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Publication Date
1970-09-01

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September 1970

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ELECTRONIC STRUCTURES AND POTENTIAL ENERGY CURVES

FOR THE LOW-LYING STATES OF THE CN RADICAL*

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ABSTRACT

At eleven internuclear separations ab initio calculations have been carried out on those 59 molecular states of CN which dissociate to atomic limits up to ^1D C + ^2D N. Four electrons are held frozen in carbon and nitrogen 1s Hartree-Fock atomic orbitals, and a full configuration interaction is carried out for the remaining nine electrons using optimized 2s and 2p Slater-type orbitals on each atom. The $^2\Pi$ calculations, which include 486 configurations, are the most complicated. Eighteen significantly bound states ($D_e \geqslant 0.84$ eV) were obtained, nine of which have been observed spectroscopically. With the exception of the third $^2\Pi$ state, the theoretical ordering of states agrees with experiment. Three of the states never observed experimentally, ($^4\Sigma^+$, $^4\Pi$, and $^4\Delta$) lie below all but three of the known states of CN. Calculated spectroscopic constants are compared with experiment. The potential curves show many interesting features, including potential maxima in the $^4\Sigma^-$, $^2\Sigma^-$, J $^2\Delta$, and $^2\Pi$ IV bound states. By performing natural orbital analyses, dominant molecular orbital configurations have been unambiguously assigned to the lowest 18 bound states. The second, third and fourth $^2\Pi$ states experience numerous avoided crossings among themselves, and natural orbitals have been

INTRODUCTION

The fact that there are four low-lying states of the carbon atom (^3P, ^1D, ^1S, ^5S) and three low-lying states (^4S, ^2D, ^2P) of the nitrogen atom guarantees the existence of a substantial number of low-lying (less than 10 eV) states of the CN molecule. Combined with the experimental interest,[1-11] particularly astrophysical, in CN, there would appear to be a great deal of motivation for ab initio calculations on the low-lying states of CN. Nevertheless we have been able to find only one such study in the literature, by Guerin.[12] He carried out calculations based on SCF orbitals and including no more than three configurations for the A $^2\Pi$, D $^2\Pi$, F $^2\Delta$, and J $^2\Delta$ states of CN. Although such calculations can be useful[13] in the study of excitation energies, it is well known[14] that diatomic molecular formation and dissociation cannot be properly described within the single configuration approximation unless one of the atoms is a closed shell species.

Over a wide range of internuclear separations, we have carried out ab initio configuration interaction (CI) calculations on all the states of CN which dissociate to atomic limits up to ^1D carbon plus ^2D nitrogen. Perhaps the most important aspect of the present work is the prediction of the existence of nine new bound states of CN.[15] A second area of emphasis in the present work involves the use of natural orbitals[16] to discuss the electronic structure of the valence-excited states of CN.

BASIS SET

Hartree-Fock atomic orbitals[17] for the ground states of C and N were used to describe the inner shell electrons. 2s and 2p Slater-type orbitals on each atom complete the basis set. The orbital exponents for the latter functions were optimized in repeated calculations on the $X\ ^2\Sigma^+$ ground state at the experimental internuclear separation. The resulting exponents for carbon were $\zeta(2s) = \zeta(2p) = 1.674$ and for nitrogen $\zeta(2s) = \zeta(2p) = 1.988$.

With the exception that the 1σ and 2σ molecular orbitals (MO's) are always doubly occupied, full CI calculations were carried out for all symmetries of interest. The calculated atomic energies for C and N are combined to give molecular dissociation limits in Table I. The comparison with experiment in Table I indicates that the **primary** deficiency in the atomic calculations is due to the fact that the ^5S state of carbon lies too low relative to the ^1D and ^1S states.

The basis set outlined above is the smallest with which one can reasonably expect to get **meaningful results** for potential surfaces. And in fact CI calculations of the same type (with molecule-optimized exponents) yielded good qualitative agreement with experiment for CO,[18] with seven of the eight known valence (i.e. non-Rydberg) states lying in the experimental order. Calculations of this type with atom-optimized exponents have also yielded qualitatively correct potential curves for O_2,[19] NH,[20] N_2,[21] and SiO.[22] Although much more accurate total energies than those reported here can be obtained using extended basis sets, the problem of treating molecular formation and dissociation is a difficult one within larger basis sets, and accurate potential curves of this type have only been reported for a few states of a few

diatomic molecules.[23]   Perhaps the primary virtue of CI treatments of the
type used here is that all molecular states dissociate smoothly to their
exact atomic limits.

Since our all-numerical methods[24] for the computation of molecular
integrals allow for the use of arbitrary orbitals, the present calculations
could equally well have been done entirely in terms of accurate Hartree-Fock
orbitals.[17]   This would have yielded much lower total energies and still
retained the correct dissociation behavior for all states.   However, as we
have shown for F_2[24] and Cl_2,[25] such a basis is optimum for the separated atoms
but far from optimum for the molecule, and this results in very poor calcu-
lated dissociation energies.   The basis set adopted here, HFAO's for the core
and STO's for the valence region, is about equally good (or bad) for both the
molecule and the separated atoms and thus yields reasonable potential curves.

CALCULATIONS

The methods used in the present study for the evaluation of integrals and construction of symmetry-adapted linear combinations of determinants are described elsewhere.[24, 26] Fifty-nine molecular states dissociate to the first seven atomic limits (see Table I) of CN. The resulting full valence CI calculations include the largest computations of this type reported to date.[18-22] The calculations are summarized in Table II, where it is seen that the largest calculation, of $^2\Pi$ symmetry, requires the ten lowest eigenvalues of a 486 × 486 matrix. Total CDC 6600 time used for all calculations was about seven hours.

The calculated total energies for 59 states at eleven internuclear separations (1.85, 2.0, 2.25, 2.5, 2.75, 3.0, 3.25, 3.5, 4.0, 5.0, 6.0) are not included here but can be obtained from the authors.[27]

SPECTROSCOPIC CONSTANTS: COMPARISON WITH EXPERIMENT

In Table III the _ab initio_ spectroscopic constants are compared with available experimental data. Eight states of CN have been fairly unambiguously identified and a ninth, designated G $^2\Pi$, has been tentatively assigned by Lutz.[11] For the eight known states our predicted ordering agrees with experiment except for the H $^2\Pi$ state. The H state is calculated to lie 0.049 eV below the E $^2\Sigma^+$ state and 0.072 eV below the F $^2\Delta$ state, but Douglas and Routly's measurements[2] indicate that the H $^2\Pi$ state in fact lies 0.156 eV _above_ the F $^2\Delta$ state. Thus if our calculated H $^2\Pi$ state were to lie 0.073 eV higher the _ab initio_ order would be in complete agreement with experiment for CN.

Our calculations predict a fourth $^2\Pi$ bound state which lies 0.95 eV above the $^2\Pi$ III state. Lutz[11] however tentatively assigns a fourth $^2\Pi$ state lying 0.04 eV below the H $^2\Pi$ state. However, inspection of Lutz's potential curves[11] shows that, if his analysis is correct, the G and H states at 60,624 cm^{-1} and 60,939 cm^{-1} are not two states but two different minima in a single $^2\Pi$ III state.

The theoretical r_e values are in all eight cases larger than experiment, the differences ranging from 0.064 to 0.104 Å. The relative differences are even better and the calculated ordering of r_e agrees with experiment except, again, for the H $^2\Pi$ state. The predicted rotational constants B_e follow the same pattern with respect to experiment, since B_e is proportional to $(1/r_e)^2$.

The calculated values of ω_e are the following percentages of experiment X $^2\Sigma^+$ 94%, A $^2\Pi$ 89%, B $^2\Sigma^+$ 82%, D $^2\Pi$ 104%, E $^2\Sigma^+$ 102%, J $^2\Delta$ 108%. Except for the B $^2\Sigma^+$ value; the theoretical ω_e's fall in the experimentally observed order.

The higher spectroscopic constants $\omega_e x_e$ and α_e are usually qualitatively similar to the experimental values. As can be seen from Table III, however, for the E $^2\Sigma^+$ state, the agreement for $\omega_e x_e$ is particularly poor.

NEW BOUND STATES OF CN

Since qualitatively correct spectroscopic constants were obtained for the known bound states of CN, it is to be expected that useful predictions can be made concerning states not yet observed experimentally. Table III predicts the existence of nine new states of CN. It is not surprising that none of these states have been observed, since six are quartet states, two are $^2\Sigma^-$, and the last is a $^2\Phi$ state. Transitions from these nine states to the ground X $^2\Sigma^+$ state are electronically forbidden.

It is perhaps surprising how low-lying some of the quartet states are. For example the $^4\Sigma^+$ state is predicted to lie only 0.251 eV above the very well characterized B $^2\Sigma^+$ state. And both the $^4\Pi$ and $^4\Delta$ states lie below the fourth known state of CN, D $^2\Pi$. Since all nine of these new states are observably bound ($D_e > 0.85$ eV), we hope that the present theoretical predictions will spur new experimental interest in the CN spectrum.

POTENTIAL CURVES

Figures 1-10 contain the calculated potential curves for 59 states of CN. In Fig. 11 the lowest bound states are seen. Several attempts were made to plot the higher bound states but the number of curve crossings makes the resulting figure virtually inscrutable. So, in Fig. 12 we indicate the energy of each of these bound states and the r_e value. This group of CN potential curves is the most interesting we have studied[18,19,22] to date, since there are a large number of significantly bound states and many more potential maxima than previously encountered.

Among the eighteen lowest bound states the $^4\Sigma^-$, $^2\Sigma^-$, J $^2\Delta$, and $^2\Pi$ IV all have potential maxima at about four bohrs. The heights of these maxima are, respectively, 0.43 eV, 0.24 eV, 0.43 eV, and 0.32 eV. All four maxima appear to be due to avoided crossings with higher states. The curves for the two lowest $^2\Sigma^-$ and $^2\Delta$ states are particularly interesting, since for both of these symmetries there are two nearly parallel bound states. Figure 6 shows that the $^4\Pi$ II state is quasi-bound. This state has a potential well of depth 1.41 eV, but the minimum nevertheless lies 0.67 eV above the dissociation limit. Two higher states having potential maxima are $^2\Delta$ III and $^4\Delta$ III.

The fact that, in our calculations, the ^{5}S state of carbon lies too low is reflected in our $^2\Sigma^+$ results. Figure 1 implies that the B state dissociates to ^{5}S carbon plus ^{4}S nitrogen, whereas in fact, it must dissociate to ^{3}P C + ^{2}D N. The $^2\Sigma^+$ IV curve is also affected, the maximum in its potential curve being a result of the ^{5}S + ^{4}S atomic limit lying too low. If we realize this limitation of the present results, one can more sensibly predict that the $^2\Sigma^+$ IV state should dissociate smoothly to ^{3}P C + ^{2}P N. Thus the $^2\Sigma^+$ IV state

is predicted to be bound with a dissociation energy of ~0.5 eV. Lutz[11] has

mentioned the possibility of the existence of a fourth $^2\Sigma^+$ state.

Several other points of interest can be seen in Figs. 1-12. The second
$^4\Sigma^+$ state has a very unusual shape, much like that of a bathtub. The lowest
$^6\Sigma^+$ state is slightly bound ($D_e \approx 0.3$ eV) with a minimum at r = 3.25 bohrs.
Furthermore, since this state dissociates to ground state carbon and nitrogen
atoms, it is very low-lying ($T_e < 6.0$ eV).

A particularly interesting series of crossing occurs for the $^2\Sigma^-$ states,
where the 3rd, 4th, 5th, and 6th potential curves avoid crossing a curve which
dissociates to a higher atomic limit than those considered here.

Mention should be made concerning the possibility of molecular
Rydberg states causing serious deviations from the predictions given here,
since our basis set is incapable of describing such Rydberg states. Table I
shows that the lowest Rydberg dissociation limit occurs 3.31 eV above the
highest dissociation limit we have considered. However, since some of the
CN Rydberg states are no doubt more bound than our higher predicted states,
there is still a possibility of some interaction. The dissociation energies
of these Rydberg states should be close to those of the lowest states of CN^+.
However the ground state dissociation energy of CN^+ is only 4.7 ± 0.4 eV[6]
which implies (see Table I) that the lowest Rydberg state of CN lies ~2.7 eV
above ground state carbon plus ground state nitrogen. Our highest reported
bound state,, $^2\Pi$ IV, lies ~2.6 eV above the ground state atoms, so if Rydberg
states affect our predicted bound states at all, it is likely that only the
very highest potential curves are altered.

ELECTRONIC STRUCTURES

Molecular orbital configurations for the low-lying states of CN have been discussed in several experimental papers.[2,3,11] In this work, we have directly investigated this problem by computing natural orbitals (NO's)[16] for the lowest state of each symmetry. The natural orbitals have a highly desirable non-arbitrary form in these calculations, since our full CI calculations assume no foreknowledge of the form of the orbitals.

A. Molecular Orbital Configurations

For the lowest state of each symmetry except $^2\Pi$ which yielded at least one of the 18 significantly bound states, natural orbital occupation numbers are given in Table IV. The fact that almost all the numbers in Table IV are nearly integral implies that most of these states are well represented by a single configuration. For the ground state, NO analyses have been carried out at five different internuclear separations. It is seen that as r becomes larger the 2π NO becomes more important. This is a manifestation of the fact[14] that for diatomic molecules made up of two open-shell atoms, as $r \to \infty$, the single configuration MO approximation becomes increasingly poorer.

Using the natural orbitals thus obtained for each symmetry, the full CI wave functions were recomputed to determine the dominant configurations in each wave function. These dominant configurations are reported in Table V and give quantitative information on the electronic structure of CN. For eight of the fourteen bound states in Table V, there is only one configuration with coefficient greater than 0.25, corresponding to ~6.25% of the total wave function. For only one state, $^4\Sigma^+$ II, is it not possible to clearly identify a single dominant configuration. Table V shows that for all eight doublet states

excluding $^2\Pi$, the predicted electron configurations of Douglas and Routly[2] and Lutz[11] are correct. For the quartet states, electron configurations have not been predicted.

B. Avoided Crossings Among the $^2\Pi$ States

The $^2\Pi$ wave functions were recomputed at five r values using X $^2\Sigma^+$ natural orbitals. This was done in order to "follow", in terms of MO configurations, the avoided crossings which occur among the second, third, and fourth $^2\Pi$ states. As can be seen in Table VI, three configurations--$5\sigma^2 1\pi^3$, $5\sigma^2 1\pi^2 2\pi$, and $1\pi^4 2\pi$--dominate these four states. By simultaneously looking at Fig. 5 and Table VI it can be seen that each avoiding crossing is accompanied by a change in the dominant electron configuration.

At its minimum, the D $^2\Pi$ state is dominated by the $5\sigma^2 1\pi^2 2\pi$ configuration (actually two $^2\Pi$ configurations arise from this orbital occupancy[26]). However, between r = 2.75 and r = 2.50, the D $^2\Pi$ states shifts to the $1\pi^4 2\pi$ configuration.

The third calculated $^2\Pi$ state (which we assume is the H state) experiences two avoided crossings. At r = 2.25 and r = 2.50, $^2\Pi$ III is dominated by $5\sigma^2 1\pi^2 2\pi$. However, at the lowest calculated energy, r = 2.75, the H state is dominated by the $1\pi^4 2\pi$ configuration. At r = 3 bohrs both the $5\sigma^2 1\pi^2 2\pi$ and $1\pi^4 2\pi$ orbital occupancies are important, indicating that this is near another avoided crossing. Finally, at R = 3.25, the $5\sigma^2 1\pi^2 2\pi$ configuration again becomes dominant.

The lowest calculated energy for the fourth $^2\Pi$ state is found at R = 3.0 bohrs, but the calculated energy is less than 0.1 eV higher at R = 2.75.

Thus the minimum of the $^2\Pi$ IV state occurs very near an avoided crossing between the third and fourth $^2\Pi$ states. For smaller r than 3.0, $^2\Pi$ IV is dominated by $5\sigma^2\ 1\pi^2\ 2\pi$, and for larger r, $1\pi^4\ 2\pi$ is the dominant configuration.

Our MO configuration assignments for the four $^2\Pi$ states at their equilibrium internuclear separations are the same as those of Lutz,[11] except for the $^2\Pi$ IV state (which he calls G), for which we cannot specify a single configuration. A final interesting point is that, at different r values the $1\pi^4\ 2\pi$ configuration dominates the second, third, and fourth $^2\Pi$ states.

C.   The Question of g and u Symmetry

Douglas and Routly,[2] on the basis of the observance and non-observance of certain transitions, have suggested that the CN radical is nearly enough homonuclear that the symbols g and u have some meaning. Carroll[3] and Lutz[11] have also discussed this matter. In particular, both Douglas and Routly[2] and Lutz[11] state that the ground state can be approximately labeled as $^1\Sigma_g^+$, and thus that the 5σ orbital is more appropriately termed $3\sigma_g$, as in the N_2 molecule.

Our 5σ natural orbital from the X $^2\Sigma^+$ r = 2.25 calculation has the form

$$5\sigma = 0.6092\ 2s(C) + 0.1888\ 2s(N)$$

$$-0.6375\ 2p(C) - 0.4958\ 2p(N)$$

in terms of the normalized STO's used to describe the valence region. This orbital does not appear to approximate g character. However, the 1π natural orbital from the same calculation has the form

$$1\pi = 0.5935 \ 2p(C) + 0.6617 \ 2p(N)$$

and thus approximates a $1\pi_u$ orbital rather closely. Similar results to the above were also found for $r = 2.5$ bohrs, and we conclude that the g and u labels are more appropriate for the π than the σ orbitals.

ACKNOWLEDGEMENTS

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table I. Calculated and experimental dissociation limits for CN radical

Atomic States C	N	Calculated total energy (hartrees)	Energy relative to ^3P C + ^{4}S N (in eV) Calculated	Experimental[a]
^3P_g	^4S_u	-91.90734	0	0
^1D_g	^4S_u	-91.83672	1.92	1.26
^5S_u	^4S_u	-91.79773	2.98	4.17
^1S_g	^4S_u	-91.78503	3.33	2.68
^3P_g	^2D_u	-91.78154	3.42	2.38
^3P_g	^2P_u	-91.73809	4.61	3.58
^1D_g	^2D_u	-91.71092	5.34	3.65
Rydberg[b]	^{4}S	——	——	7.48

[a]C. E. Moore, Atomic Energy Levels, Nat. Bur. Std. (U. S.) Circ. No. 467 (1949).

[b]First Rydberg state of the carbon atom, $1s^2 2s^2 2p3s$ ^3P state.

Table II. Summary of configuration interaction calculations on the CN radical. CDC 6600 times refer to a single internuclear separation

Symmetry	Pertinent Eigenvalues	Orbital Occupancies	Configurations	Distinct Contributing Determinants	Computation Time (sec.)
$^2\Sigma^+$	7	144	320	952	434
$^2\Sigma^-$	6	108	264	912	358
$^4\Sigma^+$	5	84	164	376	92
$^4\Sigma^-$	5	108	196	392	117
$^6\Sigma^+$	2	28	40	64	9
$^8\Sigma^+$	1	4	4	4	3
$^2\Pi$	10	138	486	832	~500[a]
$^4\Pi$	7	103	292	346	238
$^6\Pi$	1	40	52	54	9
$^2\Delta$	6	108	276	448	231
$^4\Delta$	4	76	152	172	50
$^2\Phi$	3	58	102	148	27
$^4\Phi$	1	38	44	46	8
$^2\Gamma$	1	16	20	24	5

[a] CDC 7600 time.

Table III. Spectroscopic parameters for bound states of CN molecule

State		T_e(eV)	D_e(eV)	r_e(Å)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})
$X^2\Sigma^+$ I	calc.	0	6.178	1.236[a]	1939.2	14.54[a]	1.610[a]	0.0151[a]
	exp.	0	7.75±0.2[b]	1.172[a]	2068.7[a]	13.14[a]	1.900[a]	0.0173[a]
$A^2\Pi$ II	calc.	1.883[a]	4.295	1.324[a]	1621.4[a]	16.74[a]	1.403[a]	0.0149[a]
	exp.	1.146		1.233	1814.4	12.88[a]	1.717[a]	0.0175[a]
$B^2\Sigma^+$ II	calc.	3.765[a]	4.335	1.226[a]	1765.2	32.53[a]	1.636[a]	0.0262[a]
	exp.	3.193[a]		1.151[a]	2164.1[a]	20.25[a]	1.970[a]	0.0222[a]
$^4\Sigma^+$ I	calc.	4.016	2.162	1.448	1249.4	14.82	1.174	0.0152
$^4\Pi$ I	calc.	5.326	.853	1.629	873.0	13.15	0.927	0.0154
$^4\Delta$ I	calc.	5.913	2.187	1.441	1274.4	14.42	1.184	0.0147
$D^2\Pi$ II	calc.	~ 6.593	3.008	1.590	1041.6	6.38	0.972	0.010
	exp.	6.755[c](=T_0)		1.499[c]	1004.7[c]	8.78[c]	1.162[c]	0.013[c](=α_0)
$^4\Sigma^-$ I	calc.	6.666	~ 1.42	1.446	1286.0	15.36	1.177	0.0138
$^2\Phi$ I	calc.	7.742	1.860	1.621	950.7	12.63	0.936	0.0123
$H^2\Pi$ III	calc.	7.807	1.794	1.414	1651.3	43.84	1.229	0.0021
	exp.	7.556[c](=T_0)		1.310(=r_0)[c]			1.520(=B_0)[c]	
$E^2\Sigma^+$ III	calc.	7.856[d]	1.745	1.364[d]	1717.1[d]	30.57[d]	1.322[d]	0.0151[d]
	exp.	7.334		1.320	1681.4	3.60	1.487	0.0064[d]
$F^2\Delta$ I	calc.	7.879	1.722	1.461	1253.7	15.35	1.152	0.0138
	exp.	7.400(=T_0)[c]		1.378[c](=r_0)			1.374[c](=B_0)	
$^4\Sigma^+$ II	calc.	7.898	1.263	1.749	———	———	———	———

(continued)

Table III. (continued)

State		T_e(eV)	D_e(eV)	r_e(Å)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})
$^2\Sigma^-$ I	calc.	7.988	1.613	1.453	1225.5	14.92	1.165	0.0155
$J\,^2\Delta$ II	calc.	8.432	1.169	1.457	1211.7	17.58	1.159	0.0159
	exp.	8.090[c]		1.414[c]	1121.6[c]	13.93[c]	1.305[c]	0.0207(=α_o)[c]
$^4\Delta$ II	calc.	8.619	.982	1.787	651.5	2.75	0.770	0.0057
$^2\Sigma^-$ II	calc.	8.704	2.080	1.468	1183.2	14.04	1.142	0.0157
$^2\Pi$ IV	calc.	~ 8.76	~ 0.84	1.532	1446.4	15.60	1.047	0.0005

[a]Reference 1.

[b]Reference 6.

[c]Reference 3.

[d]Reference 11.

Table IV. Occupation numbers from CI wave functions for the lowest bound state of each symmetry. The 1σ and 2σ occupation numbers are exactly 2 for each wave function

		3σ	4σ	5σ	6σ	1π	2π
$X^2\Sigma^+$	R = 2.25	1.990	1.938	1.037	0.019	3.803	0.213
	R = 2.50	1.988	1.930	1.039	0.028	3.720	0.296
	R = 2.75	1.986	1.922	1.038	0.039	3.604	0.411
	R = 3.00	1.984	1.913	1.034	0.055	3.444	0.569
	R = 3.25	1.985	1.900	1.027	0.079	3.240	0.770
$^2\Sigma^-$	R = 2.75	1.988	1.927	1.031	0.035	2.921	1.098
$^4\Sigma^+$	R = 2.75	1.987	1.943	1.023	0.040	2.782	1.225
$^4\Sigma^-$	R = 2.75	1.975	1.905	1.020	0.036	2.911	1.153
$^4\Pi$	R = 3.0	1.993	1.958	1.928	0.068	1.995	1.059
$^2\Delta$	R = 2.75	1.990	1.922	1.035	0.040	2.860	1.153
$^4\Delta$	R = 2.75	1.989	1.931	1.020	0.049	2.823	1.188
$^2\Phi$	R = 3.0	1.995	1.961	1.936	0.057	1.989	1.062

Table V. Dominant configurations for bound states of CN. The coefficients given arise from a re-computation of each wave function in terms of the natural orbitals for the lowest state of that symmetry. Each coefficient incorporates the effects of all diatomic symmetry eigenfunctions arising from the given orbital occupancy. Only configurations with coefficient greater than 0.25 are included here.

State	R(bohrs)	Configurations	Coefficient
X $^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^4$	0.9304
B $^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4$	0.8587
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.3682
E $^2\Sigma^+$	2.25	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.8976
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4$	0.2803
$^2\Sigma^-$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9528
$^2\Sigma^-$ II	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9324
$^4\Sigma^+$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9173
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi 2\pi^3$	0.2819
$^4\Sigma^+$ II	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^3 2\pi$	0.7365
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi^2$	0.5168
$^4\Sigma^-$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9348
$^4\Pi$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.9624
F $^2\Delta$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9320
J $^2\Delta$	2.75	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9378
$^4\Delta$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^3 2\pi$	0.9292
$^4\Delta$ II	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^2 2\pi^2$	0.9142
		2. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^3 2\pi$	0.2879
$^2\Phi$	3.0	1. $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.9680

Table VI. Dominant configurations for the 4 lowest $^2\Pi$ state of CN. These results arise from 486 configuration calculations carried out using the X $^2\Sigma^+$ ground state natural orbitals.

		$5\sigma^2\ 1\pi^3$	$5\sigma^2\ 1\pi^2\ 2\pi$	$1\pi^4\ 2\pi$
A $^2\Pi$	R = 2.25	0.9475	0.1395	0.0555
	R = 2.50	0.9320	0.1530	0.0485
	R = 2.75	0.9083	0.1826	0.0421
	R = 3.00	0.8704	0.2360	0.0360
	R = 3.25	0.8083	0.3122	0.0286
D $^2\Pi$	R = 2.25	0.0280	0.0608	0.8198
	R = 2.50	0.0425	0.1810	0.8255
	R = 2.75	0.1595	0.9107	0.1050
	R = 3.00	0.2354	0.8831	0.0489
	R = 3.25	0.3372	0.8346	0.0347
$^3\Pi$ III	R = 2.25	0.0727	0.9450	0.0197
	R = 2.50	0.1001	0.9247	0.1128
	R = 2.75	0.0114	0.2664	0.8052
	R = 3.00	0.0480	0.7175	0.5249
	R = 3.25	0.0804	0.8435	0.2575
$^3\Pi$ IV	R = 2.25	0.0162	0.1208	0.1001
	R = 2.50	0.0339	0.9091	0.0071
	R = 2.75	0.0427	0.8790	0.1659
	R = 3.00	0.0407	0.5458	0.6111
	R = 3.25	0.0419	0.2704	0.7082

FIGURE CAPTIONS

Fig. 1. Calculated potential energy curves for $^2\Sigma^+$ states of CN. The arrows

near the right margin indicate dissociation limits.

Fig. 2. $^2\Sigma^-$ states.

Fig. 3. $^4\Sigma^+$ states.

Fig. 4. $^4\Sigma^-$ states.

Fig. 5. $^2\Pi$ states.

Fig. 6. $^4\Pi$ states.

Fig. 7. $^2\Delta$ states.

Fig. 8. $^4\Delta$ states.

Fig. 9. $^6\Sigma^+$, $^6\Pi$, and $^8\Sigma^+$ states.

Fig. 10. $^2\Phi$, $^2\Gamma$, and $^4\Phi$ states.

Fig. 11. Potential curves for the eight lowest bound states of CN.

Fig. 12. Positions of the ninth through eighteenth lowest bound states of CN.
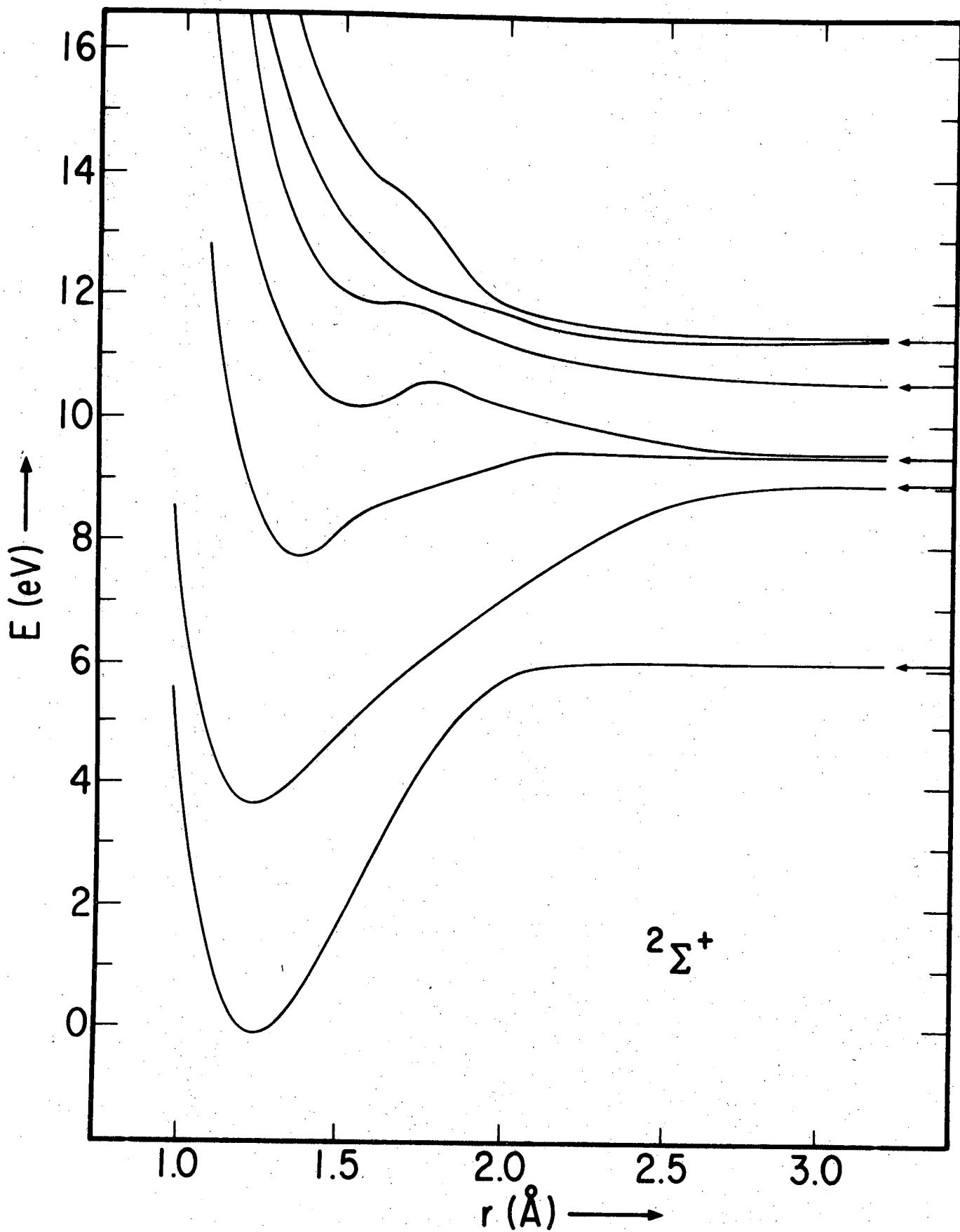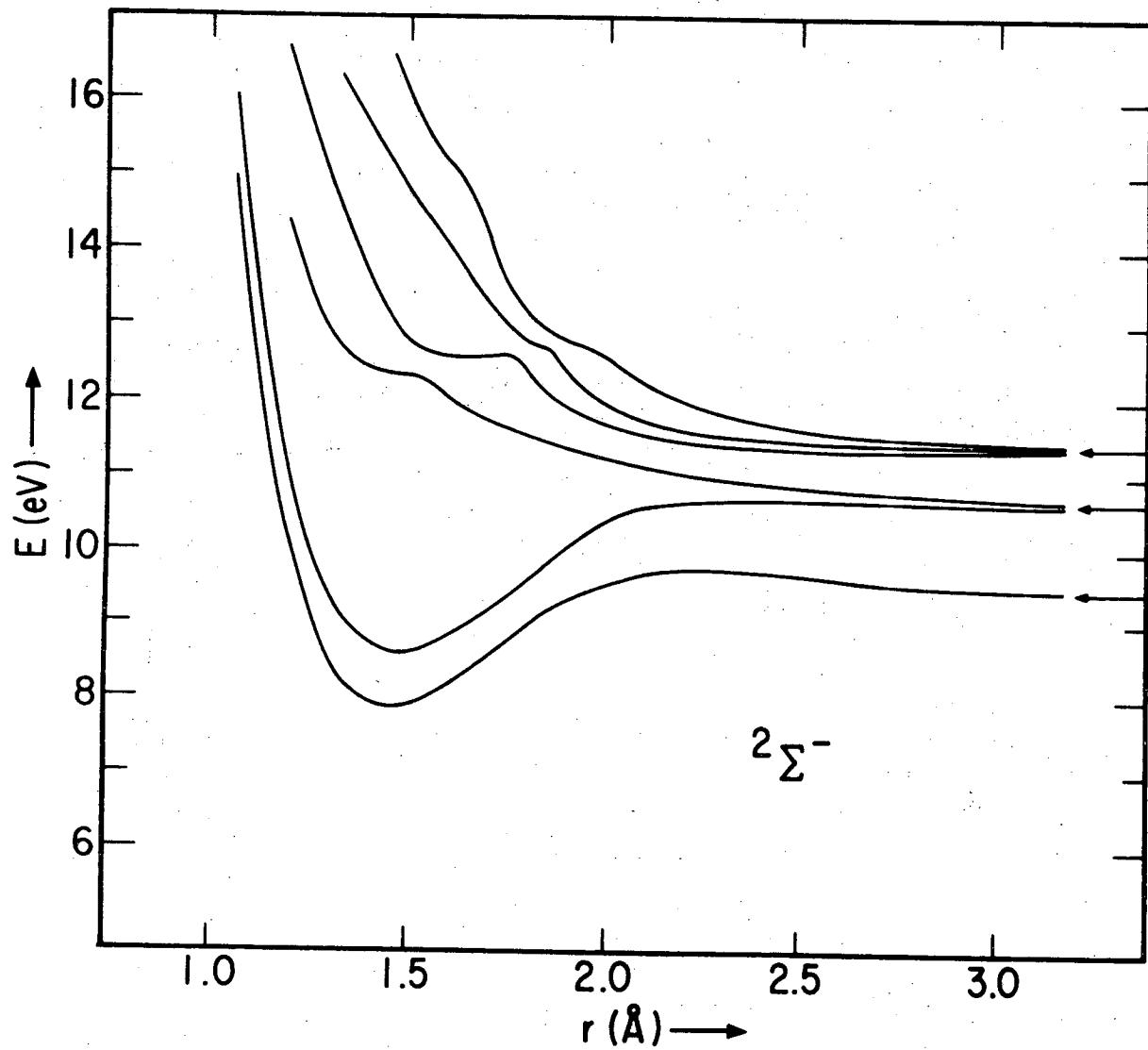
Fig. 1

Fig. 2
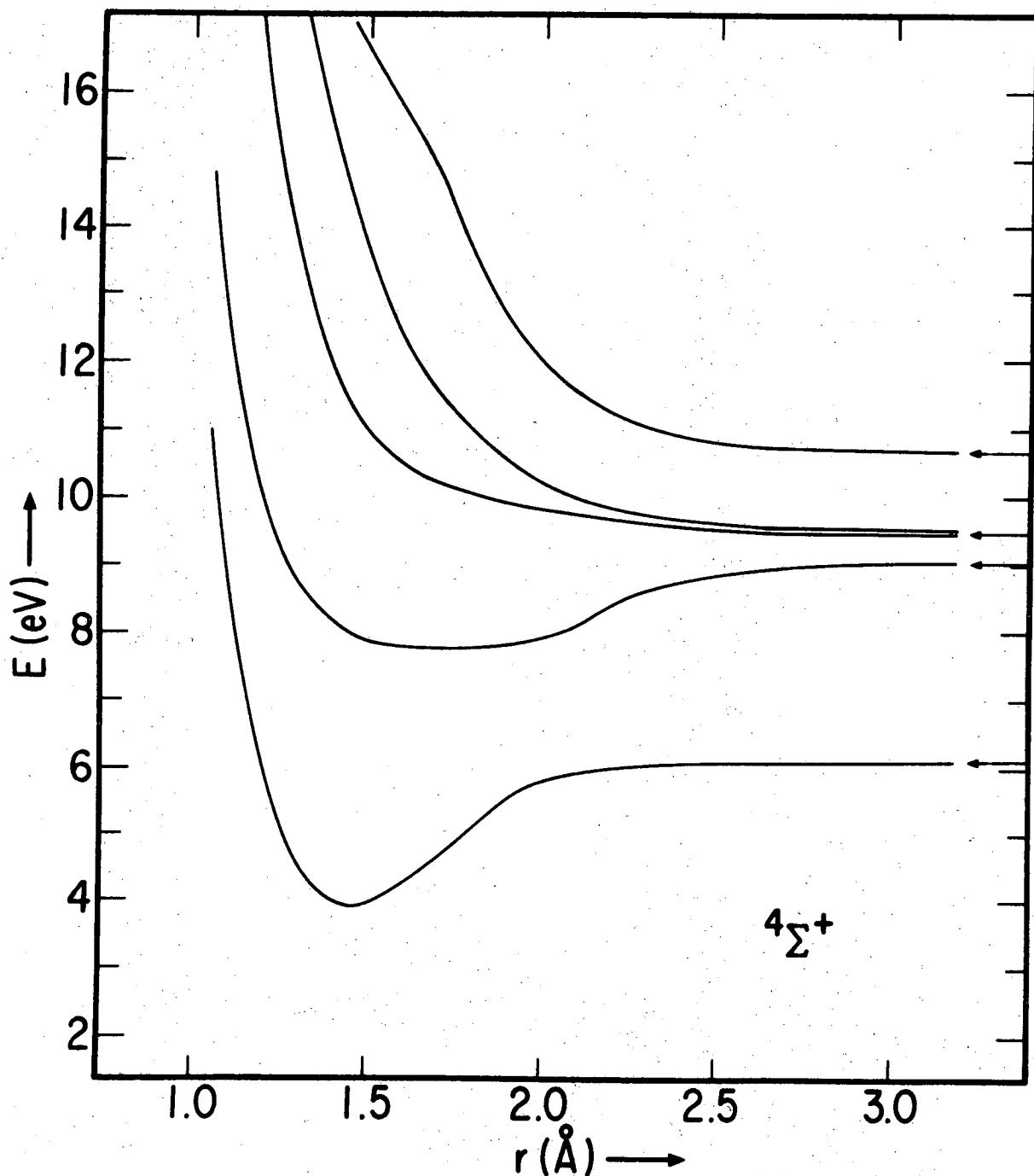
Fig. 3
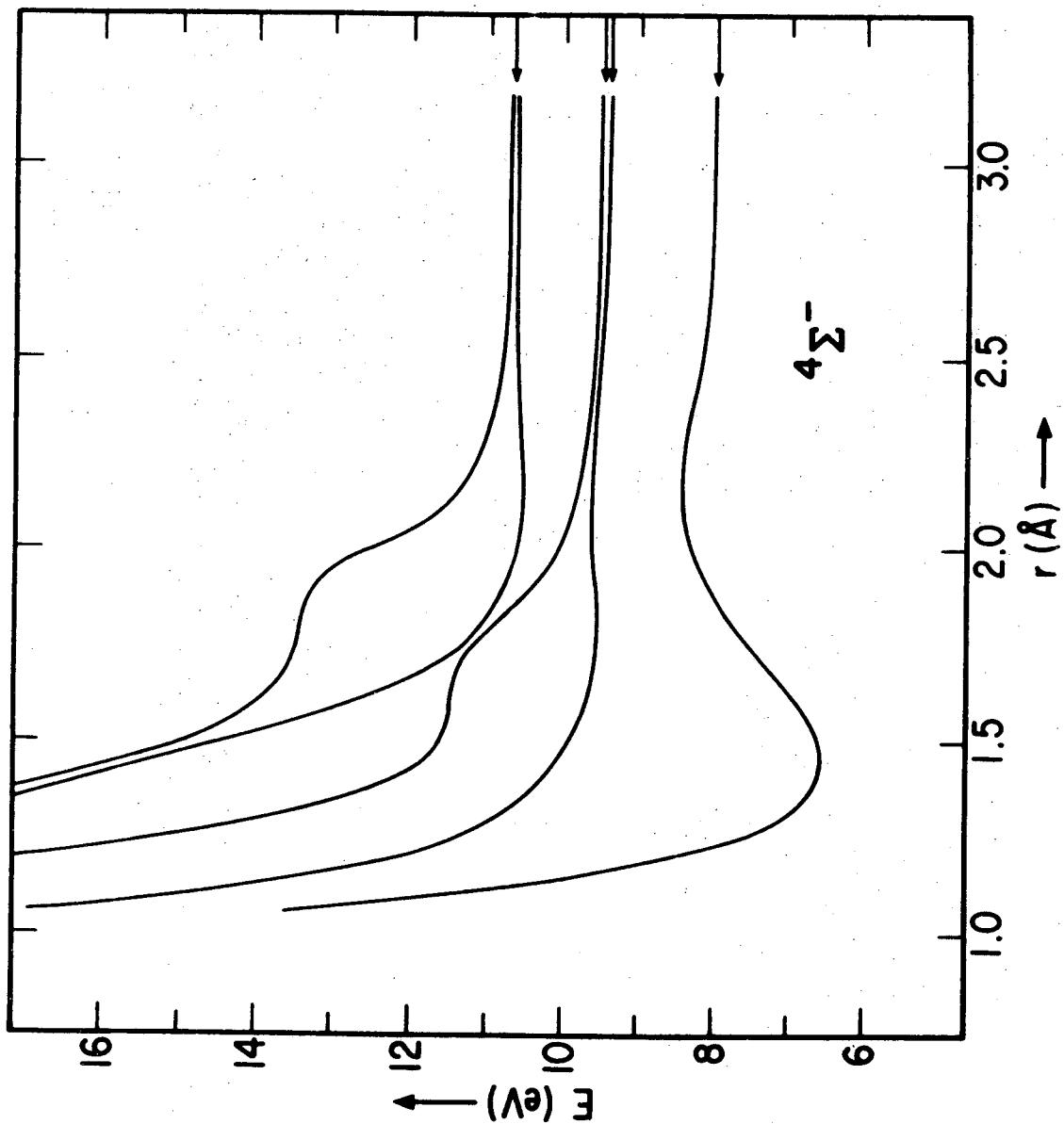
Fig. 4
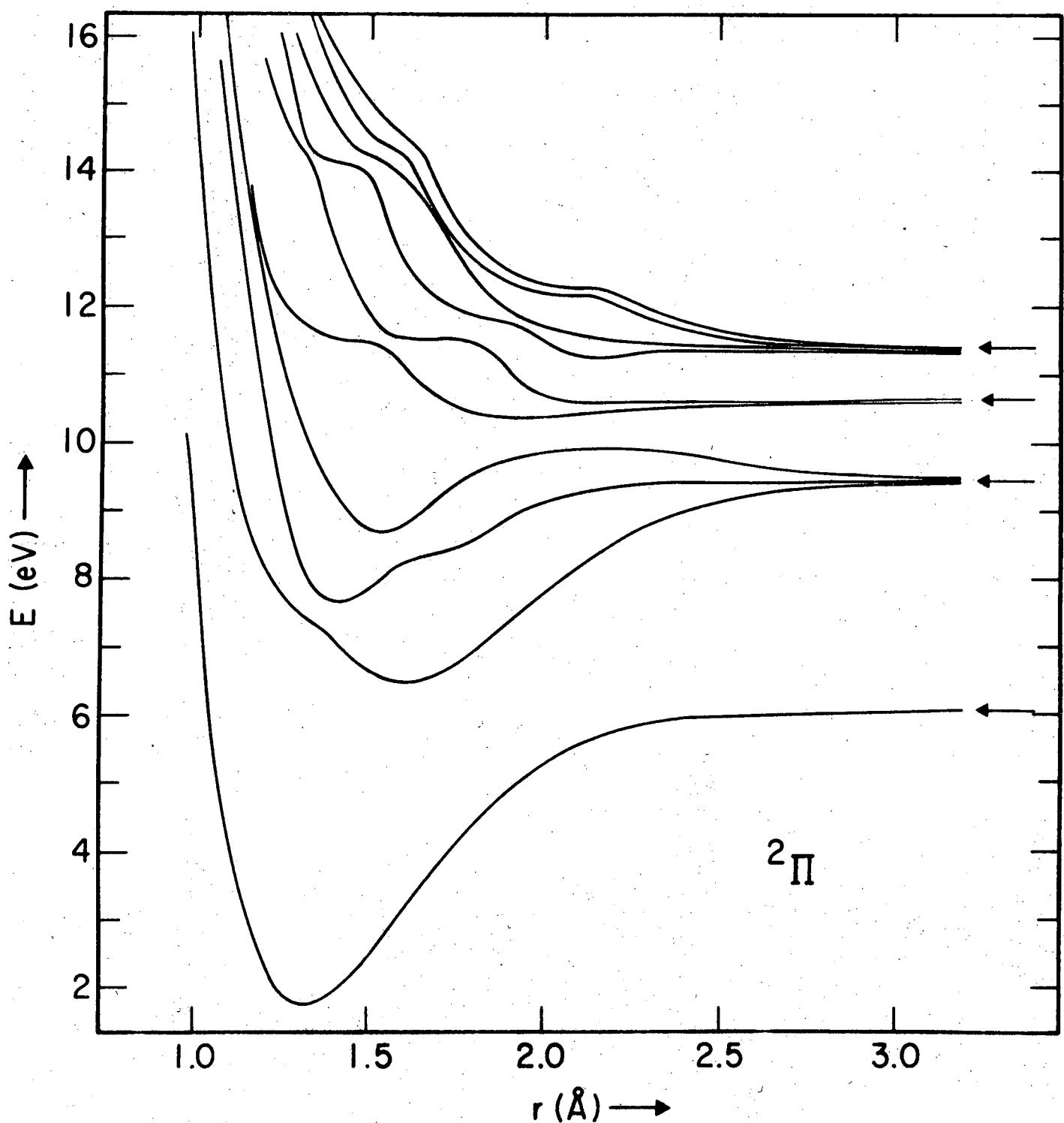
Fig. 5
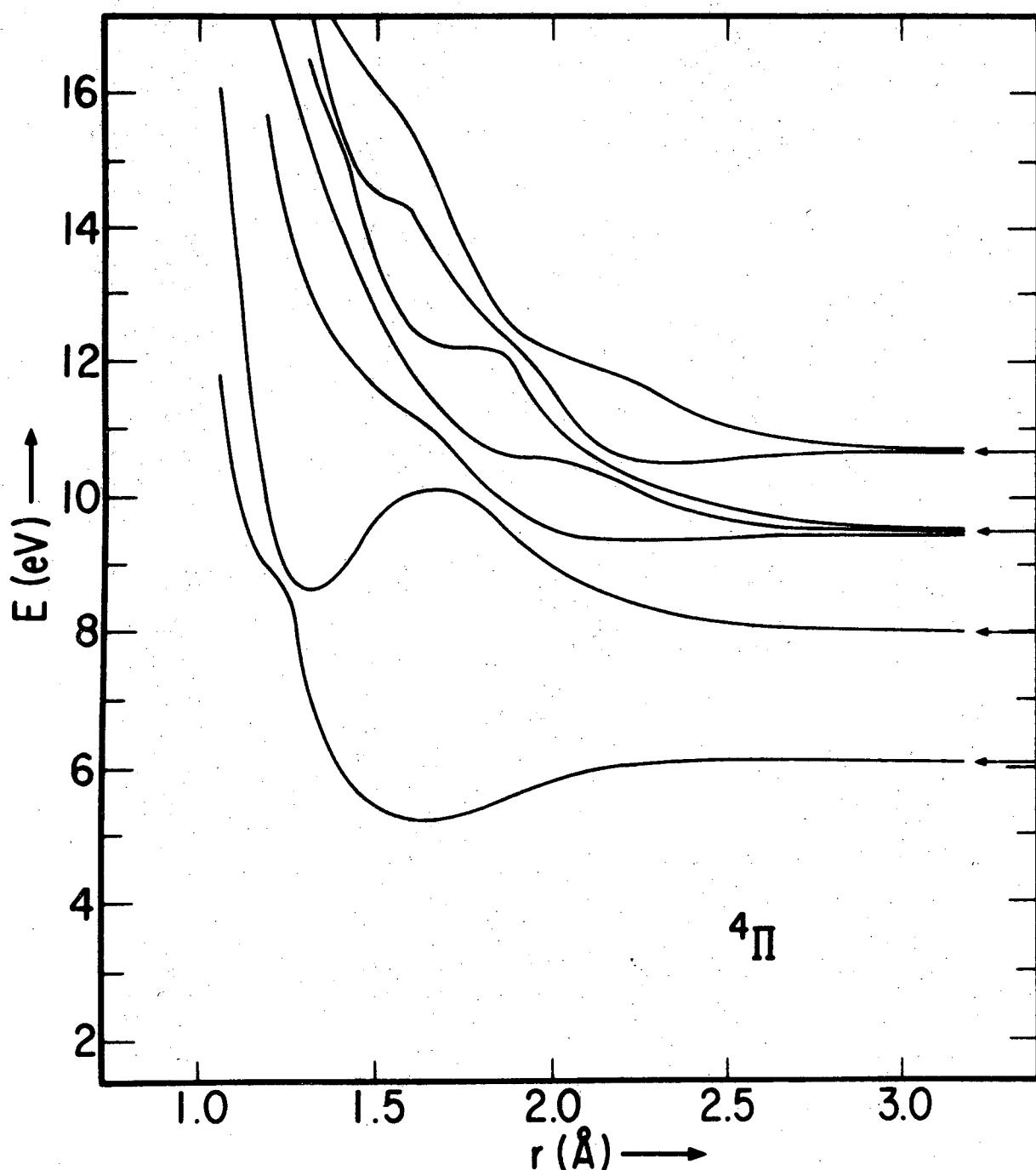
Fig. 6
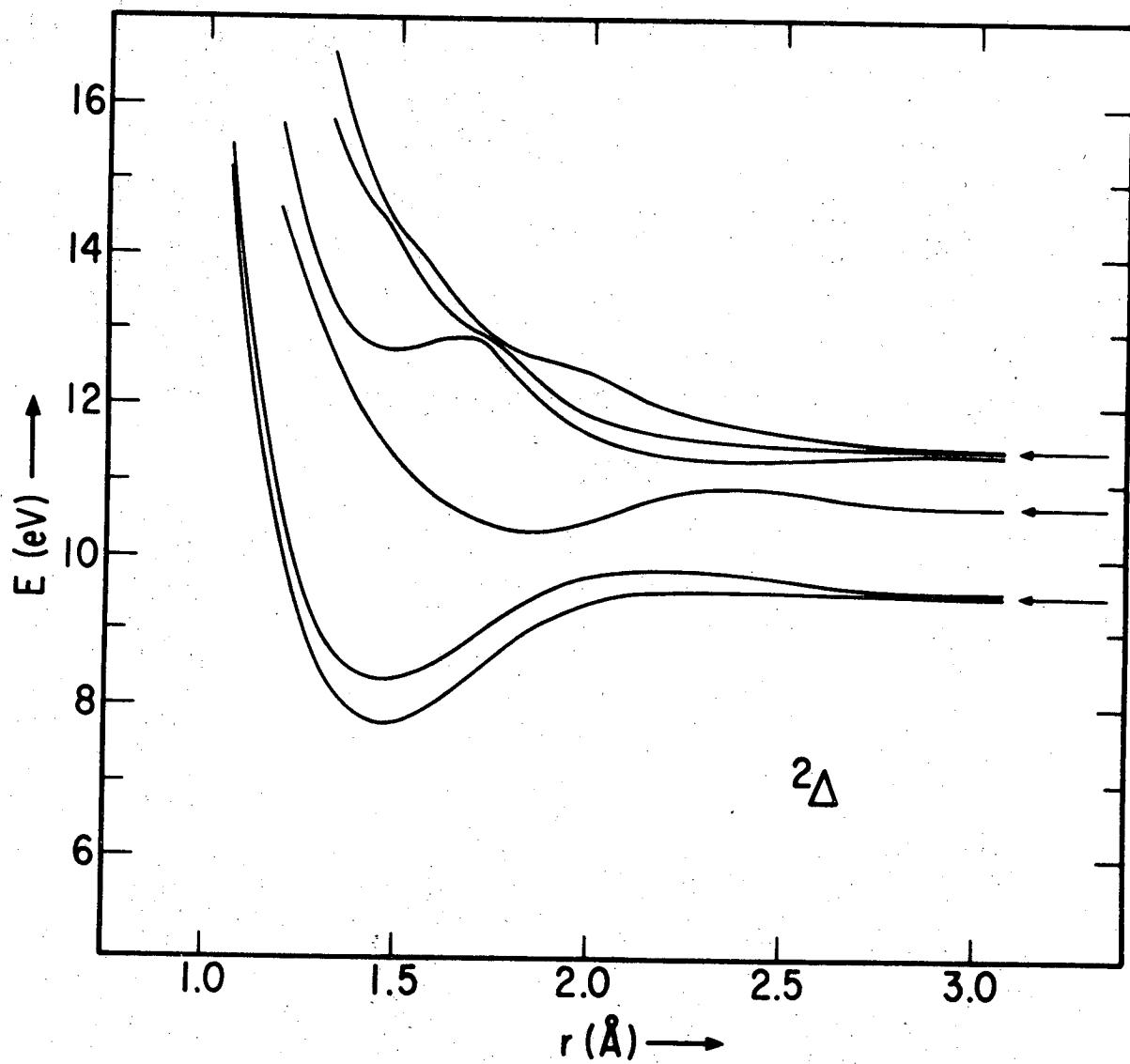
Fig. 7
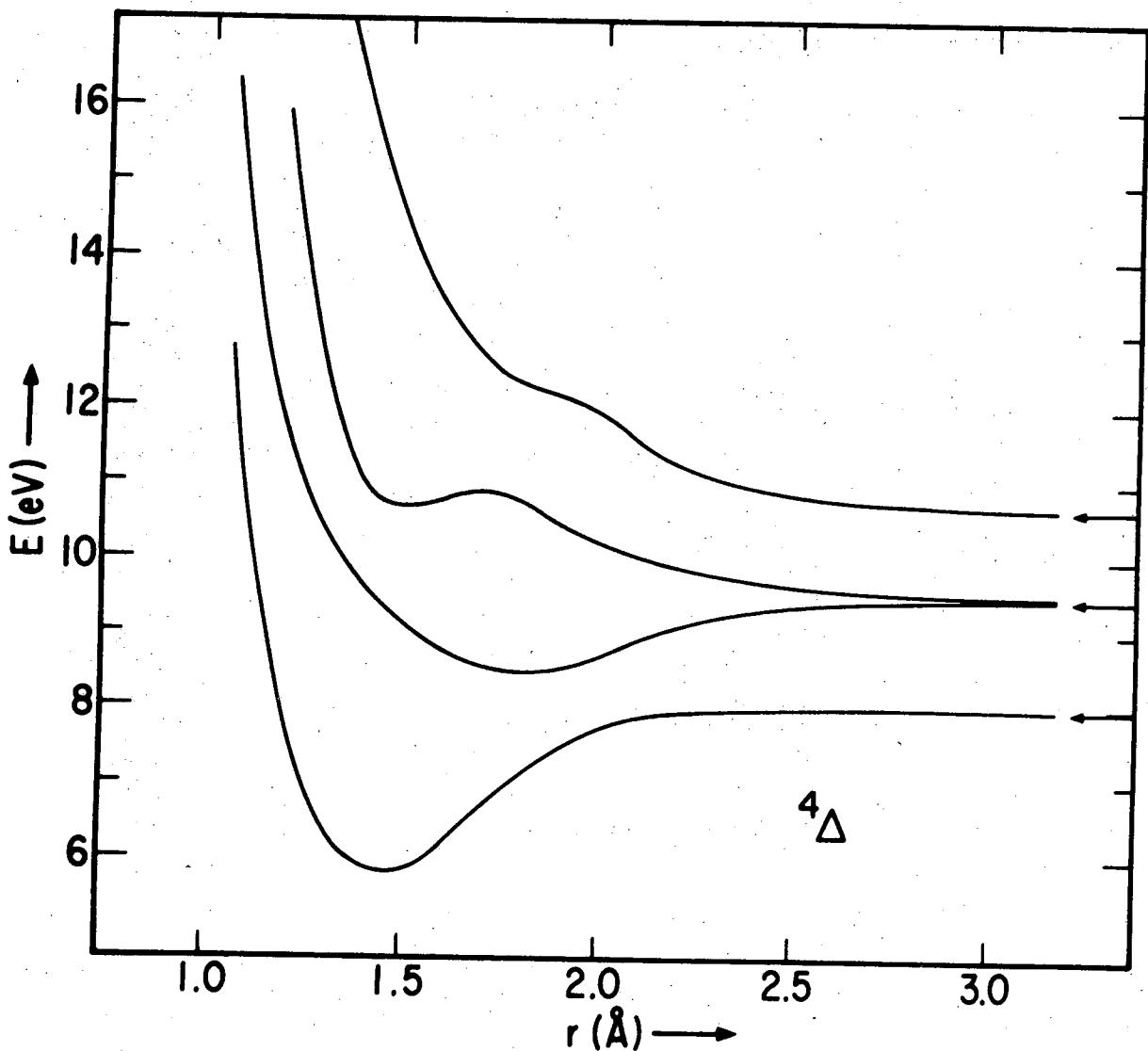
Fig. 8
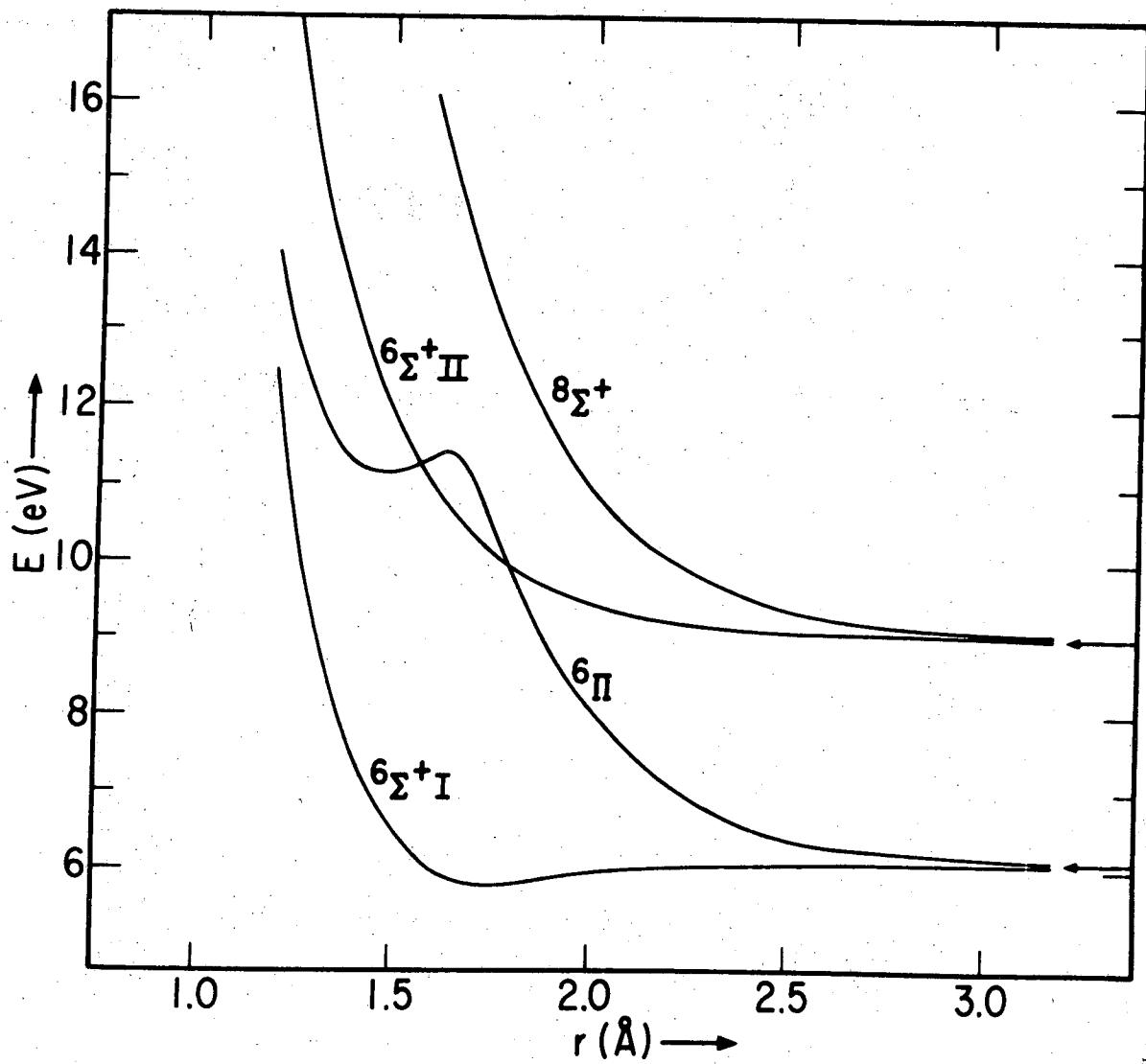
Fig. 9
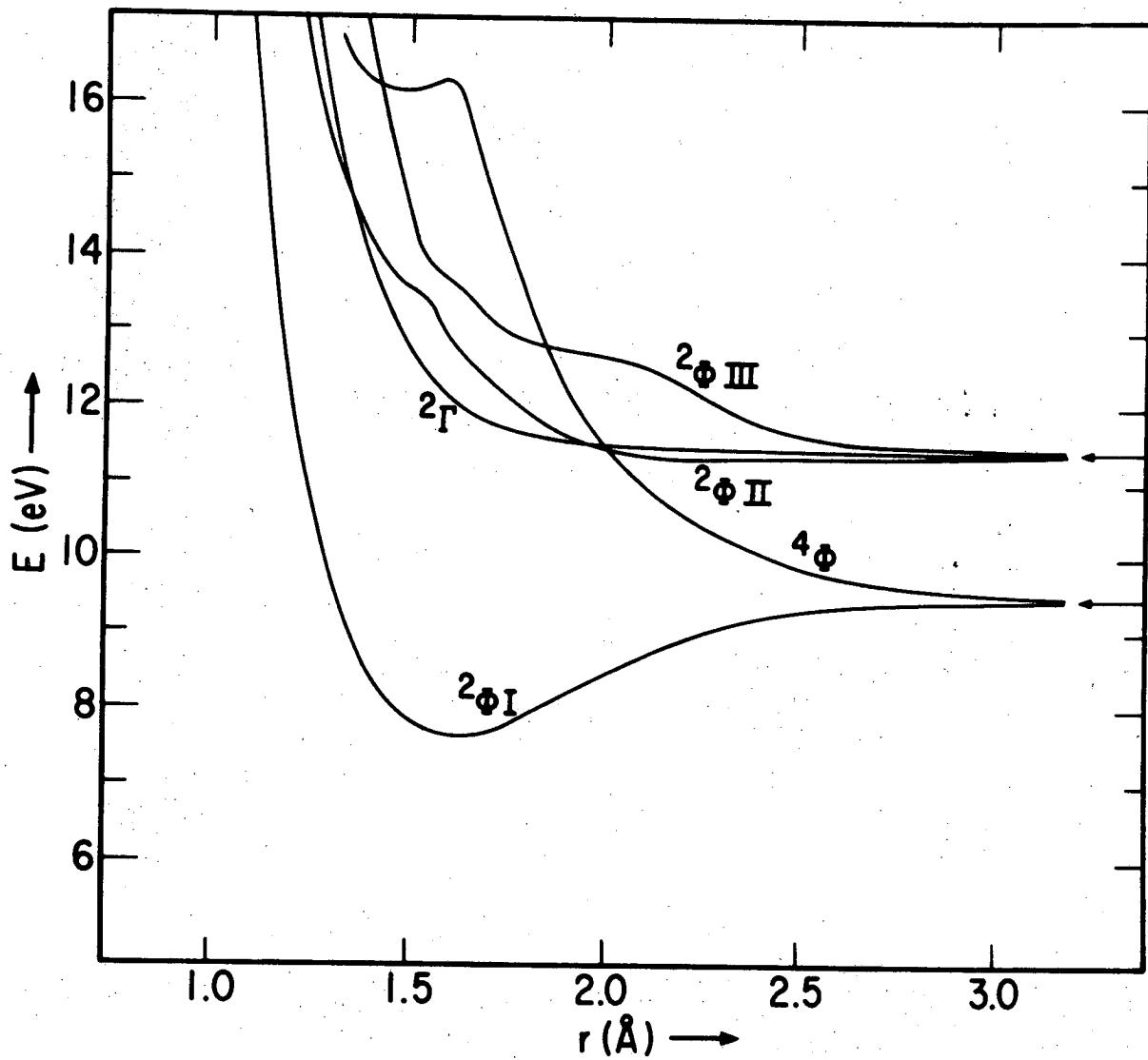
Fig. 10
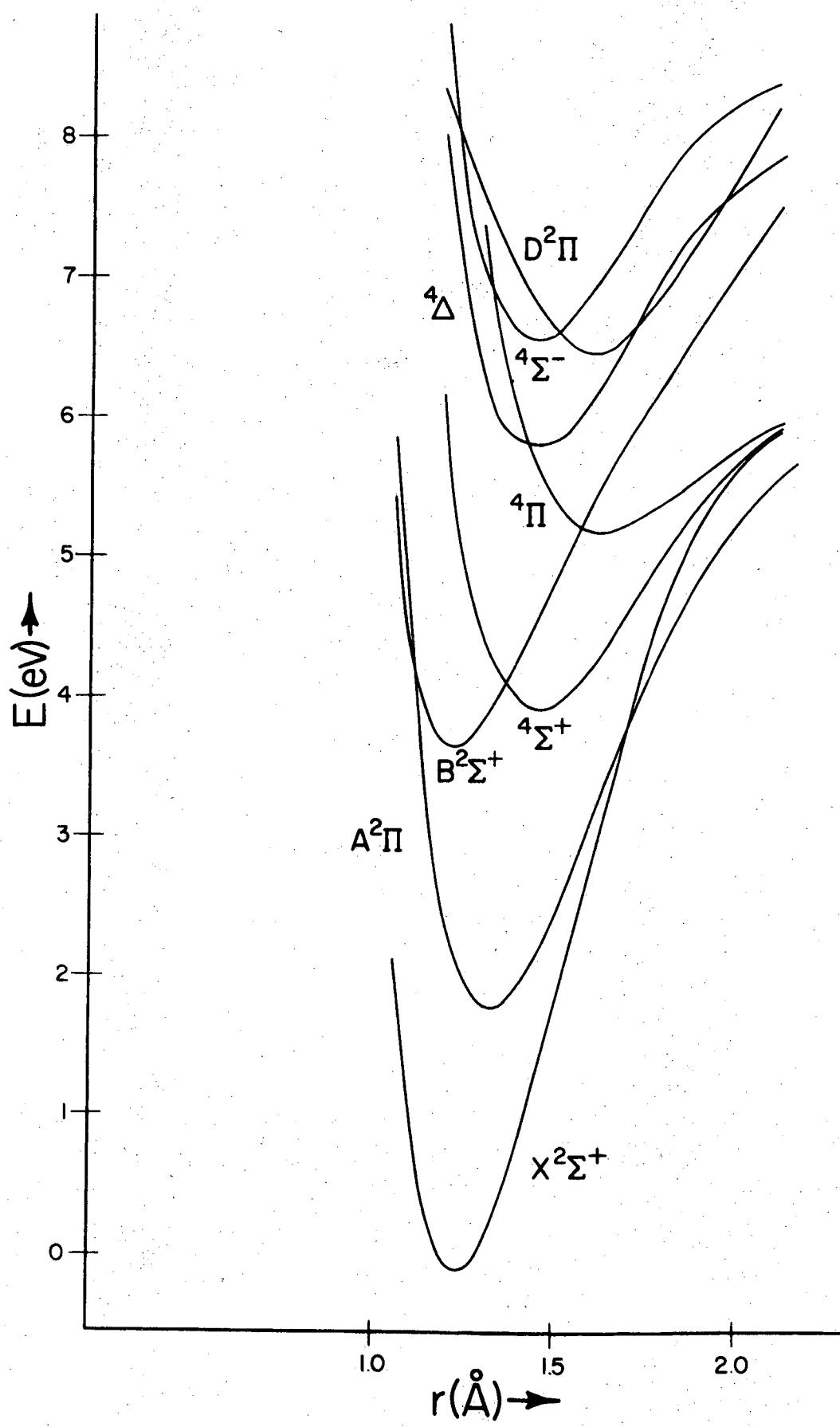
Fig. 11
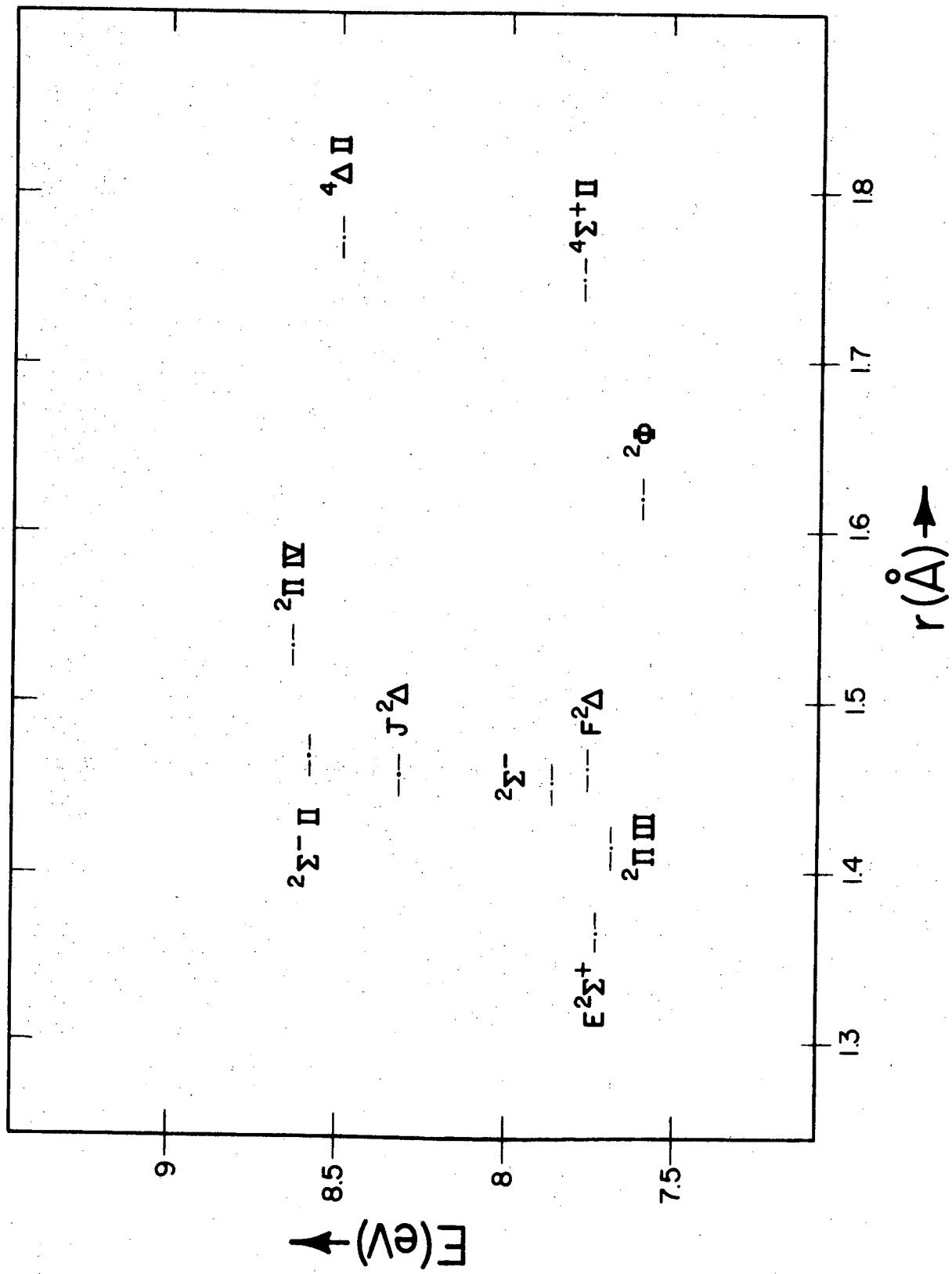
Fig. 12

APPENDIX

Calculated energies of the electronic states of CN. Internuclear distances are bohrs, energies are in hartrees.

r_{ab}	X $^2\Sigma^+$ I	B $^2\Sigma^+$ II	E $^2\Sigma^+$ III	$^2\Sigma^+$ IV	$^2\Sigma^+$ V	$^2\Sigma^+$ VI	$^2\Sigma^+$ VII
1.85	-91.92541	-91.81671	-91.41795	-91.29307			
2.0	-92.05170	-91.92967	-91.61463	-91.47580	-91.26899	-91.24878	-91.18654
2.25	-92.13039	-91.99400	-91.78686	-91.63973	-91.50946	-91.46738	-91.38378
2.5	-92.12360	-91.98617	-91.84314	-91.71378	-91.63541	-91.57168	-91.50022
2.75	-92.08199	-91.96051	-91.83694	-91.75115	-91.67936	-91.63003	-91.57552
3.0	-92.03110	-91.93502	-91.81690	-91.75501	-91.69312	-91.66146	-91.61353
3.25	-91.98340	-91.91218	-91.80795	-91.74346	-91.69558	-91.68139	-91.63600
3.5	-91.94536	-91.89320	-91.79859	-91.74531	-91.70556	-91.69053	-91.66705
4.0	-91.91206	-91.85374	-91.78168	-91.76057	-91.72309	-91.70634	-91.69955
5.0	-91.90752	-91.80493	-91.78293	-91.77813	-91.73471	-91.71263	-91.70891
6.0	-91.90744	-91.79833	-91.78200	-91.78119	-91.73778	-91.71117	-91.71072
8	-91.90734	-91.79773	-91.78154	-91.78154	-91.73809	-91.71092	-91.71092

(continued)

APPENDIX (continued)

r_{ab}	$^2\Sigma^-$ I	$^2\Sigma^-$ II	$^2\Sigma^-$ III	$^2\Sigma^-$ IV	$^2\Sigma^-$ V	$^2\Sigma^-$ VI
2.0	-91.57862	-91.53993	-91.43682	-91.34720	-91.12357	-91.05129
2.25	-91.75560	-91.72227	-91.60215	-91.51552	-91.39669	-91.26205
2.5	-91.82498	-91.79562	-91.66382	-91.59580	-91.53002	-91.42115
2.75	-91.84082	-91.81442	-91.67612	-91.65017	-91.57631	-91.51859
3.0	-91.83157	-91.80740	-91.68592	-91.66667	-91.61103	-91.56996
3.25	-91.81272	-91.78984	-91.70135	-91.66843	-91.64606	-91.62154
3.5	-91.79345	-91.77002	-91.70982	-91.68737	-91.66364	-91.65472
4.0	-91.77282	-91.74137	-91.72214	-91.70725	-91.70083	-91.68304
5.0	-91.77831	-91.73776	-91.73440	-91.71264	-91.71017	-91.70615
6.0	-91.78120	-91.73812	-91.73775	-91.71117	-91.71088	-91.71041
8	-91.78154	-91.73809	-91.73809	-91.71092	-91.71092	-91.71092

(continued)

APPENDIX (continued)

r_{ab}	$^4\Sigma^+$ I	$^4\Sigma^+$ II	$^4\Sigma^+$ III	$^4\Sigma^+$ IV	$^4\Sigma^+$ V	$^4\Sigma^-$ I	$^4\Sigma^-$ II	$^4\Sigma^-$ III	$^4\Sigma^-$ IV	$^4\Sigma^-$ V
2.0	-91.72694	-91.58613	-91.22147	-91.05762	-91.01565	-91.63047	-91.50844	-91.25074	-91.22522	-91.07808
2.25	-91.90340	-91.75110	-91.49980	-91.33458	-91.27905	-91.80656	-91.67303	-91.49953	-91.41395	-91.31096
2.5	-91.97195	-91.81604	-91.64483	-91.49795	-91.42491	-91.87468	-91.73664	-91.63820	-91.48694	-91.45478
2.75	-91.98675	-91.83680	-91.71443	-91.60222	-91.50453	-91.88908	-91.75939	-91.69640	-91.57135	-91.55834
3.0	-91.97646	-91.84259	-91.74330	-91.66881	-91.54902	-91.87848	-91.77305	-91.70814	-91.65560	-91.61358
3.25	-91.95664	-91.84447	-91.75531	-91.70972	-91.59628	-91.85852	-91.77946	-91.71574	-91.70803	-91.63272
3.5	-91.93647	-91.84371	-91.76258	-91.73509	-91.64996	-91.83861	-91.78040	-91.73953	-91.72881	-91.63875
4.0	-91.91332	-91.82982	-91.77189	-91.76353	-91.70777	-91.82113	-91.77736	-91.76802	-91.74332	-91.70721
5.0	-91.90777	-91.80166	-91.78216	-91.77903	-91.73530	-91.83257	-91.78319	-91.77954	-91.73973	-91.73551
6.0	-91.90747	-91.79806	-91.78185	-91.78130	-91.73788	-91.83628	-91.78489	-91.78135	-91.73833	-91.73789
8	-91.90734	-91.79773	-91.78154	-91.78154	-91.73809	-91.83672	-91.78503	-91.78154	-91.73809	-91.73809

(continued)

APPENDIX (continued)

r_{ab}	$^6\Sigma^+$ I	$^6\Sigma^+$ II	$^8\Sigma^+$	$^2\Pi$ I	$^2\Pi$ II	$^2\Pi$ III	$^2\Pi$ IV	$^2\Pi$ V	$^2\Pi$ VI	$^2\Pi$ VII	$^2\Pi$ VIII
1.85				-91.75829	-91.53796	-91.40212	-91.30663	-91.26002	-91.19410	-91.09881	-91.05082
2.0	-91.39728	-91.18854	-90.37320	-91.91453	-91.69880	-91.55479	-91.50524	-91.46385	-91.39586	-91.28871	-91.27736
2.25	-91.67082	-91.45330	-90.87504	-92.03645	-91.82588	-91.72580	-91.67125	-91.65687	-91.55285	-91.48610	-91.47190
2.5	-91.81253	-91.59731	-91.19654	-92.06470	-91.85761	-91.83333	-91.76018	-91.70181	-91.60773	-91.60285	-91.56034
2.75	-91.88120	-91.67776	-91.40340	-92.05023	-91.88033	-91.84566	-91.80438	-91.70645	-91.67950	-91.61415	-91.60309
3.0	-91.90996	-91.72514	-91.53809	-92.01942	-91.89208	-91.82882	-91.80796	-91.72039	-91.70593	-91.66222	-91.61889
3.25	-91.91817	-91.75485	-91.62696	-91.98620	-91.88529	-91.82057	-91.78752	-91.74077	-91.70714	-91.68839	-91.65165
3.5	-91.91741	-91.77361	-91.68609	-91.95794	-91.86844	-91.80869	-91.77420	-91.74762	-91.71463	-91.69727	-91.68453
4.0	-91.91153	-91.79022	-91.75159	-91.92452	-91.82752	-91.78778	-91.76583	-91.74595	-91.74082	-91.71740	-91.70608
5.0	-91.90811	-91.79655	-91.79115	-91.90926	-91.78782	-91.78251	-91.77553	-91.74332	-91.73975	-91.71333	-91.71093
6.0	-91.90753	-91.79760	-91.79699	-91.90764	-91.78227	-91.78176	-91.78088	-91.73877	-91.73840	-91.71129	-91.71093
∞	-91.90734	-91.79773	-91.79773	-91.90734	-91.78154	-91.78154	-91.78154	-91.73809	-91.73809	-91.71092	-91.71092

(continued)

APPENDIX (continued)

r_{ab}	$^2\Pi$ IX	$^2\Pi$ X
1.85	-90.98295	-90.96068
2.0	-91.22003	-91.18491
2.25	-91.44931	-91.41582
2.5	-91.52971	-91.52093
2.75	-91.58582	-91.56758
3.0	-91.60531	-91.59492
3.25	-91.64854	-91.63426
3.5	-91.67172	-91.66404
4.0	-91.68332	-91.67867
5.0	-91.70768	-91.70604
6.0	-91.71066	-91.71042
8	-91.71092	-91.71092

APPENDIX (continued)

r_{ab}	$^4\Pi$ I	$^4\Pi$ II	$^4\Pi$ III	$^4\Pi$ IV	$^4\Pi$ V	$^4\Pi$ VI	$^4\Pi$ VII	$^6\Pi$
2.0	-91.69635	-91.53935	-91.33330	-91.29387	-91.20198	-91.16801	-91.10254	-91.41609
2.25	-91.80031	-91.76551	-91.55409	-91.49620	-91.40891	-91.37955	-91.35021	-91.61531
2.5	-91.87533	-91.81204	-91.65587	-91.58188	-91.53377	-91.50274	-91.48433	-91.69732
2.75	-91.92309	-91.78780	-91.69521	-91.64459	-91.61032	-91.58806	-91.52768	-91.71934
3.0	-91.93800	-91.76188	-91.71588	-91.69330	-91.66853	-91.60452	-91.56207	-91.71323
3.25	-91.93628	-91.76016	-91.74018	-91.72218	-91.68095	-91.63486	-91.61589	-91.73414
3.5	-91.92754	-91.77681	-91.76287	-91.73891	-91.68477	-91.67510	-91.66363	-91.79150
4.0	-91.91057	-91.81162	-91.78518	-91.74896	-91.74095	-91.73329	-91.69054	-91.85848
5.0	-91.90623	-91.83351	-91.78348	-91.77927	-91.77448	-91.73984	-91.73096	-91.90032
6.0	-91.90725	-91.83640	-91.78187	-91.78144	-91.78076	-91.73843	-91.73731	-91.90659
8	-91.90734	-91.83672	-91.78154	-91.78154	-91.78154	-91.73809	-91.73809	-91.90734

(continued)

APPENDIX (continued)

r_{ab}	$^2\Delta$ I	$^2\Delta$ II	$^2\Delta$ III	$^2\Delta$ IV	$^2\Delta$ V	$^2\Delta$ VI
2.0	-91.57277	-91.56301	-91.42872	-91.38321	-91.15822	-91.13665
2.25	-91.75361	-91.73960	-91.59408	-91.55281	-91.42923	-91.36685
2.5	-91.82646	-91.80822	-91.66047	-91.63606	-91.55051	-91.51734
2.75	-91.84452	-91.82423	-91.70369	-91.66161	-91.59726	-91.58921
3.0	-91.83632	-91.81629	-91.73281	-91.65770	-91.63559	-91.62200
3.25	-91.81767	-91.79959	-91.74629	-91.65917	-91.65549	-91.65335
3.5	-91.79857	-91.78267	-91.75056	-91.68368	-91.67495	-91.66505
4.0	-91.78102	-91.76977	-91.73659	-91.71124	-91.70116	-91.68404
5.0	-91.78121	-91.77839	-91.73452	-91.71394	-91.70913	-91.70625
6.0	-91.78159	-91.78120	-91.73775	-91.71130	-91.71075	-91.71042
∞	-91.78154	-91.78154	-91.73809	-91.71092	-91.71092	-91.71092

(continued)

APPENDIX (continued)

r_{ab}	$^4\Delta_I$	$^4\Delta_{II}$	$^4\Delta_{III}$	$^4\Delta_{IV}$	$^2\Phi_I$	$^2\Phi_{II}$	$^2\Phi_{III}$	$^4\Phi$	$^2\Gamma$
2.0	-91.66119	-91.53012	-91.27085	-91.06518	-91.44658	-91.23860	-91.12894	-91.22189	-91.14117
2.25	-91.83624	-91.69378	-91.54576	-91.33310	-91.67464	-91.46522	-91.33548	-91.42560	-91.42221
2.5	-91.90342	-91.75687	-91.68519	-91.48303	-91.78574	-91.57472	-91.45036	-91.51102	-91.57105
2.75	-91.91695	-91.78575	-91.73559	-91.57531	-91.83424	-91.62544	-91.56300	-91.53507	-91.64690
3.0	-91.90546	-91.80779	-91.73419	-91.63582	-91.84922	-91.65310	-91.62585	-91.53105	-91.68310
3.25	-91.88442	-91.81669	-91.73039	-91.66775	-91.84668	-91.68031	-91.64969	-91.59900	-91.69892
3.5	-91.86305	-91.81686	-91.74051	-91.67988	-91.83592	-91.69959	-91.65968	-91.65966	-91.70533
4.0	-91.84074	-91.80224	-91.76257	-91.70832	-91.81011	-91.71350	-91.67342	-91.72985	-91.70944
5.0	-91.83714	-91.78372	-91.77869	-91.73534	-91.78580	-91.71258	-91.70672	-91.77401	-91.71112
6.0	-91.83685	-91.78182	-91.78127	-91.73787	-91.78210	-91.71121	-91.71057	-91.78071	-91.71103
∞	-91.83672	-91.78154	-91.78154	-91.73809	-91.78154	-91.71092	-91.71092	-91.78154	-91.71092