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Publication Date

1970-10-01

Submitted to Physical Review

UCRL-20401
Preprint c.2

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October 1970

AEC Contract No. W-7405-eng-48

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ABSTRACT

Using a (3s, 2p, 1d/2s, 1p) basis set of contracted Slater type functions and an iterative natural orbital scheme, ab initio valence configuration interaction studies have been done on the lowest three states of the imidogen radical at eight internuclear separations. Included in the CI were those configurations differing by zero, one or two space-orbitals from the Hartree-Fock configuration, except that the 1σ orbital was held doubly occupied. The size of the CI varied from 259 ($^1\Delta$) to 418 ($^3\Sigma^-$). For the ground state the computed total energy lies below that reported in any previous calculation except the 3379 configuration wave function of Bender and Davidson. From the potential curves thus obtained the spectroscopic constants r_e, ω_e, $\omega_e X_e$, B_e, and α_e are calculated, and compare well with the available experimental constants. The molecular splittings are calculated to be 2.00 eV ($X^3\Sigma^- - a^1\Delta$) and 0.79 ($a^1\Delta - b^1\Sigma^+$), but when the discrepancy between calculated and experimental atomic limits is taken into account these splittings are estimated as 1.47 eV and 1.02 eV, the latter being close to the experimental value of 1.05 eV. Dissociation energies (D_e) for the $X^3\Sigma^-$, $a^1\Delta$, and $b^1\Sigma^+$, states are calculated as 3.06 eV, 3.97 eV, and 4.13 eV, respectively.

For comparison, the Hartree-Fock dissociation energy for the $X^3\Sigma^-$ state is 2.10 eV and Gaydon's experimental value is 3.41 ± 0.16 eV. The occupation numbers and most important configurations are given at several internuclear distances for each state.

I. INTRODUCTION

The imidogen radical, NH, is of significant astrophysical import, and has been observed in the spectra of several sources, including the sun[1] and comets.[2] Laboratory investigations on NH have been numerous, some of the most interesting results being those which yield estimates of the dissociation energies of the ground state[3,4,5,6] and excited states,[7,8] and the splitting between states.[7,8,9,26] Despite the quantity of work on this molecule, there still are no reliable estimates of the singlet-triplet splittings, and the spectroscopic constants for even the second and third states remain uncertain. These considerations, together with the fact that (unlike any other diatomic molecule for which dissociation limits have been established) the lowest three states of NH arise from three different atomic limits suggest that the imidogen radical might be the subject of a very fruitful theoretical investigation.

Recent *ab initio* calculations on NH have been varying in their degree of depth and accuracy. Kouba and Ohrn[10] carried out a broad (in terms of the number of states studied) valence configuration interaction (VCI) with a small basis set, and obtained a great deal of qualitative information. Using a natural orbital scheme within the separated pair approximation, Silver *et al.*[11] performed an extensive study of the potential curve and expectation values of numerous one and two-electron operators for the $X^3\Sigma^-$ ground state. Cade and Huo[12] used a large basis set of optimized Slater type functions (STF's) to calculate accurate SCF wave functions and potential curves for the first row diatomic hydrides, and claim that their results are of essentially true Hartree-Fock accuracy. The most accurate (lowest energy) calculation on NH is included in the pioneering work of Bender and Davidson[13] on the first row hydrides, employing massive configuration interaction (CI) with large basis sets. However, due to the pecuniary impositions of such a scheme, these calculations were done at only one internuclear separation and for only one state for each hydride.

In an attempt to obtain relatively accurate potential curves with reasonable amounts of computer time, we have used configuration interaction with the iterative natural orbital method of Bender and Davidson.[14] This method has all the advantages of conventional CI, but removes one of the drawbacks thereto; namely, the large number of configurations which enter the wave function with non-negligible coefficients and cause some difficulty in obtaining a simple interpretation which is physically reasonable. The domination of the wave function by a single configuration, together with the occupation numbers ensuing from the diagonalized first order density matrix,[15] result in a wave function which is conceptually less difficult and computationally simpler (for the calculation of one-electron properties) than the conventional CI.

II. CALCULATIONS

A. Basis Set

The basis functions used for the expansion of the molecular orbitals were products of Slater-type orbitals and complex spherical harmonics. Stevens[16] has optimized a "double zeta plus polarization" basis set[17] for the ground state of NH at R = 1.91 bohrs. After several test calculations, we decided to use Stevens optimized nitrogen 3d and hydrogen 1s, 2s, and 2p STO's. However, for the s and p functions on nitrogen, we contracted the Bagus-Gilbert[18] set of five s and three p functions (obtained from their optimized calculations on the ^2D state of the N atom) to three s and two p functions. The final basis set used is seen in Table I. One measure of the completeness of this set is that the computed single configuration energy for $^3\Sigma^-$ NH and R = 1.91 bohrs is -54.9757, or less than 0.003 hartrees above the Hartree-Fock energy,[12a] -54.978 hartrees. Similarly, our single configuration energies for the $a^1\Delta$ and the $b^1\Sigma^+$ states are about 0.0025 and 0.0039 hartrees above the Huo's accurate self-consistent-field energies of -54.9020 and -54.8469.[12b]

B. Molecular Calculations

From the five s, three p, one d type contracted STO basis may be formed nine molecular orbitals of σ, four of π, and one of δ symmetry. We deleted the δ orbital and employed the remaining 9σ, 4π set. The configurations used were those arising from orbital occupancies which differed from the Hartree Fock occupancy ($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$) by zero, one or two orbitals; i.e. the HF configuration plus all single and double excitations into the remaining six σ and three π orbitals. In addition, using techniques previously described,[19] each configuration was made to be an eigenfunction of S^2, S_z, L_z, and, for Σ states, σ_v.

Initial MO's were obtained by Schmidt orthonormalizing the contracted basis in the order $1s_N$, $2s_N$, $1s_H$, $2p\sigma_N$, $2s_N'$, $2s_H'$, $2p\sigma_N'$, $2p\sigma_H$, $3d\sigma_N$, $2p\pi_N$, $2p\pi_H$, $2p\pi_N'$, $3d\pi_N$. The thirteen MO's gave rise to 2261 distinct non-zero two-electron integrals. For each internuclear separation, and for each state, the calculation proceeded in two steps. The object of the first stage was to obtain MO's which were much nearer the natural orbitals than were the initial MO's. This was accomplished by means of an iterative natural orbital (INO) scheme using a small number of configurations. The configurations selected for this stage were, in addition to the HF configuration, those arising from a) all single excitations from the HF configuration and b) double excitations of the form $X^2 \rightarrow Y^2$. With these few configurations it was economically very feasible to perform many iterations of the sequence consisting of: first, the CI calculation of the energy and eigenvector, and second, the generation and diagonalization of the first order density matrix, thus obtaining the natural orbitals upon which the next CI may be based. The usual procedure was to iterate for ten cycles or until the first natural configuration ($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$) energy rose from one cycle to the next, whichever occurred first. Since this stage involves a very limited CI, selecting only certain double excitations, it is not guaranteed, nor did we expect, that the first order density matrix, if diagonalized in one iteration, would remain so in the next. In fact, only for the $^1\Delta$ state did this first stage converge at all internuclear separations. For the $^3\Sigma^-$ and $^1\Sigma^+$ states the procedure rarely converged completely, but rather, the orbitals underwent usually small variations throughout all ten cycles.

In the second stage of the calculations the orbitals from the first step were used as the basis for the larger CI (HF plus all single and double excitations), with the chemically reasonable restriction that the 1σ orbital (essentially the nitrogen 1s) be held doubly occupied. Although several iterations with the larger CI might have been performed without undue cost, experimentation showed that one cycle was enough to determine the NO's quite well, and that in the second iteration the energy rose very slightly ($\sim 10^{-5}$ hartree). On most of the calculations therefore, one cycle at this stage was deemed sufficient. However, for those internuclear separations at which the relative importance of the various configurations was to be studied, two cycles were carried out in order to obtain near stabilization of the coefficients of the configurations in the total wave function. The sizes and times for both stages of the calculation are given in Table II.

C. Atomic Calculations

Since the nonrelativistic hydrogen atom may be solved exactly, no calculations were done on it, and in evaluating separated atom limits an energy of -0.5 was assigned to it.

To maintain compatibility with the molecular results an attempt was made to calculate the atomic energy of nitrogen by using the molecular basis set and considering the atom as pseudodiatomic. This proved unfruitful in this case since $1s^2\ 2s^2\ 2p^3\ (^2P)$ state is represented by two determinants, and taking single and double excitations with respect to both of them may give, in a variational calculation, not the ^2P state, but the $M_L = 1$ component of the ^2D state, as was verified by a test calculation.

A more workable approach was found in using our atomic CI methods to compute the dissociation limits. However, one must use considerable care to guarantee that the atomic results thus obtained are of the same relative accuracy as the corresponding molecular results. Compatibility is guaranteed if one obtains, for both atom and molecule, the energy limit of the basis set at hand, or very nearly so. Since this is essentially what is achieved by a CI which includes all single and double excitations from the HF configuration,[20] the use of an atomic program for the nitrogen atom was valid in the present case.

The CI atomic program used is the same as for previous atomic calculations.[21] All configurations arising from single and double excitations from the $1s^2\ 2s^2\ 2p^3$ occupancy were included, except that a) the 1s orbital was always doubly occupied, and b) for consistency with the molecular calculations, excitations into the 3dδ orbital were excluded. This was done by constructing L-S eigenfunctions of the proper symmetry and, for configurations containing a determinant with a 3dδ occupied, utilizing with coefficient unity each determinant, and only those determinants which did not include a 3dδ orbital.

III. RESULTS

The ab initio energies for the three lowest states of NH are given in Table III. For the ground state, comparison with some earlier investigations may be made. With a small basis CI Kouba and Ohrn[10] obtained results which were qualitatively enlightening but of relatively low absolute accuracy, with the lowest computed energy being -54.864 Hartrees. The accurate SCF calculation of Cade and Huo[12a] yielded a Hartree-Fock energy of -54.978. Going beyond the Hartree-Fock level, Silver, Ruedenberg, and Mehler's[11] separated-pair CI wave function gave, as the lowest computed energy, -55.03352 Hartrees, which is about 22% of the correlation energy suggested by Bender and Davidson[13] (-0.249). If one chooses not to study the variation of energy with internuclear distance, the time thus saved may be directed toward a very accurate calculation at one or two points. Moved by this philosophy, Bender and Davidson[13] have obtained the highest absolute accuracy to date on NH. Their 3379-configuration wave function gives an energy of -55.1620, or about 74% of the correlation energy.

In terms of both scope of study and absolute accuracy, the present work lies between that of Kouba and Ohrn, and Bender and Davidson. Our lowest energy for the ground state, -55.08397, is bested only by that of the latter work, and represents about 43% of the correlation energy. This study, however, has not been restricted to one spectroscopic state. Also, the present results were obtained relatively inexpensively, the total time for all calculations being about four hours on a CDC 6600.

A. Atomic and Molecular Splittings

Table IV shows the atomic energies calculated using the procedure described in section II. Comparison of the second and third columns of that table indicates that our basis set was incapable of describing very accurately the differences in the three pertinent states of nitrogen. No better results are to be had by accurate SCF calculations with exponents optimized for each state individually.[18] Indeed, as shown by Weiss[22] for the carbon atom, what is needed to obtain accurate atomic splittings is configuration interaction with a much larger basis set.

The discrepancies in the atomic splittings may be qualitatively understood, at least in part, by the popular but admittedly crude argument that, since the ground state is a quartet while the other two states are doublets, the parallel spins of all three electrons in the ^4S 2p orbital ensure, through the exclusion principle, that there will be less correlation energy than in the ^2D or ^2P state. Applying this reasoning to the molecular states also would lead one to the conclusion that while the $^1\Delta$ - $^1\Sigma^+$ splitting might be reasonably accurate, the triplet-singlet splittings might be expected to be less so. In fact, the calculated singlet-singlet splitting, 0.79 eV, is in reasonable agreement with the experimental value of 1.05 eV.

Comparison of the molecular triplet-singlet splittings with experiment is not possible since there are in the literature no direct experimental determinations of this parameter. The most often quoted value seems to be that of Flourent and Leach,[8] who calculated the splitting using the now-dubious dissociation energy for the ground state of 4.2 eV, and from their own dissociation energy of the $^1\Delta$ state. This in turn was obtained from the equation $D_e = \frac{\omega_e^2}{4\omega_e X_e}$, a relation which holds only if Δ G(v) is a linear function of the vibrational quantum number v. Since they only observed three $c^1\Pi$ - $a^1\Delta$ bands it is quite uncertain whether this condition holds. Their splitting (1.2 eV) is, they allow, very approximate.

Our value of the $X^3\Sigma^-$ - $a^1\Delta$ splitting of 2.00 eV thus remains neither verified nor belied by experiment. However, noting our error in the relative positions of the atomic energy levels, we can say quite probably that when an accurate experimental value for the X-a splitting does become available it will be less than our 2.00 eV. A crude estimate of the true value may be had by assuming the error in the molecular splitting to be about the same as in the atomic splitting. This yields an energy difference between the ground and first excited state of approximately 1.5 eV. It is interesting to note that this is close to Cade's[23] semi-empirical prediction of the same quantity, 1.63 ± 0.1 eV. It is also interesting to observe that the $a^1\Delta$ - $b^1\Sigma^+$ splitting estimate obtained from this scheme, 1.02 eV, is close to the experimental 1.05 eV.

B. Spectroscopic Constants

By fitting a least-squares quartic polynomial through six points (R = 1.5, 1.8, 1.91, 2.0, 2.2, 2.4) near the minimum of the potential curves and applying standard formulas[24] to the coefficients thus obtained, one may arrive at the spectroscopic constants r_e, ω_e, $\omega_e X_e$, B_e, and α_e, which are displayed in Table V. Where reliable experimental data are available for comparison, the agreement is quite good except for the anharmonicity constant $\omega_e X_e$. Of particular note is the excellent agreement (0.3%) between the experimental and theoretical r_e for the ground state. For the $^1\Delta$ and $^1\Sigma^+$ states Herzberg[24] gives r_0, the average value of r in the lowest vibrational level, rather than r_e, the r at which the potential curve has its minimum. From the general shape of the potential curves one expects r_e to be slightly less than r_0. Our results are, therefore, quite compatible with the experimental information available, and there is no reason to believe them any less accurate than the r_e of the ground state. The close agreement of the rotational constant B_e follows from the accuracy of r_0, from which it is calculated.

The vibrational constants ω_e correspond nicely to the experimentally measured numbers for all three states, and for the ground state are significantly better than the results of either SCF[12a] of separated pair[11] treatment. The ω_e's from the small basis set CI calculation of Kouba and Ohrn[10] agree well with our value for the ground state but are somewhat less accurate for either the $a^1\Delta$ or $b^1\Sigma^+$ state.

The dissociation energy of ground state NH has been unclear for some time, and for the excited states a and b the dissociation energies are still unknown. Herzberg[24] lists a 3.8 eV dissociation energy (D_0) for the ground state, indicating that this is uncertain, while Cade and Huo[12a] suggest this value as the most internally consistent. From a thermochemical argument based on D HNO = 48.6 kcal/mole Clyne and Thrush[3] deduce that D NH is 3.5 eV. Pannetier and Gaydon,[4] by means of a Birge Sponer extrapolation, arrived at a value of 4.0 eV, but after conceding the likely error of such an approximate procedure (which very often gives too big a D_0) suggest that the true D_0 is less, probably closer to 3.8 eV. More recently, Seal and Gaydon[5] have used shock tube studies to obtain a dissociation energy (D_0) of ground state NH as 3.21 ± 0.16 eV.

Since this last value is arrived at directly, using neither interpolations nor long extrapolations, we tend to favor it over the earlier values. Our calculated NH ($^3\Sigma^-$) dissociation energy (D_0), 2.86 eV, agrees rather well with that of Seal and Gaydon.

About the only certain conclusions one can draw with regard to the dissociation energies of the $a\,^1\Delta$ and $b\,^1\Sigma^+$ states are upper and lower limits. From $D_0\ a^1\Delta = T_0(c\,^1\Pi) - T_0(a^1\Delta) + D_0(c\,^1\Pi)$, the lower bound of $D_0(a^1\Delta)$ is just the experimentally known a-c splitting, 3.88 eV. Observing the "dissociation by rotation" of the c state, Krishnamurty and Narasimham[7] calculated the dissociation energy of this state to be 8713 cm^{-1} (1.08 eV), which leads to $D_0\ ^1\Delta = 4.96$ eV. But it is known that, due to the form of the effective potential curve for high rotational numbers, an estimate of a dissociation energy obtained in this manner is an upper bound to the true dissociation energy. It is quite possible therefore, and, considering all available data, even likely that the dissociation energy of the $c\,^1\Pi$ state is less than 1.08 eV. This in turn implies that $D_0\ ^1\Delta$ would be less than 4.96 eV, and closer to our calculated value of 3.76 eV.

C. Wave Function

It is of some interest to observe the changes in the wave functions as the internuclear distance varies. In the natural orbital scheme these changes are reflected in both the coefficients of the individual configurations and the occupation numbers. These are listed in Tables VI and VII.

All the states are well approximated at small internuclear distances by the single configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$, although for the $^1\Sigma^+$ state the valence shell double excitation $3\sigma^2 \rightarrow 1\pi^2$ is also important. As R becomes significantly greater than R_e, this single configuration approximation becomes less applicable, and, as may be seen from the calculation at 4.0 bohrs, it begins to break down with the onset of dissociation. At R = 2.8 bohr the double excitation $3\sigma^2 \rightarrow 4\sigma^2$ is important in all three states, while at R = 4.0 bohr the single excitation $3\sigma \rightarrow 4\sigma$ becomes quite significant in the $^3\Sigma^-$ wave function. Since all our wave functions should, at very large R, be represented by $1\sigma^2 2\sigma^2 3\sigma 4\sigma 1\pi^2$, it is expected that the $3\sigma \rightarrow 4\sigma$ excitation will become more and more important for all three states as the internuclear distance increases beyond three bohrs, and that it will eventually dominate.

From the occupation numbers for the first five σ and three π orbitals in Table VII several trends may be established. In the entries for the $^3\Sigma^-$ state it can be seen that as R varies from 1.35 to 4.00 bohr, the occupation numbers for the 2σ and 1π orbitals start off near 2.0, go through a minimum, then rise again. For the 3σ orbital, the occupation number falls monotonically from near 2.0 to a value of 1.57 at 4.0 bohr. Exactly the opposite trend is observed for the 4σ orbital, with a rise from 0.01 at 1.35 bohr to 0.42 at 4.0 bohr.

The behavior in the $^1\Delta$ state is similar to that in the $^3\Sigma^-$ state, although this might be somewhat obscured by the lack of a calculation at an internuclear distance much greater than 2.8 bohr. However, the occupation numbers for the 3σ and 1π orbitals in the $^1\Sigma^+$ state follow distinctly different trends, the former rising to a maximum then falling again, the latter dropping monotonically from 2.06 (R = 1.35), but everywhere remaining greater than 2.0.

These trends may be qualitatively understood by correlation of the molecular states with the appropriate separated atom and united atom limits. In the limit of infinite separation the system approaches a ground state hydrogen atom (^2S) and a nitrogen atom in a $(1s^2 2s^2 2p^3)\,^4S$, ^2D, ^2P state for the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ molecular states, respectively. By taking for the correlation limit a nitrogen with the correct M_L value, it can be seen that all three molecular states will be dominated at large R by the $1\sigma^2 2\sigma^2 3\sigma 4\sigma 1\pi^2$ configuration. In the limit of the united atom (Oxygen $1s^2 2s^2 2p^4$), the $^3\Sigma^-$ state correlates with the ^3P atomic state, while both the $^1\Delta$ and $^1\Sigma^+$ correlate with the ^1D state. If we again require the correct M_L value, then the $^1\Delta$ and $^3\Sigma^-$ states will be dominated at very small R by the configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$. The wave function for the $^1\Sigma^+$ state, however, will contain two strongly contributing terms, $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$ and $1\sigma^2 2\sigma^2 1\pi^4$. This last observation explains in part why the $^1\Sigma^+$ occupation numbers do not behave like those of the other two states. It also gives an indication why the double excitation $3\sigma^2 \rightarrow 1\pi^2$ is important for the $^1\Sigma^+$ state at our smallest calculated internuclear separation.

ACKNOWLEDGMENTS

We thank Dr. Richard M. Stevens for transmitting to us his optimized basis set for the ground state of NH.

FOOTNOTES AND REFERENCES

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

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Table I.

STO'S	AO'S	Basis Functions								
		$1s_N$	$2s_N$	$2s'_N$	$2p_N$	$2p'_N$	$3d_N$	$1s_H$	$2s_H$	$2p_H$
Nitrogen	ζ									
1s	10.595	0.11074	0.00128							
1s	6.026	0.92969	-0.26624							
3s	7.331	-0.04234	-0.03018							
2s	2.528	0.00218	0.53711							
2s	1.586			1.0						
2p	5.359				0.03994					
2p	2.516				0.44620					
2p	1.289					1.0				
3d	1.910						1.0			
Hydrogen										
1s	1.2083							1.0		
2s	1.2681								1.0	
2p	1.9082									1.0

Table II. Size and computation time for the CI calculations.

	Number of Orbital Occupancies		Number of Configurations		Time[a]
	Small CI	Large CI	Small CI	Large CI	(Large CI)
$^3\Sigma^-$	43	148	67	418	3.50
$^1\Delta$	43	148	49	259	1.57
$^1\Sigma^+$	51	172	63	277	3.58

[a] Time to generate Hamiltonian matrix and obtain lowest root; minutes of CDC 6600 time, not including integral calculations.

Table III. Calculated Energies of NH (hartrees).

State \ R(bohr)	1.35	1.50	1.80	1.91	2.00	2.20	2.40	2.80
$^3\Sigma^-$	-54.922 099	-55.009 182	-55.077 491	-55.083 333	-55.083 968	-55.076 260	-55.062 435	-55.028 954
$^1\Delta$	-54.849 441	-55.936 509	-55.004 350	-55.009 974	-55.010 285	-55.001 902	-54.987 263	-54.951 620
$^1\Sigma^+$	-54.820 231	-54.907 466	-54.975 398	-54.980 961	-54.981 179	-54.972 478	-54.957 377	-54.920 415

Table IV. Atomic Energies.

State	Calculated Energy (hartrees)	Relative Energy (eV)	Relative Experimental (eV)
^4S	-54.471 760	0.0	0.0
^2D	-54.364 849	2.909	2.38
^2P	-54.329 671	3.866	3.57

Table V. Spectroscopic Constants.

		D_e(eV)	D_0(eV)	r_e(Å)	ω_e(cm^{-1})	$\omega_e x_e$(cm^{-1})	B_e(cm^{-1})	α_e(cm^{-1})	T_e(eV)
$X^3\Sigma^-$	Hartree Fock[a]	2.10	1.88	1.018	3556	66.7	17.32	0.572	0
	Separated Pair[b]	2.65	2.35	1.038	4910	78.3	16.63	0.466	0
	Small Basis CI[c]	2.62	2.42	1.12	3224	117	14.28	0.564	0
	This Work	3.058	2.858	1.041	3300	120	16.56	0.760	0
	Experiment	3.41±0.16	3.21±0.16[e]	1.038[f]	3125.6[d]	78[g]	16.65[f]	0.646[d]	0
$a^1\Delta$	Hartree Fock[i]								1.83
	Small Basis CI[c]	4.01	3.80	1.13	3557	132	14.16	0.563	1.9
	This Work	3.965	3.760	1.037	3362	116	16.68	0.732	2.00
	Experiment			r_0 = 1.044[f]	3314[h]	63[h]	16.78[h]	0.67[2]	X
$b^1\Sigma^+$	Hartree Fock[i]								3.57
	Small Basis CI[c]	4.28	4.06	1.12	3628	126	14.31	0.538	2.8
	This Work	4.131	3.924	1.035	3396	113	16.73	0.712	2.79
	Experiment			r_0 = 1.046[f]	∿ 3480[f]				X + 1.05[f]

[a] See Ref. 12.

[b] See Ref. 11.

[c] See Ref. 10.

[d] See Ref. 25.

[e] See Ref. 5.

[f] See Ref. 24.

[g] See Ref. 26.

[h] See Ref. 8.

[i] See Ref. 12b

Table VI. Important configurations for several internuclear separations.

$^3\Sigma^-$		$^1\Delta$		$^1\Sigma^+$	
R = 1.30 bohr		R = 1.30 bohr		R - 1.30 bohr	
0.9842	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9860	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9654	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$
0.0436	$2\sigma \rightarrow 4\sigma$	0.0494	$3\sigma^2 \rightarrow 4\sigma^2$	0.0583	$2\sigma^2 \rightarrow 1\pi^2$
0.0362	$2\sigma \rightarrow 5\sigma$	0.0391	$1\pi^2 \rightarrow 2\pi^2$	0.0370	$3\sigma^2 \rightarrow 4\sigma^2$
0.0358	$3\sigma \rightarrow 5\sigma$	0.0332	$1\pi^2 \rightarrow 3\pi^2$	0.1858	$3\sigma^2 \rightarrow 1\pi^2$
0.0389	$3\sigma^2 \rightarrow 4\sigma^2$	0.0421	$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$	0.0475	$1\pi^2 \rightarrow 2\pi^2$
0.0379	$3\sigma^2 \rightarrow 5\sigma^2$	0.0370	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$	0.0381	$1\pi^2 \rightarrow 3\pi^2$
0.0366	$2\sigma 3\sigma \rightarrow 6\sigma 9\sigma$	0.0308	$2\sigma 1\pi \rightarrow 5\sigma 3\pi$	0.0308	$2\sigma 1\pi \rightarrow 4\sigma 2\pi$
0.0389	$2\sigma 3\sigma \rightarrow 1\pi 2\pi$	0.0405	$2\sigma 3\sigma \rightarrow 1\pi 2\pi$	0.0312	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$
0.0509	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$	0.0366	$2\sigma 3\sigma \rightarrow 1\pi 3\pi$	0.0342	$2\sigma 1\pi \rightarrow 6\sigma 3\pi$
0.0488	$3\sigma 1\pi \rightarrow 5\sigma 3\pi$	0.0603	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$	0.0333	$2\sigma^2 \rightarrow 1\pi 3\pi$
0.0395	$3\sigma^2 \rightarrow 1\pi 2\pi$	0.0389	$3\sigma 1\pi \rightarrow 6\sigma 3\pi$	0.0517	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$
				0.0320	$3\sigma 1\pi \rightarrow 5\sigma 3\pi$
				0.0486	$3\sigma^2 \rightarrow 1\pi 2\pi$
				0.0395	$3\sigma^2 \rightarrow 1\pi 3\pi$
R = 2.00 bohr		R = 2.00 bohr		R = 2.00 bohr	
0.9791	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9820	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9640	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$
0.0539	$2\sigma \rightarrow 4\sigma$	0.0879	$3\sigma^2 \rightarrow 4\sigma^2$	0.0650	$2\sigma^2 \rightarrow 4\sigma^2$

(continued)

Table VI. (Continued)

$^3\Sigma^-$		$^1\Delta$		$^1\Sigma^+$	
R = 2.00 bohr		R = 2.00 bohr		R = 2.00 bohr	
0.0412	$2\sigma \rightarrow 5\sigma$	0.0400	$1\pi^2 \rightarrow 2\pi^2$	0.0629	$2\sigma^2 \rightarrow 1\pi^2$
0.0408	$3\sigma \rightarrow 4\sigma$	0.0317	$1\pi^2 \rightarrow 3\pi^2$	0.0341	$3\sigma^2 \rightarrow 4\sigma^2$
0.0894	$3\sigma^2 \rightarrow 4\sigma^2$	0.0405	$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$	0.1702	$3\sigma^2 \rightarrow 1\pi^2$
0.0302	$2\sigma 3\sigma \rightarrow 4\sigma 5\sigma$	0.0411	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$	0.0489	$1\pi^2 \rightarrow 2\pi^2$
0.0354	$2\sigma 3\sigma \rightarrow 4\sigma 6\sigma$	0.0306	$2\sigma 1\pi \rightarrow 5\sigma 3\pi$	0.0359	$1\pi^2 \rightarrow 3\pi^2$
0.0342	$2\sigma 1\pi \rightarrow 5\sigma 2\pi$	0.0448	$2\sigma 3\sigma \rightarrow 1\pi 2\pi$	0.0452	$2\sigma 3\sigma \rightarrow 4\sigma^2$
0.0309	$2\sigma 1\pi \rightarrow 5\sigma 3\pi$	0.0445	$2\sigma 3\sigma \rightarrow 1\pi 3\pi$	0.0494	$2\sigma 1\pi \rightarrow 4\sigma 2\pi$
0.0493	$2\sigma 3\sigma \rightarrow 1\pi 2\pi$	0.0663	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$	0.0324	$2\sigma 1\pi \rightarrow 6\sigma 3\pi$
0.0394	$2\sigma 3\sigma \rightarrow 1\pi 3\pi$	0.0401	$3\sigma 1\pi \rightarrow 6\sigma 3\pi$	0.0317	$2\sigma^2 \rightarrow 1\pi 3\pi$
0.0623	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$			0.0424	$3\sigma 1\pi \rightarrow 4\sigma 2\pi$
0.0310	$3\sigma 1\pi \rightarrow 5\sigma 3\pi$			0.0463	$3\sigma 1\pi \rightarrow 5\sigma 2\pi$
0.0300	$3\sigma 1\pi \rightarrow 6\sigma 3\pi$			0.0419	$3\sigma^2 \rightarrow 1\pi 2\pi$
				0.0388	$3\sigma^2 \rightarrow 1\pi 3\pi$
R = 2.80 bohr		R = 2.80 bohr		R = 2.80 bohr	
0.9580	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9679	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	0.9544	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$
0.0335	$2\sigma \rightarrow 4\sigma$	0.1898	$3\sigma^2 \rightarrow 4\sigma^2$	0.0487	$2\sigma^2 \rightarrow 4\sigma^2$
0.1275	$3\sigma \rightarrow 4\sigma$	0.0421	$1\pi^2 \rightarrow 2\pi^2$	0.1122	$2\sigma^2 \rightarrow 1\pi^2$

(continued)

Table VI. (Continued)

$^3\Sigma^-$		$^1\Delta$		$^1\Sigma^+$	
R = 2.80 bohr		R = 2.80 bohr		R = 2.80 bohr	
0.1904	$3\sigma^2 \rightarrow 4\sigma^2$	0.0402	$2\sigma3\sigma \rightarrow 4\sigma5\sigma$	0.1467	$3\sigma^2 \rightarrow 4\sigma^2$
0.0323	$2\sigma3\sigma \rightarrow 4\sigma5\sigma$	0.0408	$2\sigma3\sigma \rightarrow 4\sigma6\sigma$	0.0974	$3\sigma^2 \rightarrow 1\pi^2$
0.0458	$2\sigma3\sigma \rightarrow 4\sigma6\sigma$	0.0395	$2\sigma1\pi \rightarrow 4\sigma3\pi$	0.0330	$1\pi^2 \rightarrow 4\sigma^2$
0.0398	$2\sigma1\pi \rightarrow 4\sigma3\pi$	0.0471	$2\sigma1\pi \rightarrow 5\sigma2\pi$	0.0520	$1\pi^2 \rightarrow 2\pi^2$
0.0386	$2\sigma1\pi \rightarrow 5\sigma2\pi$	0.0323	$2\sigma3\sigma \rightarrow 1\pi2\pi$	0.0311	$1\pi^2 \rightarrow 3\pi^2$
0.0300	$2\sigma1\pi \rightarrow 5\sigma3\pi$	0.0486	$2\sigma3\sigma \rightarrow 1\pi3\pi$	0.0871	$2\sigma3\sigma \rightarrow 4\sigma^2$
0.0424	$2\sigma3\sigma \rightarrow 1\pi2\pi$	0.0621	$3\sigma1\pi \rightarrow 4\sigma2\pi$	0.0319	$2\sigma3\sigma \rightarrow 4\sigma6\sigma$
0.0422	$2\sigma3\sigma \rightarrow 1\pi3\pi$	0.0374	$3\sigma1\pi \rightarrow 6\sigma3\pi$	0.0367	$2\sigma1\pi \rightarrow 4\sigma3\pi$
0.0570	$3\sigma1\pi \rightarrow 4\sigma2\pi$			0.0395	$2\sigma1\pi \rightarrow 5\sigma2\pi$
				0.0797	$2\sigma3\sigma \rightarrow 1\pi^2$
				0.0335	$2\sigma3\sigma \rightarrow 1\pi2\pi$
				0.0401	$2\sigma3\sigma \rightarrow 1\pi3\pi$
				0.0562	$3\sigma1\pi \rightarrow 4\sigma2\pi$
				0.0357	$3\sigma1\pi \rightarrow 5\sigma2\pi$
				0.0350	$3\sigma1\pi \rightarrow 6\sigma3\pi$

(continued)

Table VI. (Continued)

$^3\Sigma^-$		$^1\Delta$	$^1\Sigma^+$
R = 4.0 bohr			
0.8421	$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$		
0.0390	$2\sigma \rightarrow 5\sigma$		
0.3532	$3\sigma \rightarrow 4\sigma$		
0.3790	$3\sigma^2 \rightarrow 4\sigma^2$		
0.0584	$2\sigma 3\sigma \rightarrow 4\sigma 6\sigma$		
0.0417	$2\sigma 1\pi \rightarrow 4\sigma 2\pi$		
0.0405	$2\sigma 1\pi \rightarrow 5\sigma 3\pi$		
0.0503	$2\sigma 3\sigma \rightarrow 1\pi 2\pi$		
0.0327	$3\sigma 1\pi \rightarrow 7\sigma 3\pi$		

Table VII. Occupation Numbers.

R =	1.35	1.50	1.80	1.91	2.00	2.20	2.40	2.80	4.00
$^3\Sigma^-$									
1σ	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
2σ	1.9821	1.9805	1.9782	1.9777	1.9775	1.9772	1.9772	1.9774	1.9808
3σ	1.9726	1.9718	1.9671	1.9639	1.9606	1.9510	1.9372	1.8920	1.5747
4σ	0.0126	0.0151	0.0224	0.0262	0.0298	0.0401	0.0544	0.1008	0.4209
5σ	0.0107	0.0104	0.0100	0.0098	0.0097	0.0094	0.0092	0.0086	0.0064
1π	1.9924	1.9921	1.9914	1.9911	1.9909	1.9906	1.9904	1.9905	1.9932
2π	0.0120	0.0124	0.0131	0.0133	0.0134	0.0138	0.0131	0.0121	0.0077
3π	0.0090	0.0089	0.0088	0.0088	0.0087	0.0087	0.0086	0.0085	0.0069
$^1\Delta$									
1σ	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	
2σ	1.9860	1.9853	1.9839	1.9835	1.9832	1.9828	1.9824	1.9820	
3σ	1.9738	1.9725	1.9678	1.9650	1.9622	1.9542	1.9430	1.9079	
4σ	0.0117	0.0131	0.0190	0.0223	0.0254	0.0343	0.0463	0.0832	
5σ	0.0732	0.0788	0.0819	0.0818	0.0815	0.0803	0.0788	0.0754	
1π	1.9893	1.9889	1.9882	1.9879	1.9877	1.9873	1.9871	1.9872	
2π	0.0137	0.0142	0.0150	0.0152	0.0153	0.0153	0.0151	0.0142	
3π	0.0104	0.0103	0.0101	0.0101	0.0100	0.0099	0.0098	0.0094	
$^1\Sigma^+$									
1σ	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	
2σ	1.9770	1.9750	1.9699	1.9675	1.9654	1.9598	1.9533	1.9414	
3σ	1.9074	1.9095	1.9134	1.9146	1.9154	1.9165	1.9160	1.9031	
4σ	0.0109	0.0125	0.0183	0.0213	0.0242	0.0322	0.0429	0.0748	
5σ	0.0079	0.0083	0.0085	0.0085	0.0084	0.0084	0.0083	0.0080	

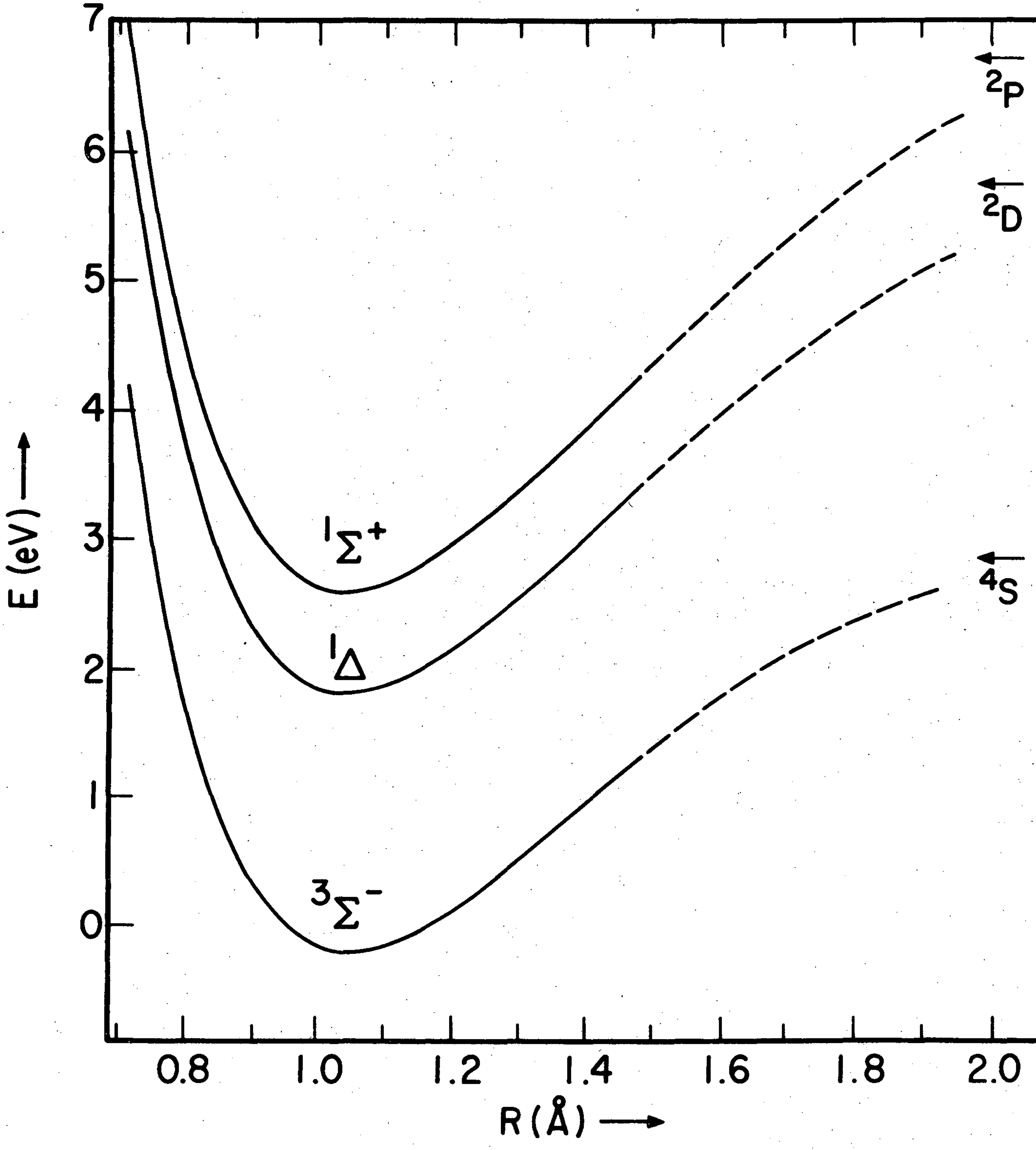
(continued)

Table VII. (Continued)

R =	1.35	1.50	1.80	1.91	2.00	2.20	2.40	2.80	4.00
1π	2.0620	2.0576	2.0544	2.0524	2.0508	2.0473	2.0440	2.0383	
2π	0.0151	0.0156	0.0163	0.0165	0.0166	0.0166	0.0164	0.0156	
3π	0.0118	0.0117	0.0114	0.0113	0.0112	0.0110	0.0107	0.0101	

FIGURE CAPTION

Fig. 1. Potential curves for the three lowest bound states of NH.



7
6
5
4
3
2
1
0
E (eV) ⟶
0.8
1.0
1.2
1.4
1.6
1.8
2.0
R (Å) ⟶
$^1\Sigma^+$
$^1\Delta$
$^3\Sigma^-$
^2P
^2D
^4S

Fig. 1

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