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ROLE OF ELECTRON CORRELATION IN A PRIORI PREDICTIONS OF THE
ELECTRONIC GROUND STATE OF BeO*

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ABSTRACT

Ab initio wave functions including electron correlation have been calculated for the $^3\Pi$ state of BeO. A (4s 2p 1d) basis set of Slater functions was centered on each atom. The iterative natural orbital method was used to optimize the set of molecular orbitals employed in each 591 configuration first-order wave function. The $^3\Pi$ energy calculated here is 0.73 eV above the $^1\Sigma^+$ energy obtained in a comparable calculation. Since near Hartree-Fock calculations result in a $^3\Pi$ energy below the $^1\Sigma^+$ energy, it seems clear that electron correlation plays a crucial role in the ordering of these states. Predicted spectroscopic constants for the $^3\Pi$ state are: $R_e = 1.463 \text{ \AA}$, $\omega_e = 1270$, and $B_e = 1.365 \text{ cm}^{-1}$. Natural orbital occupation numbers and coefficients of important configurations in the CI wave functions are presented to describe the electronic structure of $^3\Pi$ BeO.

INTRODUCTION

This is the third paper in a series^{1,2} aimed at predicting the symmetry of the ground state of BeO from theoretical calculations including consideration of electron correlation.^{3,4} Previous papers^{1,2} have treated the $^1\Sigma^+$, $^3\Sigma^+$, and $^3\Sigma^-$ states.

The long-standing interest in the undetermined symmetries of the ground states of BeO, MgO, and CaO is a matter of record.^{5,6} Candidates for ground states have been $^1\Sigma^+$, $^3\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$. The difficulty in determining which are the ground states results largely from the fact that no triplet states of these molecules have been observed experimentally. For BeO, Huo, Freed, and Klemperer⁷ have performed near Hartree-Fock (HF) calculations on the $^1\Sigma^+$, $^3\Pi$, and $^1\Pi$ states. Although the near HF results indicate that both $^1\Pi$ and $^3\Pi$ (lying a little below $^1\Pi$) lie below $^1\Sigma^+$, it is known from experiment that $^1\Pi$ really lies substantially above $^1\Sigma^+$. By assuming that correlation effects would not appreciably change the $^1\Pi - ^3\Pi$ separation, Huo et al. concluded that the $^3\Pi$ state actually lies about 1 eV above the $^1\Sigma^+$. An inescapable conclusion of the paper by Huo et al. is that electron correlation plays an important role in determining the order of the low-lying states.

The $^1\Sigma^+$, $^3\Sigma^+$, and $^3\Sigma^-$ states have already been investigated in calculations similar to those reported here. The $^3\Sigma^-$ state was found to be unbound, while the $^3\Sigma^+$ state was found to lie 1.93 eV above the $^1\Sigma^+$. The approach used in these calculations includes electron correlation through "first-order" CI wavefunctions. This method has been used to calculate potential curves for various states of O_2 ,⁸ BH,⁹ HF and HF⁺,¹⁰ and KrF⁺,¹¹ where its reliability has been verified by comparison of calculated and observed spectroscopic constants. We therefore are reasonably confident that the indicated ordering of the low-lying states of BeO is correct.

CALCULATIONS

A. Method

The basis set used here consists of contracted Slater functions: four s, two p, and one d on each atom.¹ It describes the individual atoms essentially to Hartree-Fock accuracy, while yielding a self-consistent-field (SCF) energy for $^3\Pi$ BeO at R_e roughly 0.003 hartree (0.08 eV) above that obtained by Huo et al. In turn, the Huo SCF energy probably lies about 0.005 hartree above the HF limit.

Correlation is treated through use of an approximate first-order wave function. The true first-order wave function is composed of (i) all "degeneracy effect" configurations, i.e. all arrangements of the electrons within the valence orbitals; and (ii) all single excitations thereof. Since correlation among the inner electrons is presumed to be structure-independent, such correlation is expected to be immaterial in the calculation of bonding behavior etc., and the configurations required for its description are dropped in our approximate first-order wave function. (For a full description of the configuration selection procedure, see Refs. 1 and 8.) The 591 configurations used in these calculations are shown in Table I.

As before, each calculation was performed in three stages. The first stage obtains the SCF solution (within our basis set) by performing natural orbital iterations on the reference configuration and all its single excitations, until the energy contributions of the singly-excited configurations vanish.

Now it is known that in an SCF wave function, the requirement of anti-symmetrization allows certain groups of orbitals to "mix" within a unitary transformation without changing the wave function at all: for instance, in the $^3\Pi$ reference configuration, $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3$, all rotations among the final

1σ , 2σ , 3σ , and 4σ orbitals yield equally acceptable SCF solutions, equally likely to result from our SCF stage. Since the first-order stage of our calculation does distinguish between, for instance, the 1σ and 4σ orbitals, we find it necessary to protect the first-order stage from the caprices of the SCF stage with an intermediate stage which rotates the occupied orbitals into approximate agreement with the conventional Hartree-Fock orbitals. Simultaneously a general uniformity is imposed upon the virtual orbitals. This is accomplished by transforming the virtual orbitals so as to describe the excited states of the BeO^+ ion.

The third stage then consists of natural orbital iterations on the (approximate) first-order wavefunction.

For these calculations on the $^3\Pi$ state of BeO (at each of 6 internuclear separations), typical computation times on a CDC 6600 were:

SCF stage	---	5 iterations at 26 seconds each;
rotation	---	19 seconds;
first-order	---	10 iterations at 150 seconds each

(comprising 80 sec for setting up the configuration interaction (CI) matrix, 50 sec for obtaining the lowest eigenvalue and eigenvector of the 591×591 matrix, and 16 sec for two-electron integral transformation).

B. Natural Orbital Convergence

A single natural orbital iteration consists of a CI calculation followed by an orbital transformation designed to diagonalize the first-order density

matrix corresponding to the CI wave function. The effect of the density matrix diagonalization is to rearrange the orbitals in such a way that dominant orbitals generally become more important, and higher virtual orbitals less important. As a usual concomitant effect, the contributions of a large number of configurations in the CI expansion diminish markedly, indicating that with the new orbitals, the correlation in the same CI wave function may be described with fewer configurations. In the case of a full CI calculation, a CI calculation following the density matrix diagonalization will yield exactly the same wave function (since a rotation among the orbitals does not alter the space spanned by all configurations constructed from those orbitals), but will describe it with fewer important configurations than did the first CI. In other words, a few configurations will be greatly improved in their description of the wave function.

In the case of a partial CI, one might expect that such an improvement among a few important configurations could actually result in a better wave function. And indeed, it generally results that the second CI energy is substantially lower than the first, and a third lower than the second, and thus natural-orbital iterations are continued until the downward trend in the CI energies comes to an end.

This end can come about in either of two ways: sometimes the successive improvements in the CI energy become progressively smaller and fall below some threshold, whereupon the natural orbital iterations are stopped; or sometimes a CI energy higher than the previous energy appears, indicating the onset of a period of meanderings toward higher energies, and NO iterations are, again, stopped. In this second case it becomes clear that in an incomplete CI calculation, the NO transformation is not obliged to yield a lower energy. Nonetheless, since the upward regression is usually small in comparison with energies of interest

(generally less than 0.01 eV), and since each CI calculation is itself a variational calculation, we feel justified in taking the lowest CI energy as our final value. (The final justification, naturally, comes from comparison with experiment.)

The convergence of the natural-orbital procedure was slower for some calculations on the $^3\Pi$ state of BeO than for any other calculations we have reported. Although the calculations at 2.3, 2.4, and 2.5 bohrs all ended neatly when the CI energy increased on the fifth iteration (by less than 0.01 eV in each case), the calculations at 2.7, 2.9, and 3.1 bohrs took 20, 15, and 13 iterations before the monotonic descent of the energy fell below our threshold of 10^{-5} hartree. Since convergence in about 5 iterations is customary, such slow convergence (particularly on so large a problem) is perplexing. Inspection of the orbitals at various points toward the end of each of these three calculations shows that they are changing monotonically and slowly, suggesting that the desired progress is being "damped". The most obvious way to hasten convergence would be to add an extrapolation feature to the iterative natural orbital procedure. Such a feature has proved very useful in multiconfiguration SCF calculations.¹²

RESULTS

The energies calculated are tabulated in Table II. Figure 1 shows the position of the $^3\Pi$ state in relation to the states previously calculated. The $^1\Sigma^+$ is seen to be the lowest, with a calculated minimum energy of -89.58466 hartrees. The $^3\Sigma^+$ state lies 1.91 eV ($15,430$ cm^{-1}) above the $^1\Sigma^+$, comparing well with the corresponding state of the isoelectronic molecule C_2 , which lies $13,312$ cm^{-1} above the lowest $^1\Sigma^+$. However, arguments based on the isoelectronic molecule seem shaky with a $^1\Sigma^+ - ^3\Pi$ separation of roughly 6000 cm^{-1} (versus 610 cm^{-1} in C_2), and are apparently completely misleading in the case of the $^3\Sigma^-$ state. Although we calculate the $^3\Sigma^-$ state of BeO to be repulsive, the corresponding $^3\Sigma^-$ state of C_2 is bound and lies only 6434 cm^{-1} above the lowest $^1\Sigma^+$.

A simple program which fits a fifth-degree polynomial to the tabulated potential curves calculated the spectroscopic constants shown in Tables III and IV. Since the $^3\Pi$ state has never been observed, the corresponding constants for the $^1\Pi$ state are provided for comparison. Huo et al. found the potential curves for the $^3\Pi$ and $^1\Pi$ states--in the SCF approximation--to be nearly parallel, suggesting that the $^3\Pi$ and $^1\Pi$ vibrational and rotational constants would be similar. Table III shows that the constants calculated from the first-order potential curve are reasonably close to those observed for the $^1\Pi$. Especially noteworthy is the close agreement (well within our expected error) between the calculated and observed R_e . Also note that our calculated value of 0.734 eV for the $^1\Sigma^+ - ^3\Pi$ separation (reliable to roughly 0.25 eV) is in reasonable agreement with the value estimated by Huo, Freed, and Klemperer, 1.05 eV, supporting the assumption incorporated in their semi-empirical prediction.

The nature of this description of the correlation energy of ${}^3\Pi$ BeO is best seen from tabulations of the coefficients of important configurations in the approximate first-order wave function (Table V) and the occupation numbers of the important orbitals (Table VI). The coefficient of the ${}^3\Pi$ reference configuration, 0.985, is considerably closer to unity than the corresponding coefficient for the ${}^1\Sigma^+$ state (0.973), consistent with the notion that correlation energy is more important in the ${}^1\Sigma^+$ state. The most important excitation is $1\pi^2 \rightarrow 2\pi^2$, as it was both for ${}^1\Sigma^+$ and for ${}^3\Sigma^+$, followed closely in this case by $4\sigma 1\pi \rightarrow 6\pi 2\pi$, which may correspond to the second-most-important $4\sigma 1\pi \rightarrow 5\sigma 2\pi$ in the case of ${}^1\Sigma^+$. Also indicative of the smaller role of correlation in the ${}^3\Pi$ state are the occupation numbers, which are uniformly closer to their single-configuration limits than in the ${}^1\Sigma^+$ state. The 2π and 6σ orbitals are seen to describe the greatest part of the correlation.

ADDITIONAL COMPUTATIONS ON THE $3\Sigma^-$ STATE

Since we submitted our calculations on the $3\Sigma^-$ state, Dunning and Hunt¹⁴ have conjectured that the configuration $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3 2\pi$, omitted in our calculations, may contribute substantially to the stability of that state. An SCF calculation on the $1\pi^3 2\pi$ configuration at 2.7 bohrs gave an energy of -89.295 hartrees, compared with -89.291 for the configuration used in the original calculations ($1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2$). A small calculation involving both configurations yielded a substantial energy improvement (to -89.341), but did not bring the energy below the dissociation limit (-89.382). First-order calculations are under way.

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FOOTNOTES AND REFERENCES

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Table I. Configurations included in the approximate first-order wave function for the $^3\Pi$ state of BeO.

Excitation	$^3\Pi$ Configurations per orbital occupancy	Total configurations
Reference $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3$	1	1
$1\sigma \rightarrow 5\sigma, \dots 14\sigma$	1	10
$2\sigma \rightarrow 5\sigma, \dots 14\sigma$	1	10
$3\sigma \rightarrow 5\sigma$	1	1
$3\sigma \rightarrow 6\sigma$	3	3
$3\sigma \rightarrow 7\sigma, \dots 14\sigma$	1	8
$4\sigma \rightarrow 5\sigma$	1	1
$4\sigma \rightarrow 6\sigma, \dots 14\sigma$	3	27
$5\sigma \rightarrow 6\sigma, \dots 14\sigma$	1	9
$1\pi \rightarrow 2\pi, \dots 6\pi$	4	20
$3\sigma^2 \rightarrow 5\sigma 6\sigma$	1	1
$\rightarrow 6\sigma^2$	1	1
$\rightarrow 1\pi 2\pi$	1	1
$\rightarrow 2\pi^2$	4	4
$3\sigma 4\sigma \rightarrow 5\sigma 6\sigma$	3	3
$\rightarrow 6\sigma^2$	3	3
$\rightarrow 1\pi 2\pi$	3	3
$\rightarrow 2\pi^2$	12	12
$3\sigma 5\sigma \rightarrow 6\sigma^2$	1	1
$\rightarrow 1\pi 2\pi$	1	1

(continued)

Table I. (continued)

Excitation	$^3\Pi$ Configurations per orbital occupancy	Total configurations
$\rightarrow 2\pi^2$	4	4
$3\sigma 1\pi \rightarrow 5\sigma 2\pi$	4	4
$\rightarrow 6\sigma 2\pi$	12	12
$4\sigma^2 \rightarrow 5\sigma 6\sigma$	1	1
$\rightarrow 6\sigma^2$	1	1
$\rightarrow 1\pi 2\pi$	1	1
$\rightarrow 2\pi^2$	4	4
$4\sigma 5\sigma \rightarrow 6\sigma^2$	1	1
$\rightarrow 1\pi 2\pi$	1	1
$\rightarrow 2\pi^2$	4	4
$4\sigma 1\pi \rightarrow 5\sigma 2\pi$	4	4
$\rightarrow 6\sigma 2\pi$	12	12
$5\sigma 1\pi \rightarrow 6\sigma 2\pi$	4	4
$1\pi^2 \rightarrow 5\sigma 6\sigma$	1	1
$\rightarrow 6\sigma^2$	1	1
$\rightarrow 2\pi^2$	4	4
$4\sigma^2 \rightarrow 5\sigma n\sigma \quad n=7, \dots, 14$	1	8
$\rightarrow 6\sigma n\sigma$	3	24
$\rightarrow 1\pi m\pi \quad m=3, \dots, 6$	1	4
$\rightarrow 2\pi m\pi$	9	36
$4\sigma 5\sigma \rightarrow 6\sigma n\sigma$	3	24

(continued)

Table I. (continued)

Excitation	$^3\Pi$ Configurations per orbital occupancy	Total configurations
$\rightarrow 1\pi\pi\pi$	1	4
$\rightarrow 2\pi\pi\pi$	9	36
$4\sigma 1\pi \rightarrow 5\sigma\pi\pi$	4	16
$\rightarrow 6\sigma\pi\pi$	12	48
$\rightarrow n\sigma 2\pi$	12	96
$5\sigma 1\pi \rightarrow 6\sigma\pi\pi$	4	16
$\rightarrow n\sigma 2\pi$	4	32
$1\pi^2 \rightarrow 5\sigma n\sigma$	1	8
$\rightarrow 6\sigma n\sigma$	3	24
$\rightarrow 2\pi\pi\pi$	9	36

Table II. Calculated energy of the $^3\Pi$ state at various internuclear separations.

R(Bohrs)	SCF	First-Order	Calculated Correlation
2.3	-89.4379	-89.5048	0.0669
2.4	-89.4598	-89.5273	0.0675
2.5	-89.4735	-89.5424	0.0689
2.7	-89.4838	-89.5569	0.0731
2.9	-89.4798	-89.5550	0.0752
3.1	-89.4678	-89.5449	0.0771

Table III. Spectroscopic constants calculated for the $^3\Pi$ state of BeO.

	E_{Total}	T_e (eV)	R_e (Å)	ω_e (cm $^{-1}$)	B_e (cm $^{-1}$)
SCF ^a	-89.4877	-1.03	1.447	1213	1.397
This work	-89.5577	0.73	1.463	1270	1.365

^aRef. 7.

Table IV. Summary of predicted spectroscopic constants for the low-lying states of BeO. (Experimental values^b in parentheses.)

State	T_e (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)
$1\Sigma^+$	0	1.313(1.331)	1629(1487)	1.699(1.651)
3Π	0.734	1.463	1270	1.365
1Π	(1.166)	(1.463)	(1144)	(1.366)
$3\Sigma^+$	1.93	1.384	1234	1.527
$3\Sigma^-$	REPULSIVE			

^bRef. 13.

Table V. Coefficients of important configurations in the $^3\Pi$ wave function at 2.7 bohrs.

Excitation	Coefficient
Reference - $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3$	0.985
$1\pi^2 \rightarrow 2\pi^2$	0.090
$4\sigma 1\pi \rightarrow 6\sigma 2\pi$	0.090
$1\pi \rightarrow 2\pi$	0.056
$4\sigma^2 \rightarrow 5\sigma 6\sigma$	0.054
$1\pi \rightarrow 3\pi$	0.034
$4\sigma 1\pi \rightarrow 5\sigma 2\pi$	0.026
$3\sigma^2 \rightarrow 1\pi 2\pi$	0.023
$4\sigma 5\sigma \rightarrow 1\pi 2\pi$	0.023
$4\sigma^2 \rightarrow 1\pi 4\pi$	0.023
$5\sigma 1\pi \rightarrow 6\sigma 2\pi$	0.021

Table VI. Orbital occupation numbers for the two lowest states of BeO near their equilibrium positions.

	${}^3\Pi(2.7 \text{ bohrs})$	${}^1\Sigma^+(2.5 \text{ bohrs})$
1 σ	2.0	2.0
2 σ	2.0	2.0
3 σ	1.998	1.990
4 σ	1.981	1.977
5 σ	0.999	0.023
6 σ	0.016	0.011
1 π	2.971	3.929
2 π	0.032	0.070
3 π	0.002	0.000
4 π	0.001	0.000

FIGURE CAPTION

Fig. 1. Theoretical potential energy curves for the low-lying electronic states of BeO.

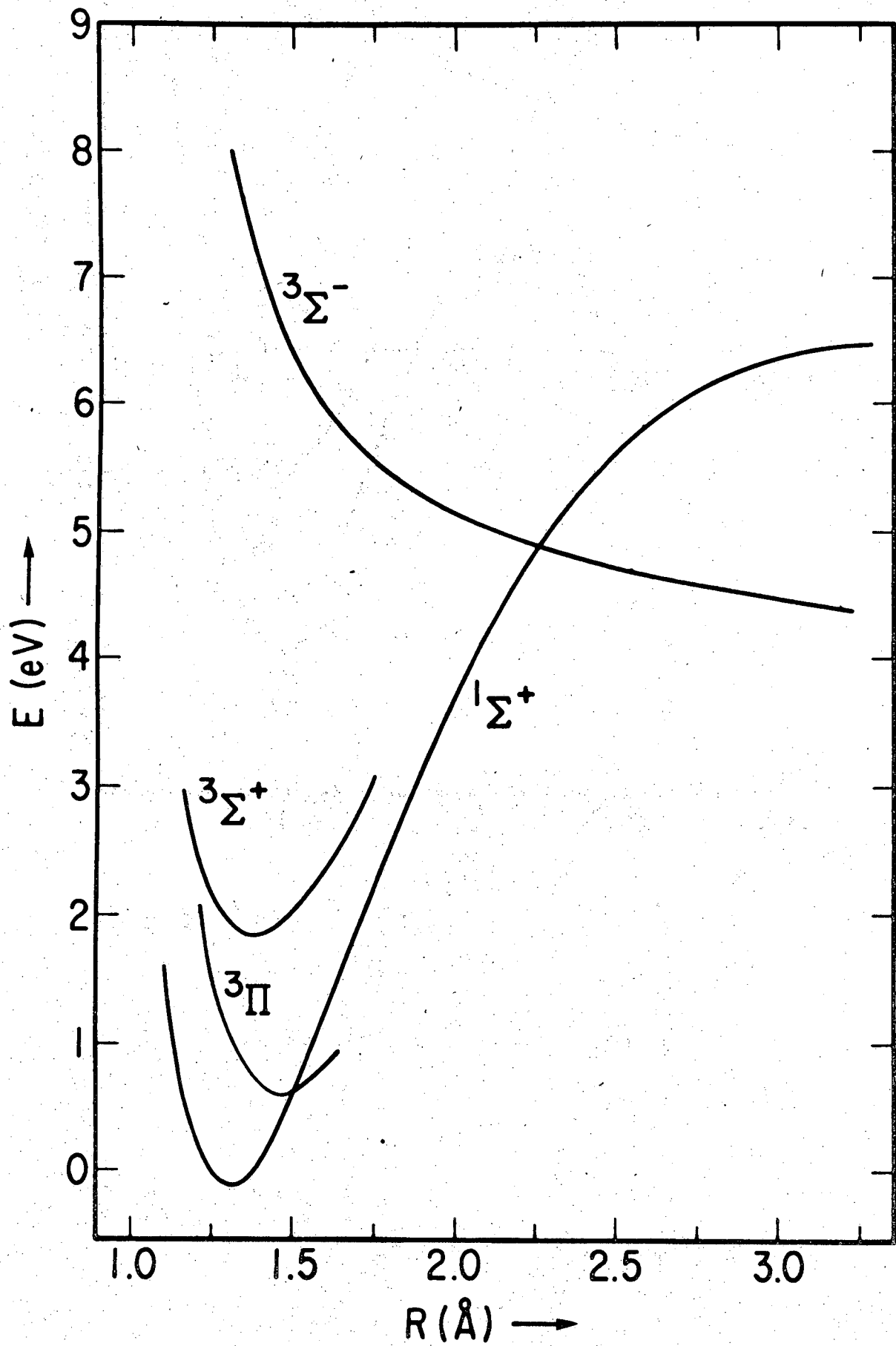


Fig. 1

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