

Electronic structure of silicon Rydberg series. II. The $(3pns)^1P^o$, $^3P^o$ and $(3pnd)^1P^o$, $^3P^o$ series

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The electronic structure of the $(3s^2 3pns)^1P^o$, $^3P^o$ and $(3s^2 3pnd)^1P^o$, $^3P^o$ Rydberg series of the silicon atom is investigated by configuration interaction (CI) calculations of various levels. For example, the calculated energies relative to the ionized state $(3s^2 3p)^2P^o$ for the first five members of the $(3s^2 3pnd)^3P^o$ Rydberg series by the largest CI calculation in the present work are -1.91 , -1.17 , -0.75 , -0.50 , and -0.35 eV and the experimental ones are -1.91 , -1.15 , -0.74 , -0.50 , and -0.36 eV. The $(3pnd)^3P^o$ series is strongly perturbed by $(3s3p^3)^3P^o$, and the perturber $(3s3p^3)^3P^o$ is almost completely smeared out over the series. The $(3pns)^1P^o$ and $(3pnd)^1P^o$ series are found to perturb each other.

I. INTRODUCTION

Two types of Rydberg series, i.e., pure and perturbed, are known. The latter is further classified into two types, i.e., weakly and strongly perturbed series.¹ In a previous paper,² called Paper I in the following, the $(3s^2 3pnd)^1F^o$, $^3F^o$, $^1D^o$, and $^3D^o$ Rydberg series of the silicon atom have been investigated by the restricted Hartree-Fock (RHF) and configuration interaction (CI) calculations of various levels. It has been shown that the $^1F^o$ and $^3F^o$ series are pure Rydberg series, whereas the $^1D^o$ and $^3D^o$ series are strongly perturbed by $(3s3p^3)^1D^o$ and $^3D^o$. The term $(3s3p^3)^3D^o$ not only acts as the perturber, but is the largest component in the first member of the $^3D^o$ series. On the other hand, such a strongly mixed state is not found below the ionized level $(3s^2 3p)^2P^o$ in the $^1D^o$ series.

In this paper, the $^1P^o$ and $^3P^o$ Rydberg series, which also arise from the configuration $3s^2 3pnd$, are studied. Experimentally, the states which lie 1.91, 1.15, and 0.74 eV below the ionized state $^2P^o$ were designated as $(3p3d)$, $(3p4d)$, and $(3p5d)^3P^o$ by Moore,³ and were redesignated as $(3p3d)$, $(3s3p^3)$, and $(3p4d)^3P^o$ by Radziemski and Andrew⁴ (see Fig. 1). Their designation was based on a semiempirical three-dimensional CI calculation, which leads to the result that the lowest and highest states are predominantly $3p3d$ and $3p4d$, respectively, but the middle state contains almost equal amounts of the $3p3d$, $3p4d$, and $3s3p^3$ configurations (see Ref. 5):

$$\Psi_1(^3P) = 0.81(3p3d) + 0.54(3s3p^3) + 0.21(3p4d), \quad (1a)$$

$$\Psi_2(^3P) = 0.55(3p3d) - 0.60(3s3p^3) - 0.58(3p4d), \quad (1b)$$

$$\Psi_3(^3P) = 0.19(3p3d) - 0.59(3s3p^3) + 0.79(3p4d) \quad (1c)$$

Since then, their assignment has been widely accepted.⁵⁻¹¹

Their result, Eq. (1), shows that $(3s3p^3)^3P^o$ contributes almost equally to the three states and acts as a series perturber. It is expected that if we add more Rydberg-like configurations to the calculation the contribution of the perturber $(3s3p^3)^3P^o$ in the first three states will decrease and the term $3s3p^3$ will be smeared out over the series. In this

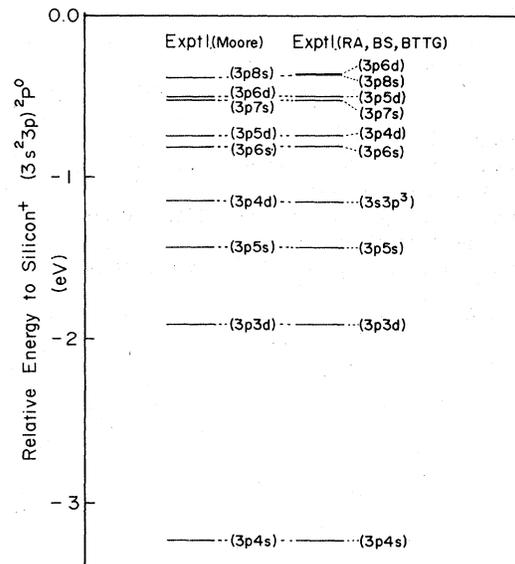


FIG. 1. Experimental designations for the silicon $(3s^2 3pnd)^3P^o$ and $(3s^2 3pns)^3P^o$ Rydberg series. Moore; see Ref. 3. The symbols RA, BS, and BTTG indicate Radziemski and Andrew (Ref. 4), Bashkin and Stoner (Ref. 9), Brown, Tilford, Tousey, and Ginter (Ref. 10), respectively.

paper the designation for the series will be re-examined from this viewpoint.

The energy levels of the $(3pns)^3P^o$ series are near those of the $(3pnd)^3P^o$ series^{3,4,9-11} (see Fig. 1). It is probable therefore that the two series perturb each other.

Since the configurations $3s3p^3$, $3pnd$, and $3pns$ yield $^1P^o$, it is interesting to examine whether $(3s3p^3)^1P^o$ acts as a series perturber and whether the series $(3pnd)^1P^o$ and $(3pns)^1P^o$ perturb each other.

In view of all this, the present paper is devoted to the study of the $(3pnd)^1,^3P^o$ and $(3pns)^1,^3P^o$ series by theoretical calculations, where the magnetic terms such as spin orbit one are not included in the Hamiltonian.

In Sec. II, we discuss the energy levels and characters of the Rydberg series. The effects of the perturber and the electronic correlation on the

quantum defects are discussed in Sec. III. The concluding remarks are given in Sec. IV.

II. ENERGY LEVELS AND CHARACTER OF THE RYDBERG SERIES

A. $(3pns)^3P$ and $(3pnd)^3P$ series

In the first stage, four CI calculations are performed.¹² The configurations employed for the respective CI's are (a) $3s^23pns$ ($n=4-13$), (b) $3s^23pnd$ ($n=3-13$), (c) $3s^23pns+3s^23pnd$, and (d) $3s^23pns+3s^23pnd+3s3p^3$. We call these CI's A , B , $A+B$, and $A+B+PT$. The purpose of making the A and B calculations is to obtain the energies of the RHF accuracy. The $A+B$ calculation is performed because the experimental energy levels of the $(3pns)^3P^o$ and $(3pnd)^3P^o$ series are close, especially for the higher levels. The purpose of the calculation $A+B+PT$ is to study the effect of the

TABLE I. Results of A , B , $A+B$, and $A+B+PT$ for the $^3P^o$ series.

Configurations		Total energy (a.u.)							
A: $3pns$ ($n=4-13$) ^a		$(3pns)^3P^o$ series			$(3pnd)^3P^o$ series				
B: $3pnd$ ($n=3-13$) ^a		A	A+B	A+B+PT	B	A+B	A+B+PT		
A+B: $3pns_A+3pnd_B$ ($n=4-13, m=3-13$) ^b									
A+B+PT: $3pns_A+3pnd_B+3s3p^3$ ($n=4-13, m=3-13$) ^b									
State	Method								
1		-288.6822	-288.6826	-288.6826	-288.6290 ^c	-288.6288	-288.6364		
2		-288.6228	-288.6228	-288.6229	-288.6049	-288.6049	-288.6116		
3		-288.6015	-288.6015	-288.6015	-288.5934	-288.5933	-288.5977		
4		-288.5912	-288.5912	-288.5913	-288.5870	-288.5870	-288.5897		
5		-288.5852	-288.5852	-288.5852	-288.5831	-288.5831	-288.5846		
	$3s^23p$	-288.5728 ^a	-288.5728	-288.5728	-288.5728	-288.5728	-288.5728		
	$3s3p^3$	288.5554 ^d			-288.5554				
		Relative energy to $^2P^o$ (eV)							
State	Method	$(3pns)^3P^o$ series				$(3pnd)^3P^o$ series			
		A	A+B	A+B+PT	Expt.	B	A+B	A+B+PT	Expt.
1		-2.977	-2.988	-2.990	-3.233 ^e	-1.531	-1.525	-1.731	-1.910 ^e
2		-1.361	-1.362	-1.364	-1.428 ^e	-0.875	-0.874	-1.058	-1.146 ^e
3		-0.781	-0.782	-0.782	-0.811 ^f	-0.560	-0.560	-0.679	-0.741 ^e
4		-0.503	-0.503	-0.503	-0.524 ^f	-0.387	-0.387	-0.461	-0.502 ^e
5		-0.337	-0.338	-0.338	-0.368 ^f	-0.282	-0.282	-0.323	-0.364 ^e
	$3s^23p$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$3s3p^3$	0.473				0.473			

^aThe $1s$, $2s$, $3s$, $2p$, and $3p$ orbitals are fixed to RHF ones for $(3s^23p3d)^3D^o$ (see Paper I).

^bThe basis sets for $1s$, $2s$, $3s$, $2p$, and $3p$ are the same as those of a. For ns ($n=4-13$) and nd ($n=3-13$) orbitals, we have employed the optimum orbitals resulting from the A and B calculations. They are expressed by ns_A and nd_B .

^cUsing nine s , eight p , and eight $3d$ STO's ($\{9s, 8p, 8d\}$) given in Paper I, we have made a RHF calculation for $(3s^23p3d)^3P^o$. The resulted energy is -288.6290 a.u. This agrees with the result of the lowest solution of the B calculation.

^dThe total energy for $(3s3p^3)^3P^o$ by the present basis is higher than the RHF result by 0.67 eV (RHF: -288.5799 a.u.). The basis of RHF is $\{9s, 8p\}$ given in Paper I.

^eSee Ref. 9.

^fSee Ref. 10.

TABLE II. Wave functions of $A+B+PT^a$ for the ${}^3P^0$ series

Weight of configurations (%) ($3pns$) ${}^3P^0$ series				
Solution	Most important configuration and its weight	$\sum' 3pns_A$ ^b	$\sum 3pnd_B$	$3s3p^3$
1	$3p4s_A$: 99.47	0.00	0.47	0.06
3	$3p5s_A$: 99.78	0.00	0.15	0.07
5	$3p6s_A$: 99.88	0.01	0.05	0.07
7	$3p7s_A$: 99.83	0.01	0.11	0.06
9	$3p8s_A$: 99.42	0.01	0.51	0.07
($3pnd$) ${}^3P^0$ series				
Solution	Most important configuration and its weight	$\sum' 3pnd_B$ ^b	$\sum 3pns_A$	$3s3p^3$
2	$3p3d_B$: 78.13	7.09	0.27	14.51
4	$3p4d_B$: 58.20	27.35	0.06	14.39
6	$3p5d_B$: 46.74	44.87	0.05	8.35
8	$3p6d_B$: 43.38	51.39	0.14	4.59
10	$3p7d_B$: 50.29	46.42	0.56	2.73

^a See Table I.

^b The symbol \sum' indicates that the summation over n is performed except for the most important configuration given in the second column.

term $3s3p^3$ on the ($3pns$) ${}^3P^0$ and ($3pnd$) ${}^3P^0$ series.

The atomic orbitals (AO's) for $1s$, $2s$, $3s$, $2p$, and $3p$ for these CI calculations are the RHF orbitals for ($3p3d$) ${}^3D^0$.² For diffuse orbitals, ten $3s$ and eleven $3d$ Slater-type orbitals (STO's) are used in the A and B calculations, respectively, whereas the optimum orbitals resulting from A and B , which will be called ns_A and nd_B in the following, are employed in the $A+B$ and $A+B+PT$ calculations. The total energies and the energies relative to ${}^2P^0$ are given in Table I together with the experimental values.

The present basis set is expected to give the energies close to those of the RHF calculation¹³ for the first several solutions in the A and B calculations. For example, the lowest energy for the ($3pnd$) ${}^3P^0$ series, -288.6290 a.u., by the B calculation agrees well with the RHF energy (see footnote c in Table I) and the calculated quantum defects are nearly constant for the first four solutions (see Sec. III).

For the ($3pns$) ${}^3P^0$ series, the calculation A leads to rather good agreement with experiment. And the results change only slightly in going to the calculations $A+B$ and $A+B+PT$. The weights of the configurations obtained from the $A+B+PT$ calculation are given in Table II. The wave functions of $A+B+PT$ for the series almost entirely consist of the corresponding $3pns_A$ ones; the series is al-

most a pure one.

For the ($3pnd$) ${}^3P^0$ series, the B calculation leads to poor agreement with experiment. The $A+B$ calculation gives nearly the same results as the B calculation, whereas considerable improvement is obtained by $A+B+PT$. One finds from Table II that ($3s3p^3$) ${}^3P^0$ mixes with the configurations $3pnd_B$ and strongly perturbs the latter. For example, at the fourth member of the series, the sum of the Rydberg configurations other than the main one is over 51%, although the contribution of $3s3p^3$ is less than 5%. Since the matrix elements between the Rydberg configurations ($3pnd_B$) are zero, the mixing arises from the interaction of the Rydberg configurations with $3s3p^3$. We can expect from the results given in Tables I and II that $3s3p^3$ strongly perturbs the rest of the series just as the cases of the ${}^1D^0$ and ${}^3D^0$ series.

One might wonder why ($3s3p^3$) ${}^3P^0$ acts as a perturber for ($3pnd$) ${}^3P^0$, but does not for ($3pns$) ${}^3P^0$. The off-diagonal matrix elements between the perturber and the Rydberg configurations ($3pns_A$) ${}^3P^0$ and ($3pnd_B$) ${}^3P^0$ are given by

$$H_{PT, 3pns_A} = -\frac{\sqrt{2}}{3} \iint R_{3p}^*(r_1) R_{ns_A}(r_1) \frac{r_1}{r_2} R_{3p}^*(r_2) \times R_{3s}(r_2) r_1^2 dr_1 r_2^2 dr_2 \quad (2a)$$

and

$$H_{PT, 3pnd_B} = -\frac{1}{3} \iint R_{3p}^*(r_1) R_{nd_B}(r_1) \frac{r_1}{r_2} R_{3p}^*(r_2) \times R_{3s}(r_2) r_1^2 dr_1 r_2^2 dr_2. \quad (2b)$$

The magnitude of the matrix element depends on the radial overlap of $R_{3p}^* R_{ns_A}$ and $R_{3p}^* R_{nd_B}$. The R_{ns_A} 's oscillate in a region where R_{3p} takes appreciable values because of the orthogonality to the $2s$ and $3s$ orbitals. This makes the radial overlap small. On the other hand, R_{nd_B} 's ($n \neq 3$) have the first peak in this region¹⁴ and it makes the radial overlap large compared with the case of ns_A 's.

We recall that the second member of the series, which lies 1.15 eV below ${}^2P^0$, was designated as ($3s3p^3$) ${}^3P^0$ by Radziemski and Andrew.⁴ The configuration $3s3p^3$ contributes significantly to the first and second solutions, but the weight of the term is not large enough to designate any one of them as $3s3p^3$. The weights of the Rydberg configurations amount to 85% for the two states. The weight of the Rydberg configuration increases for the higher solutions.

We note that the present $A+B+PT$ calculation has the following defect. The term ($3s3p^3$) ${}^3P^0$ calculated by RHF lies 0.19 eV below ${}^2P^0$ whereas the corresponding diagonal element of the $A+B+PT$

TABLE III. Atomic orbitals for the $^3P^o$ and $^1P^o$ Rydberg series.

<i>s</i> type	$1-2s_{\text{HF}}(^3D^o)$	$3-4s_{\text{NO}}(^2P^o)$
	$3s^a$ 1.19	$3s$ 0.79
	$3s$ 0.35	$3s$ 0.23
	$3s$ 0.10	$3s$ 0.069
		$3s$ 0.046
<i>p</i> type	$2p_{\text{HF}}(^3D^o)$	$3-4p_{\text{NO}}(^2P^o)$
	$3p^b$ 0.71	$3p$ 0.41
		$3p$ 0.24
<i>d</i> type	$3-13d_{\text{NO}}(^2P^o)$	
<i>f</i> type	$4-7f_{\text{NO}}(^2P^o)$	

^a $3s$ -type STO.^b $3p$ -type STO.

calculation lies 0.47 eV above $^2P^o$. Thus the weights of $3s3p^3$ in the $A+B+PT$ wave functions are probably underestimated. So we have performed a rather extensive CI calculation, where $(3pns, n=4-13)^3P^o$ and $(3pnd, n=3-13)^3P^o$ as well as $(3s3p^3)^3P^o$ are treated as the reference functions. The AO's for this CI are given in Table III. Except for ns orbitals, the AO's are the same as those of Paper I.

The one- and two-electron excitations of the M -shell electrons and the Rydberg electron of the reference functions to the correlating orbitals (see Paper I for details) are considered. The excited configuration-state functions (CSF's) are selected as follows.

(a) The pairwise excitations $(nl'n'l') \rightarrow (\alpha k \alpha' k')$ are considered in order to express the correlation effects between the ion core and an outer electron and the correlations in $(3s3p^3)^3P^o$. In some excitations the angular momentum conservation between the excited and exciting pairs is imposed.

(b) In order to express the correlation effects

TABLE IV. Reference configurations and results for the $^3P^o$ series.

Reference functions $3s^23pnd$ ($n=3-13$)		$3s^23pns$ ($n=4-13$)	
		$3s3p^3$	
Dimension of CI		1245	
$(3pns)^3P^o$ series			
Solution	Total energy (a.u.)	Relative energy to $^2P^o$ (eV)	CI
			Expt.
1	-288.7518	-3.178	-3.233 ^a
3	-288.6970	-1.414	-1.428 ^a
5	-288.6646	-0.804	-0.811 ^b
7	-288.6539	-0.514	-0.524 ^b
10	-288.6477	-0.345	-0.368 ^b
$^2P^o$	-288.6350	0.0	0.0
$(3pnd)^3P^o$ series			
2	-288.7053	-1.913	-1.910 ^a
4	-288.6779	-1.168	-1.146 ^a
6	-288.6625	-0.748	-0.741 ^a
8	-288.6536	-0.504	-0.502 ^a
9	-288.6481	-0.355	-0.364 ^a
$^2P^o$	-288.6350	0.0	0.0

^aSee Ref. 9.^bSee Ref. 10.

in the ion core of the Rydberg configurations, the ion core is described by the 18 CSF's.² The Rydberg CSF's thus obtained are expected to cover the most part of the correlation energy of the ion core (90%-94%).² The dimension of the CI calculation for the $^3P^o$ series reaches 1245.

The total energies and the relative energies to $^2P^o$ are collected in Table IV together with the experimental values. The relative energies are also plotted in Fig. 2 together with those of the

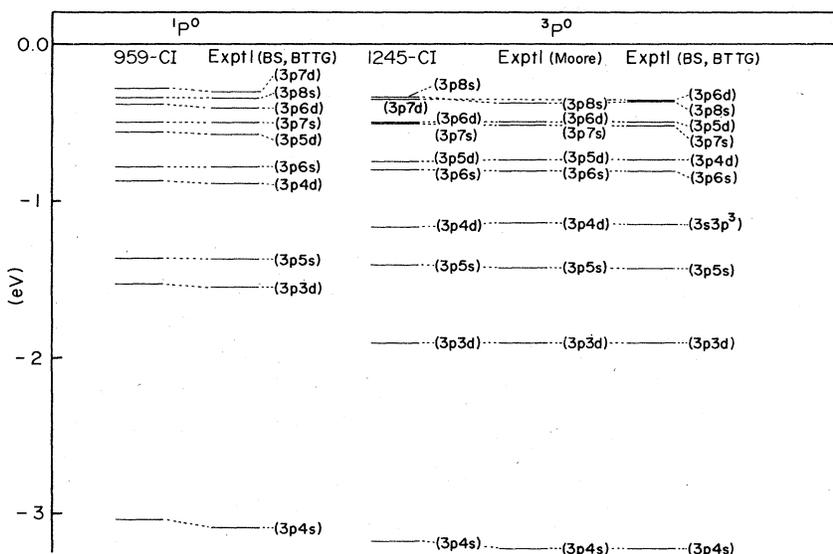


FIG. 2. Relative energies with respect to $\text{Si}^+ 3s^23p^2P^o$, of the silicon $(3s^23pnd)^1, ^3P^o$ and $(3s^23pns)^1, ^3P^o$ Rydberg series. The symbols 959-CI and 1245-CI indicate the 959- and 1245-dimensional CI calculations (see text) for the $^1P^o$ and $^3P^o$ series, respectively. The symbols BS and BTTG indicate Bashkin and Stoner (Ref. 9) and Brown, Tilford, Tousey, and Ginter (Ref. 10), respectively. Moore: see Ref. 3.

TABLE V. Important configurations and results of NO analysis for the $^3P^o$ series.

(a) Important configurations (%)						
$(3pns)^3P^o$ series						
Solution / CSF's	$\sum 3s^23pns$	$\sum 3p^3ns$	$\sum' 3s3p3dns^a$	$\sum 3p^24pns$	$\sum 3s^23pnd$	
1	92.47	2.55	2.35	0.95	0.39	
3	93.44	2.65	2.51	0.44	0.17	
5	93.72	2.69	2.55	0.34	0.04	
7	92.48	2.77	2.53	0.30	0.87	
10	92.72	2.64	2.53	0.30	1.13	
$3s^23p$	93.92	2.66	2.55	0.26	...	
$(3pnd)^3P^o$ series						
Solution / CSF's	$\sum 3s^23pnd$	$\sum 3p^3nd$	$\sum' 3s3p3dnd^a$	$\sum 3s3d^2np$	$3s3p^3^b$	$\sum 3s^23pns$
2	71.59	2.66	1.40	0.78	21.65	0.21
4	72.85	2.35	1.92	0.59	21.07	0.12
6	82.13	2.40	2.28	0.36	11.82	0.06
8	86.74	2.48	2.40	0.21	6.20	1.00
9	88.59	2.52	2.44	0.15	4.17	1.16
$3s^2sp$	93.92	2.66	2.55
(b) Occupation numbers for each NO						
$(3s^23pns)^3P^o$ series						
Solution, designation	NO	s'	p'	s''	$\langle r_{s''} \rangle^c$	
	1: $3p4s$	1.900	1.058	0.984	6.730	
	3: $3p5s$	1.905	1.055	0.995	14.682	
	5: $3p6s$	1.906	1.054	0.998	25.816	
	7: $3p7s$	1.905	1.056	0.989	41.678	
	10: $3p8s$	1.906	1.054	0.987	66.410	
	$3s^23p$	1.907	1.053	0.002	2.630	
$(3s^23pnd)^3P^o$ series						
Solution, designation	NO	s'	p'	d'	$\langle r_{d'} \rangle^d$	
	2: $3p3d$	1.692	1.476	0.775	6.605	
	4: $3p4d$	1.702	1.456	0.778	14.695	
	6: $3p5d$	1.792	1.274	0.875	24.833	
	8: $3p6d$	1.847	1.167	0.924	38.429	
	9: $3p7d$	1.866	1.130	0.943	55.427	
	$3s^23p$	1.907	1.053	0.032	2.364	

^aThe symbol \sum' indicates that the summation over n is performed except for $n=3$.

^bThe contribution from $\sum' 3s3p^2np$ is also included. The weights of $\sum' 3s3p^2np$ are 1.54%, 1.88%, 1.28%, 0.77%, and 0.54% for the respective solutions.

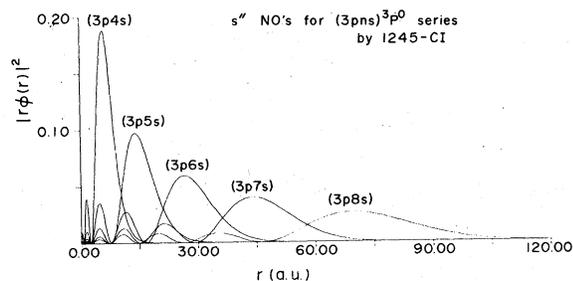
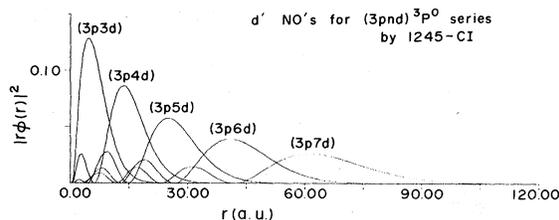
^cThe symbol $\langle r_{s''} \rangle$ indicates $\langle s'' | r | s'' \rangle$.

^dThe symbol $\langle r_{d'} \rangle$ indicates $\langle d' | r | d' \rangle$.

$^1P^o$ series.

For the $(3pns)^3P^o$ series, one finds that the agreement between the calculation and experiment is satisfactory. The first and second parts of Table V show the important configurations and the results of natural orbital (NO) analysis. The s -, p -, and d -type NO's with the largest occupation number are denoted by s' , p' , and d' and the s -type NO with the second largest one by s'' . The occupation number of s' approaches that of $^2P^o$ as the state becomes higher. The occupation number of the s'' orbitals is around one and they are Rydberg-like orbitals as are expected (see Fig. 3).

The agreement between the calculation and experiment is also satisfactory for the $(3pnd)^3P^o$ series and the error is one order of magnitude smaller than that by the $A+B+PT$ calculation. This is mainly due to the inclusion of the correlation effect and is partly due to the improvement of the description of the perturber $3s3p^3$. The weight of $3s3p^3$ in each member of the series becomes larger. Nevertheless it is not large enough again to designate any one of them as $(3s3p^3)^3P^o$. The sum of the weights of $3pnd$ is 71.6%–88.6% for the first five members of the series. The d' NO's have large occupation numbers and they show

FIG. 3. s'' NO's for the $(3s^2 3pns)^3P^o$ Rydberg series.FIG. 4. d' NO's for the $(3s^2 3pnd)^3P^o$ Rydberg series.

the typical shape of the Rydberg orbitals (see Fig. 4). Thus the designations for the first five members of the series are $(3pnd, n=3-7)^3P^o$. The present designation is in accord with that given by Moore.³

The weight of $(3s3p^3)^3P^o$ does not exceed 22% in any one of the members of the $(3pnd)^3P^o$ series and the sum of the weights of $3s3p^3$ from $3p3d$ to $3p7d$ reaches 64.9%. This indicates that $3s3p^3$ is to be smeared out over the series. An analogous case was found by Weiss in the aluminum $(3s^2nd)^2D$ Rydberg series.¹

B. $(3pns)^1P^o$ and $(3pnd)^1P^o$ series

We have performed five CI calculations. The first four CI's are A , B , $A+B$, and $A+B+PT$ whose configurations are $3pns$, $3pnd$, $3pns+3pmd$, and $3pns+3pmd+3s3p^3$, respectively. The basis set for the A and B calculations is just as that for the corresponding calculations in Sec. II A. For the $A+B$ and $A+B+PT$ calculations, the core orbitals are the same as those of the A and B calculations and the diffuse ones are the ns_A 's and nd_B 's resulting from the A and B calculations for the $^1P^o$ series. The final calculation is an extensive CI one similar to the 1245-dimensional CI

TABLE VI. Results of A , B , $A+B$, and $A+B+PT$ for the $^1P^o$ series.

Configurations									
$A: 3pns$ ($n=4-13$) ^a									
$B: 3pnd$ ($n=3-13$) ^a									
$A+B: 3pns_A+3pmd_B$ ($n=4-13, m=3-13$) ^b									
$A+B+PT: 3pns_A+3pmd_B+3s3p^3$ ($n=4-13, m=3-13$) ^b									
State	Method	Total energy (a.u.)							
		A	$(3pns)^1P^o$ series		B	$(3pnd)^1P^o$ series			
			$A+B$	$A+B+PT$		$A+B$	$A+B+PT$		
1		-288.6762	-288.6781	-288.6781	-288.6255 ^c	-288.6260	-288.6263		
2		-288.6210	-288.6210	-288.6210	-288.6029	-288.6031	-288.6034		
3		-288.6007	-288.6006	-288.6007	-288.5922	-288.5923	-288.5925		
4		-288.5909	-288.5908	-288.5908	-288.5862	-288.5862	-288.5863		
5		-288.5850	-288.5850	-288.5850	-288.5825	-288.5825	-288.5827		
$3s^2 3p$		-288.5728 ^a	-288.5728	-288.5728	-288.5728	-288.5728	-288.5728		
$3s3p^3$		-288.3821 ^d			-288.3821				
State	Method	Relative energy to $^2P^o$ (eV)							
		A	$A+B$	$A+B+PT$	Expt.	B	$A+B$	$A+B+PT$	Expt.
1		-2.814	-2.866	-2.867	-3.093 ^e	-1.436	-1.448	-1.457	-1.556 ^e
2		-1.314	-1.312	-1.313	-1.372 ^e	-0.820	-0.827	-0.834	-0.885 ^e
3		-0.761	-0.759	-0.760	-0.781 ^f	-0.528	-0.531	-0.536	-0.574 ^e
4		-0.493	-0.491	-0.492	-0.503 ^f	-0.365	-0.366	-0.370	-0.406 ^e
5		-0.333	-0.333	-0.333	-0.348 ^f	-0.266	-0.266	-0.269	-0.304 ^e
$3s^2 3p$		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$3s3p^3$		5.187				5.187			

^aSee footnote a in Table I.^bSee footnote b in Table I.^cThe RHF energy for $(3s^2 3p3d)^1P^o$ by $\{9s, 8p, 8d\}$ in Paper I is -288.6256 a.u.^dThe RHF energy for $(3s3p^3)^1P^o$ by the basis of $\{9s, 8p\}$ in Paper I is -288.4288 a.u.^eSee footnote e in Table I.^fSee footnote f in Table I.

TABLE VII. Wave function of $A+B^2$ for the $^1P^o$ series.

Weight of Configurations (%)				
$(3pns)^1P^o$ series				
Solution	Most important configurations in		$\sum' 3pns_A^b$	$\sum' 3pnd_B^b$
	$3pns_A$	$3pnd_B$		
1	$3p4s$: 97.86	$3p3d$: 1.23	0.05	0.86
3	$3p5s$: 82.26	$3p3d$: 16.09	0.04	1.62
5	$3p6s$: 82.17	$3p4d$: 16.09	0.03	1.71
7	$3p7s$: 84.57	$3p5d$: 13.62	0.02	1.79
9	$3p8s$: 91.27	$3p6d$: 6.67	0.00	2.06
$(3pnd)^1P^o$ series				
2	$3p5s$: 15.89	$3p3d$: 82.20	1.78	0.13
4	$3p6s$: 15.91	$3p4d$: 82.06	1.92	0.11
6	$3p7s$: 13.47	$3p5d$: 84.45	2.00	0.08
8	$3p8s$: 6.56	$3p6d$: 91.07	2.35	0.02
10	$3p8s$: 1.51	$3p7d$: 95.20	3.29	0.00

^aSee Table VI.^bThe symbol \sum' indicates that the summation over n is performed except for the most important configuration given in the second or third columns.

calculation for the $^3P^o$ series. The total energies and the relative energies to $^2P^o$ of the first four CI calculations are collected in Table VI.

For the $(3pns)^1P^o$ series, the A , $A+B$ and $A+B+PT$ calculations give almost the same results except for the first state. The agreement between the calculations and experiment is good. For the $(3pnd)^1P^o$ series, this agreement becomes a little worse than that of $(3pns)^1P^o$.

TABLE VIII. Reference configurations and results for the $^1P^o$ series.

Reference functions	$3s^2 3pnd$ ($n=3-13$)		
	$3s^2 3pns$ ($n=4-13$)		
	$3s 3p^3$		
Dimension of CI	959	Relative energy	
$(3pns)^1P^o$ series		CI	Expt.
Solution	Total energy (a.u.)		
1	-288.7468	-3.041	-3.093 ^a
3	-288.6852	-1.364	-1.372 ^a
5	-288.6638	-0.782	-0.781 ^b
7	-288.6535	-0.504	-0.503 ^b
9	-288.6475	-0.339	-0.348 ^b
$^2P^o$	-288.6350	0.0	0.0
$(3pnd)^1P^o$ series			
2	-288.6913	-1.532	-1.556 ^a
4	-288.6669	-0.868	-0.885 ^a
6	-288.6554	-0.555	-0.574 ^a
8	-288.6491	-0.384	-0.406 ^a
10	-288.6453	-0.280	-0.304 ^a
$^2P^o$	-288.6350	0.0	0.0

^aSee Ref. 9.^bSee Ref. 10.

The weights of the configurations by the $A+B$ calculation are given in Table VII. The weights of the most important configuration shows that $3pnd_B$ and $3p(n+2)s_A$ perturb each other. A rather small contribution of $3pns_A$'s in $(3p7d)^1P^o$ is probably caused by the insufficiency of the s -type basis set. The effects of the mutual perturbation on the spectra are small as is shown in Table VI.

The weights of $3s3p^3$ for the two series are very small in the $A+B+PT$ wave functions [$(3pns)^1P^o$, 0.20%–0.00%; $(3pnd)^1P^o$, 0.05%–0.00%] and the character of the wave functions is essentially the same as that of the $A+B$ calculation.

The results of the extensive CI calculation are given in Table VIII and Fig. 2. For $(3pns)^1P^o$, the agreement as for the relative energies to $^2P^o$ is satisfactory: the error is less than 0.009 eV except for the first solution.

For $(3pnd)^1P^o$, a considerable improvement is obtained by this CI calculation, but the calculated term energies are always higher than experimental values by ~ 0.02 eV. The error is mainly caused by a neglect of the spin-orbit interaction in the Hamiltonian which will be discussed in Sec. III.

The character of the wave functions for the extensive CI calculation for the $^1P^o$ series is essentially the same as that for the $A+B$ calculation.

III. QUANTUM DEFECTS

The quantum defect μ and the energy lowering ΔE from the ionization limit $^2P^o$ are related by

$$\Delta E = R_y / (n - \mu)^2.$$

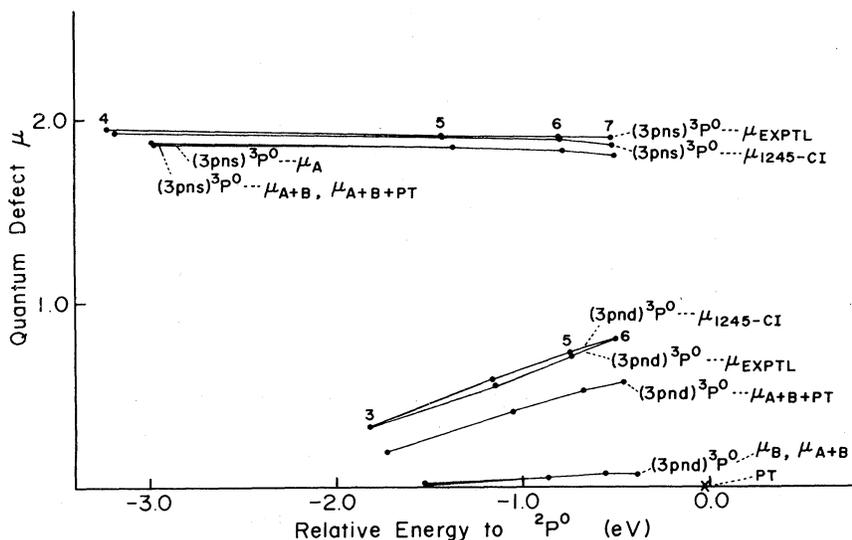


FIG. 5. Quantum defects μ for the $(3s^2 3pns) \ ^3P^\circ$ and $(3s^2 3pnd) \ ^3P^\circ$ Rydberg series. The suffixes, $A, B, A+B$, and $A+B+PT$ of μ indicate the kind of the CI calculation used to compute μ (cf. text). The suffixes, 1245-CI and EXPTL indicate the 1245-dimensional CI calculation and an experimental value. The mark \times on the abscissa indicates the energy of $(3s3p^3) \ ^3P^\circ$ relative to the ionized state $^2P^\circ$.

The calculated and experimental quantum defects for the $^3P^\circ$ series are given in Fig. 5. The $A, A+B$, and $A+B+PT$ calculations give almost the same results for the $(3pns) \ ^3P^\circ$ series.

For the $(3pnd) \ ^3P^\circ$ series, the quantum defect μ_B is small and slightly increases with n . Reflecting the existence of the perturber, μ_{A+B+PT} shows a considerable increase as the state becomes higher. The difference between μ_{EXPTL} and μ_{A+B+PT} is still large. The correlation effects for the $(3pnd) \ ^3P^\circ$ series are more important than those for the pure Rydberg series, $(3pns) \ ^3P^\circ$, which is partly due to the large contribution of $3s3p^3$ in the wave function. The agreements between μ_{EXPTL} and μ_{CI} are excellent.

The quantum defects for the $^1P^\circ$ series are given in Fig. 6. The experimental quantum defects for $(3pnd) \ ^1P^\circ$ are positive, while μ_B, μ_{A+B} , and μ_{A+B+PT} are negative. The μ_{959-CI} 's are positive, however the error of μ_{959-CI} is large for the higher member of the series compared with the results for the others. This indicates that the magnetic terms such as spin orbit interaction are important for the $(3pnd) \ ^1P^\circ$ series. In order to estimate the effect of the magnetic terms, we have performed a three-dimensional CI calculation, which includes only the spin orbit interaction as the magnetic term. The configurations employed are $(3pnd) \ ^1P_1^\circ, (3pnd) \ ^3P_1^\circ$, and $(3pnd) \ ^3D_1^\circ$.¹⁵ For the nonmagnetic part of the diagonal terms, we have

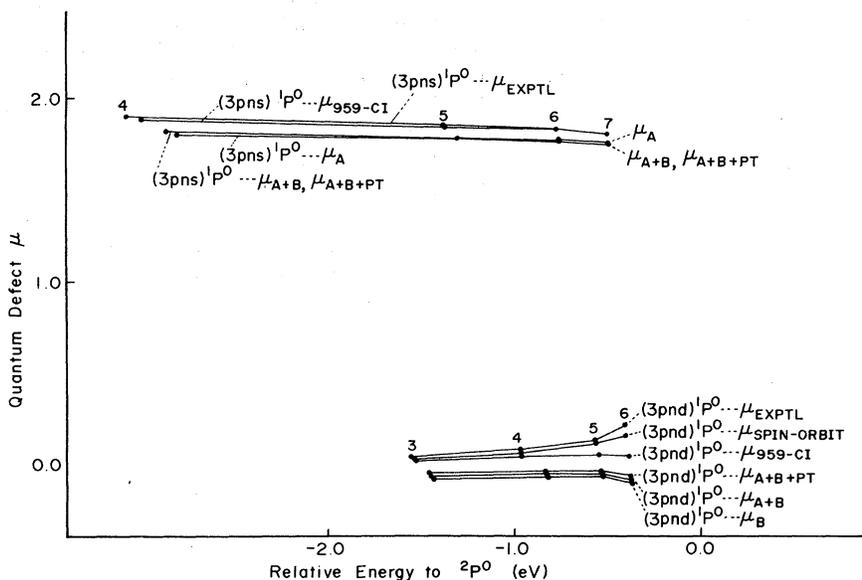


FIG. 6. Quantum defects μ for the $(3pns) \ ^1P^\circ$ and $(3pnd) \ ^1P^\circ$ Rydberg series. See the legend of Fig. 5 for the meaning of suffixes of μ except for the suffixes 959-CI and SPIN-ORBIT, which indicate the 959-dimensional CI calculation and the three-dimensional CI calculation including the spin orbit interaction, respectively.

adopted the total energies of 959-CI for $^1P^o$, 1245-CI for $^3P^o$ and 838-CI for $^3D^o$ which is given in Paper I. The improvement is considerable as is shown in Fig. 6.

IV. CONCLUDING REMARKS

The $(3pns)^{1,3}P^o$ and $(3pnd)^{1,3}P^o$ Rydberg series of the silicon atom have been investigated by CI calculations at various levels. The agreement of the calculated term values by the largest CI in the present work with experimental ones is excellent for the $(3pns)^{1,3}P^o$ and $(3pnd)^{3}P^o$ series.

It has been found that the $(3pnd)^{3}P^o$ series is strongly perturbed by $(3s3p^3)^{3}P^o$, but the $(3pns)^{3}P^o$ series is not. The term $3s3p^3$ is almost smeared out over the $(3pnd)^{3}P^o$ series. This is reflected in a marked increase in the quantum defect which approaches a unity for the higher members. Radziemski and Andrew⁴ designated the state which lies 1.15 eV below the ionized state as $3s3p^3$, but the present calculation shows that its appropriate

designation should be $3p4d$. Thus the designation given to the series by the present work is in accord with that given by Moore.³

Making a strong contrast with $(3s3p^3)^{3}P^o$, the term $(3s3p^3)^{1}P^o$ does not act as a series perturber for both the $(3pns)$ and $(3pnd)^{1}P^o$ series. The $(3pns)^{1}P^o$ and $(3pnd)^{1}P^o$ series perturb one another. The effects on the spectra are small, however. It has been found that for the $(3pnd)^{1}P^o$ series the spin orbit interaction is very important.

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$$\zeta_{nd} = \frac{z^4 n'^3 l' (l' + \frac{1}{2}) (l' + 1) \zeta_{n'p}}{z^4 n^3 l (l + \frac{1}{2}) (l + 1)}$$

where $z' = 2$, $n' = 3$, $l' = 1$, $z = 1$, and $l = 2$. See, e.g., E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1964), p. 269.