree-Fock atomic orbitals gave slow convergence. By first carrying out a molecular SCF calculation, convergence was greatly improved. For example, at R = 2.4 bohrs, the energies of the successive INO iterations were -89.57126, -89.57675, -89.58124, -89.58220, -89.58251, and -89.58253 hartrees. For R = 2.1, 2.3, 2.5, 2.7, and 2.9 bohrs the above procedure, beginning with molecular SCF orbitals, was followed and similar trends were observed. However, at larger separations, the natural orbitals are expected to be closer to the atomic than to the molecular SCF orbitals. For this reason at 4 and 6 bohrs the most useful starting orbitals were just the atomic SCF orbitals. At 6 bohrs only a single INO iteration was carried out and at 4 bohrs only two iterations were required.

SPECTROSCOPIC CONSTANTS

Table III gives the calculated total energies at eight internuclear separations. Calculated spectroscopic constants are compared with Yoshimine's near Hartree-Fock values and experiment in Table IV. Except for D_e, the experimental spectroscopic constants are those of Lagerquist.[32]

The experimental value of D_e given in Table IV deserves special attention.[1] For the lowest $^1\Sigma^+$ state of BeO, vibrational levels up to v = 16 (at 2.56 eV) are known[32] and extrapolation yields a value of D_0 of 5.9 eV. However, by the Wigner-Witmer rules,[3] the A $^1\Pi$ state of BeO must also dissociate to ^1S Be + ^1D O. For the A $^1\Pi$ state vibrational levels up to v = 25 (lying 4.4 eV above the v = 0 level of the $^1\Sigma^+$ state) have been observed[33] and extrapolate to a value of 6.78 eV. Gaydon weights the A $^1\Pi$ extrapolation heavier and concludes[1] that the spectroscopic value of D_0 for the $^1\Sigma^+$ state of BeO is 6.6 ± 0.4 eV. Adding $\frac{1}{2}\,\omega_e = 0.093$ eV, we obtain for D_e the value 6.69 ± 0.4 eV given in Table IV.

Our ab initio value of the dissociation energy of $^1\Sigma^+$ BeO is within experimental error. For the O_2 molecule, a nearly comparable calculation[16] yielded a dissociation energy 0.49 eV less than the precisely known experimental value. However, our basis set for O_2 yielded an SCF energy 0.53 eV above the Hartree-Fock energy,[34] whereas for BeO our SCF energy is only 0.23 eV above the Hartree-Fock energy.[9] Thus we see that for O_2 our ab initio D_e differed from experiment by almost exactly the deviation of our SCF energy from the Hartree-Fock energy. If we add 0.23 eV to our calculated D_e for BeO we obtain a value 6.81 eV, which is close to the 6.87 eV obtained by Lagerqvist's extrapolation of the A $^1\Pi$ vibrational levels. For comparison, the mass-spectrometric value[35] (which refers to the as yet unknown ground state) is

6.68 ± 0.1 eV. Although we will not make any conclusions concerning the ground state until calculations are completed on other states ($^3\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$), the fact that ab initio calculations of dissociation energies now seem to be in a position to rival experiment indicates a significant advance in theoretical chemistry.

Table IV also shows that our calculated spectroscopic constants are in significantly better agreement with experiment than the Hartree-Fock constants.[9] The percentages of experiment obtained were r_e 98.6%, ω_e 109.5%, $\omega_e x_e$ 103.7%, B_e 102.9%, α_e 91.6%. Our calculated potential energy curve is compared with the Hartree-Fock curve in Fig. 1.

ELECTRONIC STRUCTURE

For five internuclear separations, the most important configurations are given in Table V. One inevitable result seen in Table V is that as R becomes larger the single configuration approximation becomes progressively worse, that is the coefficient of the first natural configuration becomes smaller. It is significant that all of the most important configurations involve only the valence orbitals 3σ-6σ, 1π, and 2π, which, in a simpler approximation arise from the 2s and 2p atomic orbitals on Be and O. Near r_e the double excitation $1\pi^2 \rightarrow 2\pi^2$ is the second most important configuration. As expected, at our largest separation the excitation $1\pi^2 \rightarrow 5\sigma^2$, required to describe the ^1D state of the oxygen atom, becomes very important. However, near r_e this configuration is rather unimportant, contrary to the hypothesis of Carlson, et al.[11] concerning CaO. Carlson, et al.[11] suggest that strong configuration interaction between the $\sigma^2\pi^4$ and $\sigma^2\pi^2\sigma^2$ configurations is responsible for the lowering of the $^1\Sigma^+$ state relative to the triplet states of CaO. It is our general contention that the correlation problem is rather complicated and that visualizing configuration interaction between "nearly physical states" can be misleading.

For each geometry, after our last natural orbital iteration the first order reduced density matrix is diagonalized.[36] The resulting natural orbital occupation numbers are given for five internuclear separations in Table VI. These occupation numbers provide a simple, clear picture of the electronic structure of $^1\Sigma^+$ BeO. The occupation number vary is a rather smooth way with changing R. For example, the 4σ and 1π become less occupied as R increases while the 5σ and 2π orbitals become more important. It is seen that, after the highest valence orbitals 6σ and 2π, the occupation numbers drop off sharply.

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FOOTNOTES AND REFERENCES

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Table I. Be atom basis set for calculations on the BeO molecule. Each orbital is a linear combination of normalized Slater-type orbitals. The O atom basis was the same as that described previously.[16]

Orbital Exponent	1s	2s	2s'	2s"	2p	2p'	3d
1s(ζ = 5.748)	0.20331	-0.01969					
1s(ζ = 2.945)	0.89756	-0.21113					
3s(ζ = 3.630)	-0.11149	-0.02030					
2s(ζ = 1.290)			1.0				
2s(ζ = 0.854)				1.0			
2p(ζ = 2.1033)					1.0		
2p(ζ = 0.8352)						1.0	
3d(ζ = 1.8)							1.0

Table II. Configurations in the approximate first-order wave function for the $^1\Sigma^+$ state of BeO.

Type Excitation	$^1\Sigma^+$ configurations per orbital occupancy	Total Configurations
$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$	1	1
$1\sigma \rightarrow 5\sigma, 6\sigma, \ldots 14\sigma$	1	10
$2\sigma \rightarrow 5\sigma, 6\sigma, \ldots 14\sigma$	1	10
$3\sigma \rightarrow 5\sigma, 6\sigma, \ldots 14\sigma$	1	10
$4\sigma \rightarrow 5\sigma, 6\sigma, \ldots 14\sigma$	1	10
$1\pi \rightarrow 2\pi, 3\pi, 4\pi, 5\pi, 6\pi$	1	5
$3\sigma^2 \rightarrow 5\sigma^2, 5\sigma 6\sigma, 6\sigma^2, 2\pi^2$	1	4
$3\sigma 4\sigma \rightarrow 5\sigma^2, 6\sigma^2, 2\pi^2$	1	3
$3\sigma 4\sigma \rightarrow 5\sigma 6\sigma$	2	2
$3\sigma 1\pi \rightarrow 5\sigma 2\pi, 6\sigma 2\pi$	2	4
$4\sigma^2 \rightarrow 5\sigma^2, 5\sigma 6\sigma, 6\sigma^2, 2\pi^2$	1	4
$4\sigma 1\pi \rightarrow 5\sigma 2\pi, 6\sigma 2\pi$	2	4
$1\pi^2 \rightarrow 5\sigma^2, 5\sigma 6\sigma, 6\sigma^2$	1	3
$1\pi^2 \rightarrow 2\pi^2$	3	3
$4\sigma^2 \rightarrow 5\sigma 7\sigma, 5\sigma 8\sigma, \ldots 5\sigma 14\sigma$	1	8
$4\sigma^2 \rightarrow 5\sigma 8\sigma, 5\sigma 8\sigma, \ldots 5\sigma 14\sigma$	1	8
$4\sigma^2 \rightarrow 2\pi 3\pi, 2\pi 4\pi, 2\pi 5\pi, 2\pi 6\pi$	1	4
$4\sigma 1\pi \rightarrow 5\sigma 3\pi, 5\sigma 4\pi, 5\sigma 5\pi, 5\sigma 6\pi$	2	8
$4\sigma 1\pi \rightarrow 6\sigma 3\pi, 6\sigma 4\pi, 6\sigma 5\pi, 6\sigma 6\pi$	2	8

(continued)

Table II. (Continued)

Type Excitation	$^1\Sigma^+$ configurations per orbital occupancy	Total Configurations
$4\sigma 1\pi \rightarrow 7\sigma 2\pi,\ 8\sigma 2\pi,\ \ldots\ 14\sigma 2\pi$	2	16
$1\pi^2 \rightarrow 5\sigma 7\sigma,\ 5\sigma 8\sigma,\ \ldots\ 5\sigma 14\sigma$	1	8
$1\pi^2 \rightarrow 6\sigma 7\sigma,\ 6\sigma 8\sigma,\ \ldots\ 6\sigma 14\sigma$	1	8
$1\pi^2 \rightarrow 2\pi 3\pi,\ 2\pi 4\pi,\ 2\pi 5\pi,\ 2\pi 6\pi$	3	12
TOTAL		153

Table III. Calculated total energies, in hartrees, for the lowest $^1\Sigma^+$ state of the BeO molecule. Internuclear separations are in bohrs. The computed correlation energy is the difference between the SCF and first-order energies.

	Self-Consistent Field	First Natural[a] Configuration	First-Order	Computed Correlation Energy
R = 2.1	-89.39311	-89.38818	-89.52208	0.12897
R = 2.3	-89.43917	-89.43266	-89.57325	0.13408
R = 2.4	-89.44563	-89.43839	-89.58252	0.13689
R = 2.5	-89.44460	-89.43615	-89.58455	0.13995
R = 2.7	-89.42757	-89.41696	-89.57355	0.14598
R = 2.9	-89.39943	-89.38620	-89.55082	0.15139
R = 4.0		-89.26641	-89.42211	
R = 6.0		-89.25988	-89.34422	
R = ∞			-89.34295	

[a] Note that, as must be the case, the first natural configuration energy is always higher than the self-consistent-field energy calculated within the same basis set.

Table IV. Spectroscopic constants for $^{1}\Sigma^{+}$ $^{9}\mathrm{Be}^{16}\mathrm{O}$. Energies are given in hartrees for calculations at 2.5 bohrs internuclear separation. The dissociation energies refer to $^{1}\mathrm{S}$ Be + $^{1}\mathrm{D}$ O.

	E(hartrees)	D_e(eV)	r_e(Å)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})
Near Hartree-Fock[a]	-89.45299	4.13	1.29	1736	10.66	1.754	0.0157
This work	-89.58455	6.58	1.313	1629	12.27	1.699	0.0174
Experiment		6.69 ± 0.4[b]	1.331[c]	1487[c]	11.83	1.651[c]	0.0190[c]

[a] Reference 8.

[b] From spectroscopic extrapolations of the $A^{1}\Pi$ and $X^{1}\Sigma^{+}$ state vibrational levels. See text.

[c] Reference 32.

Table V. Important configurations in the approximate first-order wave function for the $^1\Sigma^+$ state of BeO. The effects of all $^1\Sigma^+$ configurations arising from a given orbital occupancy are included in the coefficients.

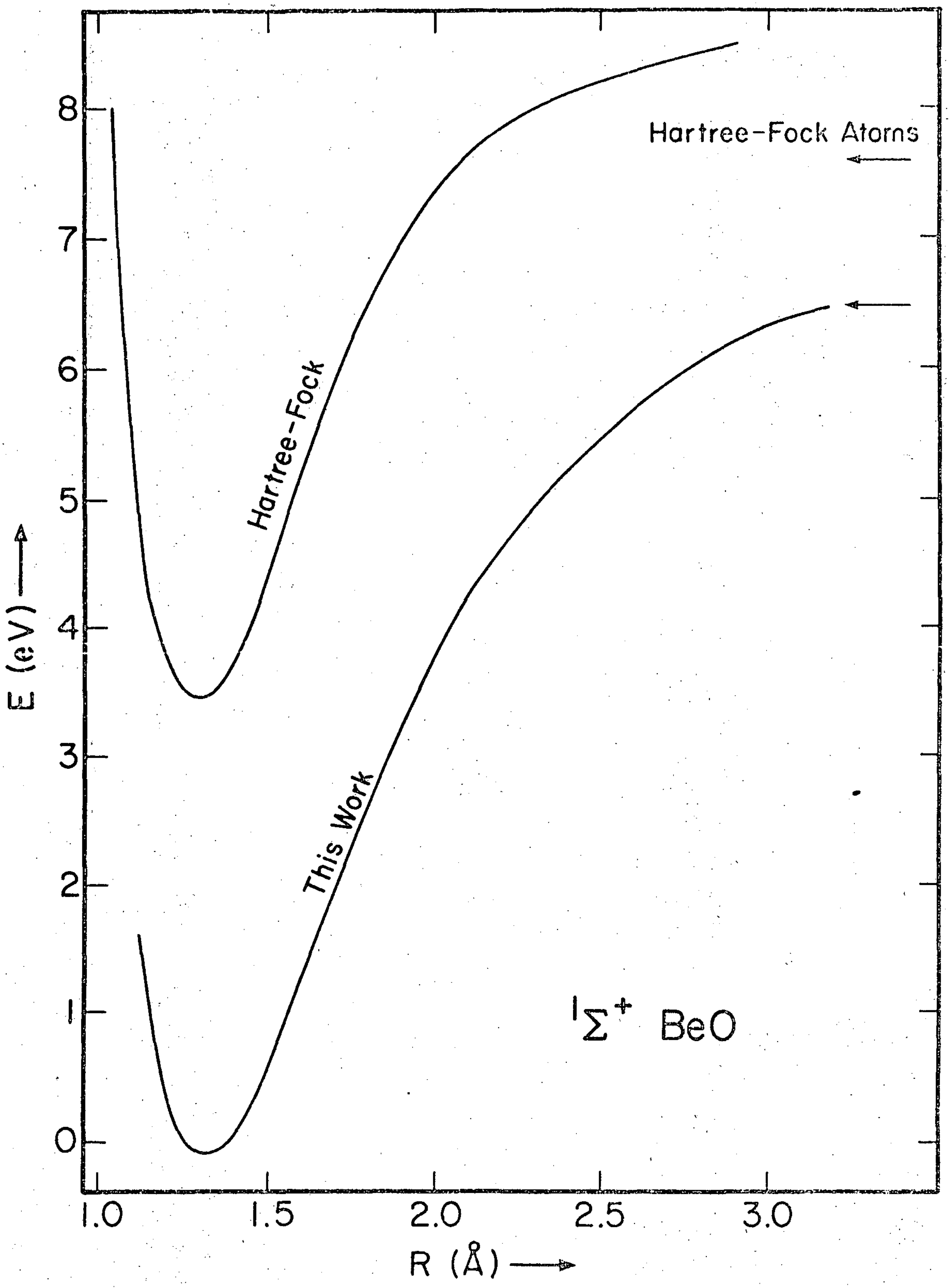
R(bohrs) Excitation	2.1	2.5	2.9	4.0	6.0
$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$	0.9784	0.9734	0.9669	0.8811	0.7805
$1\pi^2 \rightarrow 2\pi^2$	0.1448	0.1566	0.1506	0.0906	0.0009
$4\sigma 1\pi \rightarrow 5\sigma 2\pi$	0.0839	0.1142	0.1469	0.2492	0.1708
$3\sigma 1\pi \rightarrow 6\sigma 2\pi$	0.0716	0.0723	0.0705	0.0270	0.0007
$4\sigma^2 \rightarrow 5\sigma^2$	0.0360	0.0538	0.0896	0.2836	0.0073
$3\sigma 4\sigma \rightarrow 5\sigma 6\sigma$	0.0393	0.0431	0.0473	0.0241	0.0128
$1\pi^2 \rightarrow 5\sigma^2$	0.0314	0.0234	0.0308	0.0805	0.4920
$4\sigma^2 \rightarrow 2\pi^2$	0.0144	0.0180	0.0274	0.0760	0.2026
$4\sigma^2 \rightarrow 6\sigma^2$	0.0198	0.0132	0.0123	0.0304	0.1468
$4\sigma^2 1\pi^2 \rightarrow 5\sigma^2 2\pi^2$				0.0907	0.1338
$4\sigma^2 1\pi^2 \rightarrow 5\sigma^2 6\sigma^2$				0.0095	0.0910

Table VI. Natural orbital occupation numbers for $^1\Sigma^+$ BeO. The 1σ and 2σ occupation numbers are almost exactly 2.0 for all internuclear separations.

	3σ	4σ	5σ	6σ	7σ	1π	2π	3π
R = 2.1 bohrs	1.9893	1.9844	0.0145	0.0117	0.0002	3.9411	0.0577	0.0006
R = 2.5	1.9896	1.9765	0.0232	0.0108	0.0002	3.9288	0.0701	0.0003
R = 2.9	1.9900	1.9565	0.0431	0.0102	0.0003	3.9245	0.0755	0.0005
R = 4.0	1.9960	1.7303	0.2619	0.0138	0.0011	3.8754	0.1166	0.0041
R = 6.0	1.9996	1.7877	0.5687	0.0622	0.0005	3.4347	0.1457	0.0008

FIGURE CAPTION

Fig. 1. Approximate first-order and near Hartree-Fock potential curves for the lowest $^1\Sigma^+$ state of BeO. The arrows in the right margin indicate dissociation limits. See text for a discussion of the first-order dissociation limit.


Hartree-Fock Atoms
Hartree-Fock
This Work
$^1\Sigma^+$ BeO
E (eV)
R (Å)
0
1
2
3
4
5
6
7
8
1.0
1.5
2.0
2.5
3.0

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TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720