Calculations on π unp Rydberg Terms of the Nitrogen Molecule

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distributions of photodetached (or impact-detached) electrons and of angular distributions of detached electrons, all as functions of excitation energy, are measurements that test the theory or can be used with it to give information about particular molecules. The information may be such simple facts as the energies of autoionizing states or as detailed as their lifetimes and symmetries.

We have left for future development certain obvious extensions and refinements. These include the treatment of vibrational perturbations of the bound Rydberg states, whose spectra do show clearly certain perturbations that have been identified phenomenologically.[18] They also include the effects of strong coupling and many-step transitions, of molecular rotation and of the other perturbation terms, both vibrational and electronic, which were discussed briefly here but omitted from the calculations. And, following from these other

terms, the calculations should clearly be extended to many-electron molecules, where orthogonality–exclusion effects must play a role, and where we can test the generality of the calculations presented here.

Calculations on $\pi_u np$ Rydberg Terms of the Nitrogen Molecule

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A more thorough calculation is made of the lowest terms in the Worley–Jenkins Rydberg series in molecular nitrogen. A complete variation of the energy is made with respect to the screening parameters in the Rydberg functions for $n=3$, 4 and limited variation with parameters for functions with $n=5$, 6, 7. In every case investigated, a stable minimum in the term energy was found. Terms with $n=5$, 6, 7 agree with experimental terms to about 10%, and differences appear to decrease slightly with increasing n.

Some variation was made in parameters of the core function and the effect of this limited variation on the Rydberg terms is discussed. A brief discussion is made of results on computed Rydberg defects.

I. INTRODUCTION

THERE are a number of recent publications concerned with various aspects of the theoretical interpretation of Rydberg states of atoms and molecules. We can refer here only to those which have a direct relation to the present work or which have been helpful in interpretation of results to be reported here. Of particular interest is a general theory of Rydberg states which has been developed by Mulliken.[1] Limiting forms of Rydberg terms near ionization have been discussed by Kotani.[2] A stimulating general discussion of one-center approximations to molecular problems, given

by Hauk,[3,4] may be applicable to the problem of suitable radial forms of Rydberg functions. Actual calculation of molecular Rydberg terms have been made in several cases.[5–8]

In a former publication,[9] referred to here as (I), an approximate calculation of the three lowest terms in the Worley–Jenkins[10] Rydberg series in molecular nitrogen was reported. The purpose of the present work is to extend the calculations to higher members of the same series and to remove some of the arbitrary features

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[1] R. S. Mulliken, J. Am. Chem. Soc. 86, 3183 (1964).
[2] M. Kotani, in *Molecular Orbitals in Chemistry, Physics and Biology*, P.-O. Löwdin and B. Pullman, Eds. (Academic Press Inc., New York, 1964), p. 539.

[3] P. Hauk, R. G. Parr, and H. F. Hameka, J. Chem. Phys. 39, 2085 (1963).
[4] P. Hauk and R. G. Parr, J. Chem. Phys. 43, 548 (1965).
[5] C. A. Coulson and J. G. Stamper, Mol. Phys. 6, 609 (1963).
[6] F. A. Matsen and J. C. Browne, in Ref. 2, p. 151.
[7] H Lefebvre-Brion and C. M. Moser, J. Chem. Phys. 43, 1394 (1965).
[8] S. R. LaPaglia, J. Chem. Phys. 41, 1427 (1964).
[9] A. B. F. Duncan, J. Chem. Phys. 42, 2453 (1965).
[10] R. E. Worley, Phys. Rev. 64, 207 (1943).

TABLE I. Rydberg orbitals for $n=3, 4$.

	Core A		Core B	
	ϕ_3	ϕ_4	ϕ_3	ϕ_4
a_{2n}	0.26724	0.17468	0.23579	0.17858
a_{3n}	−1.03455	−0.90004	−1.03257	−1.02315
a_{4n}		1.35255		1.42930
ζ_{2n}	1.1927	1.1463	1.1330	1.0830
ζ_{3n}	0.4274	0.4124	0.4010	0.3910
ζ_{4n}		0.2784		0.2772

of the former work. At the same time, the essential simplifying features of the model are retained.

II. COMPUTATIONAL METHODS AND RESULTS

Wavefunctions for the Rydberg states are taken to be antisymmetrized products of the form $(\phi_{\text{core}}\phi_n)$; ϕ_n is the Rydberg function. It is assumed that the core function is essentially unchanged by excitation of the Rydberg function. The ϕ_n are assumed to satisfy one-electron eigenvalue equations

$$\mathbf{H}_{\text{eff}}\phi_n = (E_n - E_{\text{core}})\phi_n = \epsilon_n\phi_n.$$

The one-electron Hamiltonian, $\mathbf{H}_{\text{eff}}$ [see (I)], contains conventional two-electron Coulomb and exchange operators for the core electrons. The ϵ_n are approximations to the negatives of the experimental term values.

Rydberg terms in the Worley–Jenkins series are believed to be $(^1\pi_u)$ and we assume trial-orbital forms

$$^1\pi_u(np_x) = \phi_n = \sum_{k=2}^{n} a_{kn}(kp_x)_C,$$

with coordinates measured from the molecular midpoint, the $(kp_x)_C$ are normalized Slater functions with radial forms $r_C^{k-1}\exp(-\zeta_{kn}r_C)$. Only integral powers of r_C were used. In (I) the ζ_{kn} were arbitrarily fixed, with ζ_{2n} taken as 1.95 and the other ζ_{kn} as $(1/k)$. In the present work we have varied the energies of the terms with respect to the ζ_{kn}.

The simplified nature of the core function described in (I) is retained. In the present treatment the Rydberg energies and wavefunctions depend on the core function only through the two-electron Coulomb and exchange operators in the Hamiltonian, and therefore primarily on the screening parameters, ζ_c, of the core orbitals. A moderate variation of the energy of the nine-electron determinantal core function was made with respect of some of the screening parameters, in order to determine the effect of change of ζ_c on the Rydberg energies. The core function constructed as in (I) is referred to here as Core A and the core function after variation as Core B. The energy of Core Function B is about 1 a.u. lower than the energy of Core Function A.

The Rydberg terms were varied with respect to fixed cores, either Core A or Core B. The selection of screening parameters was not controlled automatically, but all other computations were performed automatically on an IBM 7074 computer. Double-precision (16 digit) arithmetic was used.

After a minimum in the energy of a Rydberg term with respect to a ζ_{kn} was located approximately, a best (or optimized) value of this ζ_{kn} was found by parabolic interpolation of three values of the energy near the minimum. A cycle of successive variation of the $(n-1)\zeta$ parameters in each ϕ_n should be made, and additional cycles of variation made until a stable common minimum with respect to each parameter in each function is achieved. This systematic procedure obviously requires a very large amount of computing time, which grows rapidly with increasing n, and it was practical to carry it through only for terms with $n=3$ and 4. The procedure was carried through, however, for both Cores A and B. The values of ζ_{kn} and a_{kn} obtained in this way are reported in Table I.

The treatment of Rydberg orbitals with $n=5, 6, 7$ was less systematic. In general, values of ζ_{kn} from previously determined $\zeta_{k,n-1}$ were adopted, or hydrogenic values were used to obtain the a_{kn} shown for ϕ_5, ϕ_6, and ϕ_7 in Table II, for the two cores. The significance of values listed under ϕ_6' and ϕ_7' are discussed in relation to the Rydberg defects (δ) of these orbitals.

Behavior of the energy of ϕ_3 with variation of the parameters indicate a higher sensitivity to ζ_{33} than to ζ_{23}. This behavior (with Core B) is shown in Fig. 1, which refers to the last cycle of variation. This figure shows also that the energy is stable against variation of both parameters. A similar behavior for ϕ_4 is shown in the same figure, but it is observed that the sensitivity of energy to all ζ_{k4} is reduced. For this reason we performed only one cycle of variation for the ζ_{k5}. Since ζ_{55} in ϕ_5 turned out to be almost hydrogenic, we used also hydrogenic values for ζ_{kn} for $k=5, 6$; $n=6$, and for $k=5, 6, 7$; $n=7$. A similar procedure was followed initially for Rydberg terms computed with Core A. The results were very similar and it is not necessary to show them.
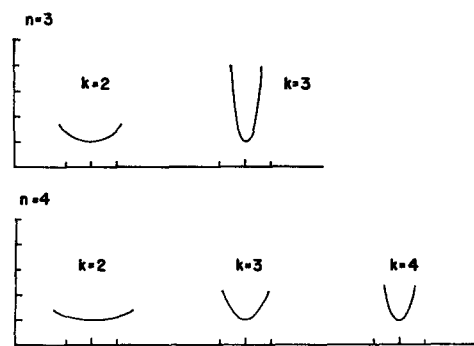

FIG. 1. Variation of relative energy of terms with ζ_{kn} for $n=3, 4$. Ordinate, 0.0005 hartree atomic units; abscissa, ζ_{kn} in units 0.1.

TABLE II. Rydberg orbitals for $n = 5, 6, 7$.

	Core A					Core B		
	ϕ_5	ϕ_6	ϕ_6'	ϕ_7	ϕ_7'	ϕ_5	ϕ_6	ϕ_7
a_{2n}	0.12801	0.11712	0.092749	0.10782	0.09430	0.13547	0.12326	0.11272
a_{3n}	−0.71598	−0.69206	−0.63977	−0.66499	−0.68087	−0.85551	−0.82687	−0.79180
a_{4n}	1.67512	1.97767	2.04214	2.17174	2.48800	1.75784	2.05784	2.24149
a_{5n}	−1.68533	−3.33548	−3.68730	−4.82430	−5.87984	−1.63831	−3.33911	−4.88192
a_{6n}		2.46363	2.74973	6.20424	7.40926		2.51517	6.35164
a_{7n}				−3.49459	−3.90428			−3.52621
ζ_{2n}	1.1463	1.1463	1.1213	1.1463	1.1213	1.083	1.083	1.083
ζ_{3n}	0.4124	0.4124	0.3854	0.4124	0.3854	0.3910	0.3910	0.3910
ζ_{4n}	0.2712	0.2712	0.2562	0.2712	0.2562	0.2772	0.2772	0.2772
ζ_{5n}	0.2017	0.2017	0.1944	0.2017	0.1944	0.2000[a]	0.2000	0.2000
ζ_{6n}		0.1666	0.1648	0.1666	0.1648		0.1666	0.1666
ζ_{7n}				0.1428	0.1428			0.1428

[a] A better interpolated value for this parameter is $\zeta_{55} = 0.1963$, but the coefficients for ϕ_6 and ϕ_7 have been obtained with $\zeta_{55} = 0.2000$.

Comparison of experimental and calculated defects (δ) in the Rydberg term formula, $T_n = 1/2(n-\delta)^2$, is of some interest.[1,11,12] Figure 2 shows values of δ calculated with Cores A and B and for experimental terms.[10] The irregular behavior, at high values of n led us to consider the fact that we did not perform independent variation of ζ_{kn} with $n=6$, but carried over the parameters used in ϕ_5. Therefore we carried out one cycle of variation of all parameters in ϕ_6. The results are shown in Table II, in column headed ϕ_6' and the effect on $\delta(6)$ is shown in the dotted line, Fig. 2, Core A. The better values of ζ_{k6} obtained by this variation were used in a recalculation of ϕ_7. The results are shown under ϕ_7' in Table II and in continuation of the dotted curve in Fig. 2, Core A. The dotted curve shows that δ is indeed very sensitive to the ζ_{kn}. It is to be noted that after one

cycle of variation, ζ_{77} did not change from its hydrogenic value significantly.

Finally, we show in Table III, the final values of Rydberg terms, T_n, computed with Cores A and B, along with corresponding experimental and hydrogenic terms for comparison. Figure 3 shows clearly the trend of terms with n, for Core B only.

The program for these computations was tested originally by recomputation of the terms reported in (I), with the same parameters for core and Rydberg functions. In these tests, some errors were discovered in the previously reported terms. It is found that lowering the single parameter ζ_{2n} from its original value 1.95 in (I) to the final values reported in Tables I, II, has a very much larger effect on the terms than these
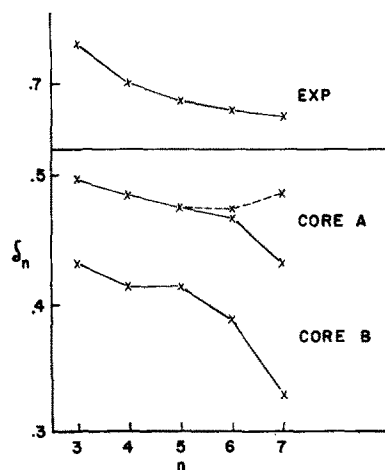

FIG. 2. Trends of δ with n from experimental terms and terms calculated with Cores A and B.

[11] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 137.
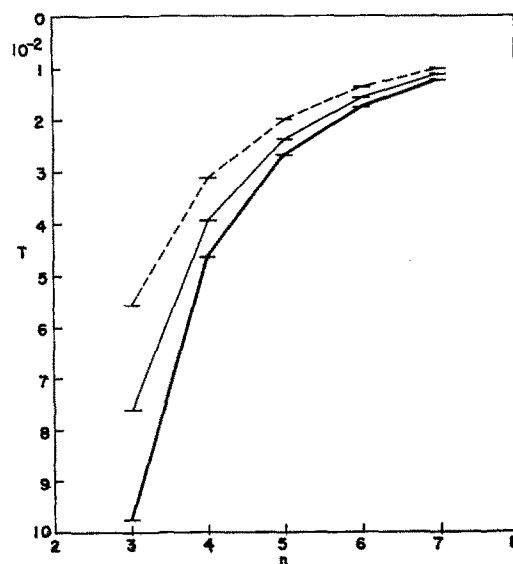[12] D. B. Cook and J. N. Murrell, Mol. Phys. **9**, 417 (1965).

FIG. 3. Comparison of experimental and hydrogen terms with terms (T_n) calculated with Core B (hartree atomic units). - - - -, hyd; ———, calc; ▬▬▬, exptl.

TABLE III. Rydberg terms (T_n) in Rydberg atomic units.[a]

n	T_n(Core B)	Δ_1	T_n(Core A)	Δ_2	$T_n{}'$(Core A)	Δ_3	T_n(exptl)	T_n(hyd)
3	0.07570	0.02133	0.07979	0.01724	...	...	0.09703	0.05555
4	0.03905	0.00684	0.04046	0.00543	...	...	0.04589	0.03125
5	0.02376	0.00312	0.02442	0.00246	...	...	0.02688	0.02000
6	0.01587	0.00178	0.01634	0.00131	0.01637	0.00127	0.01765	0.01388
7	0.01123	0.00125	0.01159	0.00090	0.01177	0.00072	0.01249	0.01020

[a] $T_n{}'$ indicates values of T_6, T_7 after the variation of parameters in ϕ_6, ϕ_7. Differences in columns headed Δ_1, Δ_2, Δ_3 are T_n (experimental) minus T_n (Core B), T_n (Core A), $T_n{}'$ (Core A), respectively.

errors. Therefore it does not appear necessary to report in detail how the errors occurred, but report only the corrected terms.[13]

All term values are reported in hartree atomic units. An interatomic distance in $N_2{}^+$ ($2.10934a_0$) was assumed in calculation of two-center integrals.

III. DISCUSSION AND CONCLUSIONS

The results in Table III show that the trial Rydberg functions and core model are adequate for approximate calculation of Rydberg terms of this particular series. An agreement between calculated and experimental terms for $n=5$, 6, 7 to 10% is good, especially in view of the fact that the terms are computed as small differences between much larger numbers. A general comparison of corresponding terms calculated with Cores A and B show only small differences, although the core energy has been varied alone with respect to the ζ_c, and has attained a value about 1 a.u. lower than Core A.

A substantial improvement in calculated terms has resulted in variation of ζ_{kn} in the Rydberg functions. The largest single factor has resulted from a reduction of ζ_{2n} from 1.95, used in (I), to the lower values in Tables I, II. Although the variation of the higher terms is not complete, we do not look for any substantial improvement with the present functional forms. The use of other forms, such as those suggested by Mulliken,[1] should be explored. These forms for a specific n can be expressed in terms of two parameters, δ and ζ. The latter could be taken as equal to ζ_c for the ($2p_x$) core orbital. The reduction in number of variational parameters might make it possible to investigate higher terms in a series with somewhat smaller computational effort.

The many-term Rydberg functions are somewhat complicated because of requirements of orthogonality (ϕ_n, ϕ_{n+1}) and of ϕ_n to the core function. The actual forms are more clearly visualized from the normalized radial distribution curves in Figs. 4, 5, and 6, drawn for Core B. In Fig. 5 it is seen that the innermost loop of ϕ_3 is totally inside the radial distribution drawn for ($2p_x$)$_{core}$, ($n=2$ in Fig. 4). The other figures show that the innermost loops of all functions are very similar

and the inward shift of the first node (after the origin) is very small as n is increased. The curves also show the small fraction of total charge which is in the first loop and that this fraction becomes smaller with increasing n. Comparison with hydrogenic functions with the same n and l shows that the innermost loops of our functions are closer to the origin and are much less diffuse than the corresponding hydrogenic loops. The curves appear to indicate that the outer parts of the functions behave correctly; each node is shifted inward relative to the corresponding hydrogenic node, as is expected.

The actual energy of the core ($N_2{}^+$, less four $1s$ electrons) is of some interest. The total energy of Core A is calculated to be about -21 a.u. After limited variation which results in Core B, the value is about -22 a.u. An estimate of core energy of a nine-electron model of $N_2{}^+$, based on data of Scherr,[14] gave about -21 a.u. These values are consistent in order of magnitude with results[15] obtained from a ten electron, valence bond calculation of N_2, -23.5 a.u., with $1s$ electrons omitted.

The change from Core A to Core B should not be viewed as a proper variation of core energy to a minimum, but rather as a change in electron distribution of the nine-electron core function. The change, which
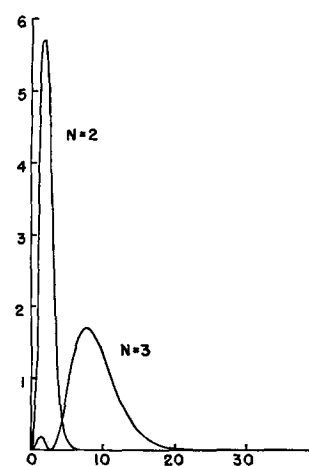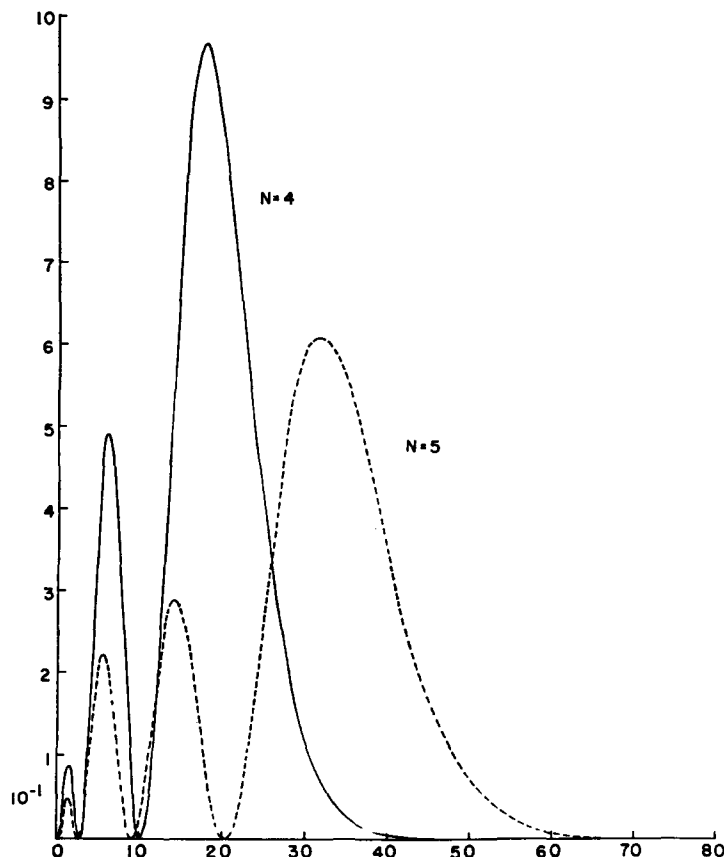

FIG. 4. Radial distribution curves for Rydberg function, $n=3$, compared with distribution of ($2p_x$) core orbital ($n=2$). Ordinate, $4\pi r^2 R_{nl}{}^2(r)$.

[13] The corrected values for T_3, T_4, and T_5 were 0.06656, 0.03303, 0.01897, respectively.

[14] C. W. Scherr, J. Chem. Phys. 23, 569 (1955).
[15] H. J. Kopineck, Z. Naturforsch. 7a, 314 (1952).

FIG. 5. Radial distribution curves for Rydberg functions, $n=4$, 5. Ordinate, $4\pi r^2 R_{nl}^2(r)$.

resulted in a lower core energy, has actually modified the shape of the radial distribution curve by moving the maximum inward. The outer regions of Core B are less diffuse than the outer regions of Core A. The total average radial distribution of the core orbitals is shown in Fig. 7, where the closed curve refers to Core A and the dotted curve to Core B. The latter shows a higher total density between the nuclei and a pronounced maximum at the nuclei. If penetration of the Rydberg electron occurs mostly in the outer regions, and if δ is some measure of penetration, δ is expected

TABLE IV. Parameters for core functions.

Core function	ζ_C (Core A)	ζ_C (Core B)	ζ_C (Huzinaga)
$(2s)_C$	1.36	2.25	1.95
$(3p_z)_C$	2.59	2.84	1.80
$\Sigma^a \begin{matrix}(\zeta_{2s})\\(\zeta_{3s})\end{matrix}$	1.36 2.92	0.900 3.304	··· ···
$(2p_x)_C$	1.1878	1.1878	1.0
$(2p_y)_C$	1.1878	1.1878	1.0
Energy	−21.05	−22.09	···

ᵃ $\Sigma = a_1(2s)_C + a_2(3s)_C$.

to be somewhat smaller for Core B. This is observed qualitatively.

The possibility that the core may be improved by another method for choice of ζ_c for the core orbitals may be considered. Huzinaga[16] has discussed the normal state of N_2 as if the molecule resembled a "semiunited" atom (magnesium, with two extra $1s$ electrons). He has computed overlap integrals between SCF–MO functions[17] of N_2 and atomic functions centered at the molecular midpoint as a function of ζ of the atomic functions. The criterion of maximum overlap can be made an alternate basis of choice for the ζ_c of core orbitals. Values of ζ_c from the maxima of Huzinaga's curve are shown in Column 4, Table IV. It is observed that Huzinaga's value for the replacement function $(2s)_C$ is between our values for this function in Cores A and B, that for $(2p_x)_C$ our value is not very different from Huzinaga's value, but our values for $(3p_z)_C$, the replacement function for $(\sigma_u 2s)$ are significantly larger. Huzinaga uses no linear combination which is equivalent to our Σ, so no comparison can be made here. While there are differences between corresponding ζ in the two methods of choice, a method of maximum overlap may be very helpful.

[16] S. Huzinaga, Mem. Fac. Sci. Kyushu Univ. Ser. B 3, 57 (1962).
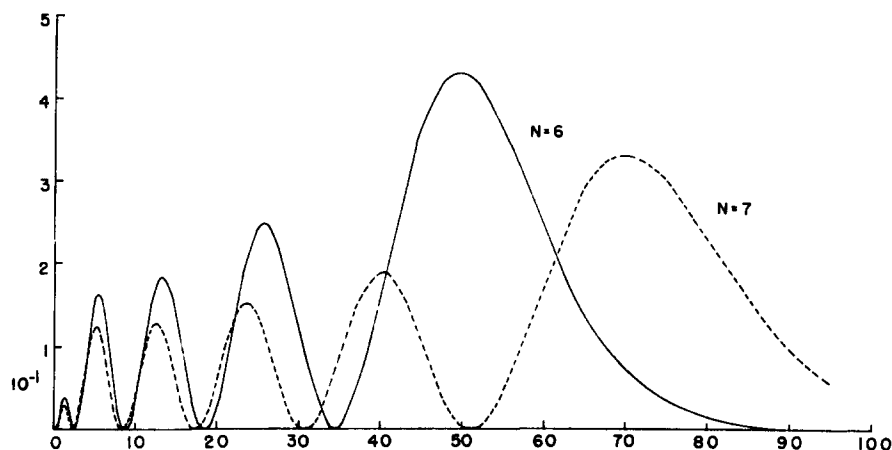
[17] B. J. Ransil, Rev. Mod. Phys. 32, 245 (1960).

FIG. 6. Radial distribution curves for Rydberg functions, $n=6$, 7. Ordinate, $4\pi r^2 R_{nl}^2(r)$.

It is probable that part of the residual errors in calculated terms (Δ in Table III) and in δ are to be ascribed to other effects than to an approximate core and the present forms of Rydberg functions. Early treatments of Rydberg defects in the helium atom[11] suggested the idea of polarization of the inner electron by the outer (Rydberg) electron. This idea has been considered recently[12] in further calculations of Rydberg states of helium and of lithium. It does not appear to be promising to attempt a formal perturbation calculation of the effect of such polarization in the Rydberg states of molecular nitrogen at the present time.

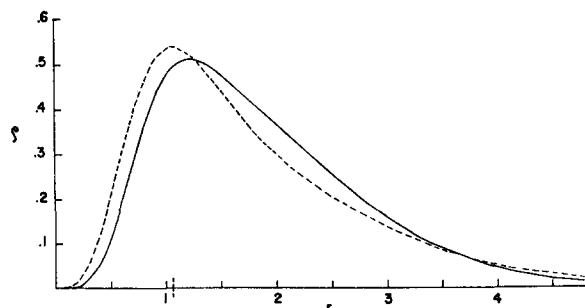We should note that Lefebvre–Brion and Moser[7]

FIG. 7. Normalized average density distributions $\rho(r)$ of Cores A (closed curve) and B (dotted curve). Ordinate, $[4\pi r^2\rho(r)]$ per electron in hartree units.

have made accurate SCF calculations on lower excited states of N_2. Some of their computed energies are very close to the experimental terms with $n=3$, 4 of the Worley–Jenkins series. They have not identified positively these calculated terms with members of a specific experimental $(n\pi_u)$ Rydberg series and indeed the original identification of Worley[10] has been the subject of recent controversy.

We do not know how far the complete SCF calculations can be carried toward higher Rydberg terms, where the interpretation of experimental terms is less controversial. Certainly the lower terms derived from a SCF calculation, with an accurate SCF core must be more reliable, simply because the excited electron is closer to the core on an average, and its function is more sensitive to core details than a function for a higher term. It may not be possible, in fact, to ever obtain accurate *lower* terms without an accurate core. This is not necessarily true for higher-series terms, where the details of the core probably are much less important.

ACKNOWLEDGMENTS