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# Electronic structure of silicon Rydberg series. I. The $(3pnd)\ {}^1D^o$, ${}^3D^o$, ${}^1F^o$, and ${}^3F^o$ series

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The $(3s^23pnd)\ {}^1D^o$, ${}^3D^o$, ${}^1F^o$, and ${}^3F^o$ Rydberg series of the silicon atom are investigated by a restricted Hartree-Fock calculation and configuration interaction (CI) calculations of various levels. The relative energies with respect to the ionized level $(3s^23p)^2P^o$ given by the largest CI calculation in the present work are −2.63, −1.46, −0.85, −0.55, −0.38, and −0.28 eV, respectively, for the first six members of the ${}^3D^o$ series, while the experimental values are −2.56, −1.45, −0.85, −0.55, −0.38, and −0.27 eV. The agreement between the two is excellent. The configuration $(3s3p^3)^3D^o$ is predominant in the first member of the ${}^3D^o$ series, and it also acts as a strong series perturber in the rest of the series. For the ${}^1D^o$ series the relative energies with respect to ${}^2P^o$ by the largest CI calculation are −2.27, −1.16, −0.70, −0.46, and −0.32 eV, respectively, whereas the experimental values are −2.31, −1.17, −0.70, −0.47, and −0.34 eV. In this series, $(3s3p^3)^1D^o$ acts as a series perturber just as $3s3p^3$ does in the ${}^3D^o$ series. At any levels of the approximations, $(3s3p^3)^1D^o$ is not found below the ${}^2P^o$ state. The $(3s^23pnd)\ {}^1F^o$ and ${}^3F^o$ series are found to be pure Rydberg series.

## I. INTRODUCTION

The silicon atom is astrophysically important because it is a dominant contributor of the electrons in the outer part of the solar photosphere. A systematic study of the spectra of the silicon atom was made first by Fowler[1] and then by Kiess.[2] The data up to 1938 are collected in Ref. 3 (AEL 1). Since then several experimental and theoretical investigations have been performed,[4-11] and they have expanded our knowledge about the Rydberg series with high principal quantum numbers.

In AEL 1, Moore[3] assigned the state which lies below the ionized level by 2.14 eV as $(3s3p^3)\,{}^3D^o$. The state is situated between $(3s^23p3d)$ and $(3s^23p4d)\,{}^3D^o$ (see Fig. 1). However, Shenstone has suggested that the first ${}^3D^o$ state is to be assigned as $(3s3p^3)\,{}^3D^o$ and the state which was designated as $(3s3p^3)\,{}^3D^o$ in AEL 1 is not a member of this series and thus the series terms $(3s^23pnd;\ n=4-8)\,{}^3D^o$ in AEL 1 have $n$ decreased by one (see Fig. 1).[12] These assignments for ${}^3D^o$ have been widely accepted.[4-11,13,14]

Radziemski and Andrew[4] have carried out a semiempirical multiconfiguration calculation and have found that the configuration $3s3p^3$ and $3s^23p3d$ contribute almost equally to the lowest two ${}^3D^o$ states,

$$\psi^1({}^3D^o) \sim 0.75(3p3d) - 0.61(3s3p^3) + 0.25(3p4d)\,, \tag{1a}$$

$$\psi^2({}^3D^o) \sim 0.66(3p3d) + 0.70(3s3p^3) - 0.27(3p4d)\,. \tag{1b}$$

(See Ref. 11.) The results of their calculation mean that we had better interchange Shenstone's designation. From (1a) and (1b), we find that the couplings of $3s3p^3$, $3p3d$, and $3p4d$ are large. This suggests that $(3s3p^3)\,{}^3D^o$ acts as a series perturber.

Series perturbers are classified into two types. One of them is a "weak perturber" which disturbs the member of the Rydberg series only in its vicinity. The other is a "strong perturber" which is strongly coupled to a considerable number of the series members and has a widespread effect on the spectra.[15] It will be interesting to investigate the character of the perturber $3s3p^3$ in detail by theoretical calculations.

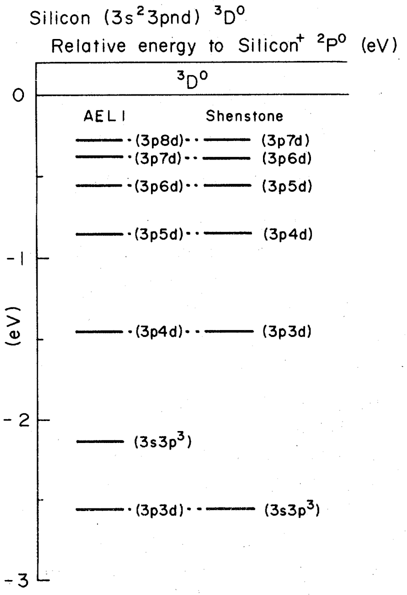

FIG. 1. Experimental designations for the ${}^3D^o$ Rydberg series.

TABLE I. Basis set for RHF calculations.[a]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $s$ type | $1s$ | 14.5344 | $1s$ | 22.6052 | $2s$ | 13.0783 | $2s$ | 5.0446 |
| | $3s$ | 4.0 | $3s$ | 2.97 | $3s$ | 1.78 | $3s$ | 1.19 |
| | $3s$ | 0.79 | | | | | | |
| $p$ type | $2p$ | 5.7795 | $2p$ | 11.1182 | $3p$ | 4.0 | $3p$ | 2.83 |
| | $3p$ | 2.0 | $3p$ | 1.41 | $3p$ | 1.0 | $3p$ | 0.71 |
| $d$ type | $3d$ | 1.7 | $3d$ | 1.13 | $3d$ | 0.76 | $3d$ | 0.50 |
| | $3d$ | 0.34 | $3d$ | 0.22 | $3d$ | 0.15 | $3d$ | 0.10 |
| | ($3d$ | 0.066 | $3d$ | 0.044 | $3d$ | 0.030)[b] | | |

[a] The exponents of the first four $s$-type and the two $p$-type STO's are those given by Clementi (Ref. 17) for the ionized state $(3s^2 3p)\,^2P^o$. The other exponents are selected to cover the charge distribution of $3s$, $3p$, and $3d$ electrons.

[b] The $d$-type STO's in the parentheses are the orbitals augmented for the CI with the Rydberg-like configurations $(3s^2 3pnd)$.

The $^1D^o$ states also arise from the configurations $3s3p^3$ and $3pnd$. The problem of whether $(3s3p^3)\,^1D^o$ lies below the ionized level $^2P^o$ or not has received considerable attention,[4,9] but it has not been settled. The problem of whether $(3s3p^3)\,^1D^o$ acts as a series perturber or not is of another interest.

The $(3pnd)\,^3F^o$ and $^1F^o$ Rydberg series are studied in order to compare with results of the $^3D^o$ and $^1D^o$ series. Throughout this paper magnetic interactions such as the spin orbit one are not included in the Hamiltonian.

In Sec. II, the energy levels and characters of the members of the Rydberg series $^3D^o$, $^1D^o$, $^3F^o$, and $^1F^o$ are discussed. The effects of the perturber and the electronic correlation on the quantum defects are discussed in Sec. III. Concluding remarks are given in Sec. IV.

## II. ENERGY LEVELS AND THE CHARACTERS OF THE RYDBERG SERIES

### A. $^3D^o$ series and its perturber

Firstly, the restricted Hartree-Fock (RHF) calculations[16] are performed for the ground state $(3s^2 3p^2)\,^3P$, $(3s3p^3)\,^3D^o$, $^1D^o$, $(3s^2 3p3d)\,^3D^o$, $^1D^o$, $^3F^o$, $^1F^o$ and the ionized state $(3s^2 3p)\,^2P^o$. The basis set is composed of Slater-type orbitals (STO's) and is common for all the states under consideration. The STO's employed are given in Table I. The total energies are collected in Table II together with those of Clementi[17] for the ground state $(3s^2 3p^2)\,^3P$ and the ionized state $(3s^2 3p)\,^2P^o$. The present result for $^2P^o$ agrees with that of Clementi and the result for $^3P$ differs by only 0.0002 a.u. from that of Clementi. The $s$- and $p$-type basis set will be sufficient for describing the orbitals for $3s3p^3$ and those of the ion core for the Rydberg series.

In RHF, $(3s^2 3p3d)\,^3D^o$ is below the ionized state $^2P^o$ by 1.64 eV. For $(3s^2 3pnd,\ n \geq 4)\,^3D^o$, the RHF wave functions are not orthogonal with each other. In order to obtain the wave functions and $nd$ orbitals in the RHF level, which are mutually orthogonal, a configuration-interaction (CI) calculation[18] with the configurational space $(3s^2 3pnd,\ n = 3\text{–}13)\,^3D^o$ is performed, where $1s$, $2s$, $3s$, $2p$, and $3p$ orbitals are fixed to the RHF ones for $(3s^2 3p3d)\,^3D^o$. The $d$-type basis set is composed of three diffuse $3d$ STO's in addition to those used in RHF calculation (see Table I). We call this calculation PRHF and the resulted $nd$ orbital $nd_{\mathrm{PRHF}}$. The total energies, relative energies to $^2P^o$, and the calculated quantum defects are collected in Table III. The energy of the ionized state, $^2P^o$, calculated with the present $s$ and $p$ orbitals agrees with that of the RHF calculation for $^2P^o$ within the error of 0.00001. Thus the ion core of the series is well described. The quantum defects are al-

TABLE II. Results of RHF.

| State | RHF energy (a.u.) | Relative energies to $^2P^o$ (eV) RHF | Relative energies to $^2P^o$ (eV) Expt.[a] |
|---|---|---|---|
| Present | | | |
| $(3s3p^3)\,^1D^o$ | −288.4661 | 2.903 | |
| $(3s^2 3p)\,^2P^o$ | −288.5728 | 0.0 | 0.0 |
| $(3s3p^3)\,^3D^o$ | −288.6197 | −1.276 | −2.557 |
| $(3s^2 3p3d)\,^1F^o$ | −288.6266 | −1.464 | −1.557 |
| $(3s^2 3p3d)\,^3D^o$ | −288.6329 | −1.635 | −1.452 |
| $(3s^2 3p3d)\,^3F^o$ | −288.6394 | −1.812 | −1.978 |
| $(3s^2 3p3d)\,^1D^o$ | −288.6401 | −1.831 | −2.303 |
| $3s^2 3p^2\,^3P$ | −288.8540 | −7.652 | −8.175 |
| Clementi[b] | | | |
| $(3s^2 3p)\,^2P^o$ | −288.5728 | 0.0 | 0.0 |
| $(3s^2 3p^2)\,^3P$ | −288.8542 | −7.657 | −8.175 |

[a] The difference of the center of the gravities between $^2P^o$ and the lowest state in each symmetry is given for the relative energy to $^2P^o$ of experiment. See Ref. 10.

[b] Reference 17.

TABLE III. Results of PRHF for $^3D^o$ series.

| | Configurations ($3s^23pnd$, $n=3$–13) | | | |
|---|---|---|---|---|
| State | Total energy (a.u.) | Relative energy to $^2P^o$ PRHF (eV) | Relative energy to $^2P^o$ Expt. (eV) | Quantum defect PRHF (eV) |
| $3p^{\infty}d$ | −288.5728 | 0.0 | 0.0 | ··· |
| $3p9d$ | −288.5777 | −0.136 | −0.159 | −1.02 |
| $3p8d$ | −288.5803 | −0.204 | −0.206 | −0.16 |
| $3p7d$ | −288.5833 | −0.285 | −0.272 | 0.10 |
| $3p6d$ | −288.5873 | −0.394 | −0.375 | 0.13 |
| $3p5d$ | −288.5938 | −0.573 | −0.548 | 0.13 |
| $3p4d$ | −288.6061 | −0.906 | −0.851 | 0.13 |
| ($3s3p^3$) [a] | (−288.6197) | (−1.276) | −2.558 | ··· |
| $3p3d$ | −288.6329 | −1.638 | −1.452 | 0.12 |

[a] This value is quoted from Table II.

TABLE IV. Configuration interaction with $3pnd_{\mathrm{PRHF}}$ and $3s3p^3$ for $^3D^o$ series.

Configurations $3s^23pnd_{\mathrm{PRHF}}$ and $3s3p^3$
Dimension of CI 12
Matrix elements for the first six members [a]

| | $3d_{\mathrm{PRHF}}$ | $4d_{\mathrm{PRHF}}$ | $3p^3$ | $5d_{\mathrm{PRHF}}$ | $6d_{\mathrm{PRHF}}$ | $7d_{\mathrm{PRHF}}$ |
|---|---|---|---|---|---|---|
| Diagonal | −0.0326 | −0.0057 | 0.0000 | 0.0066 | 0.0131 | 0.0171 |
| Off diagonal | −0.0229 | 0.0166 | ··· | 0.0123 | 0.0098 | 0.0074 |

| Solution | Total energy (a.u.) | Relative energy to $^2P^o$ (eV) PRHF + PT | Relative energy to $^2P^o$ (eV) Expt. [b] |
|---|---|---|---|
| 1 | −288.6666 | −2.554 | −2.558 |
| 2 | −288.6237 | −1.386 | −1.452 |
| 3 | −288.6025 | −0.808 | −0.851 |
| 4 | −288.5920 | −0.524 | −0.548 |
| 5 | −288.5861 | −0.362 | −0.375 |
| 6 | −288.5825 | −0.264 | −0.272 |

Weight of configurations (%)

| Solution | The largest configuration in $3pnd_{\mathrm{PRHF}}$ and its weight | $3s3p^3$ | Others |
|---|---|---|---|
| 1 | $3p3d$... 25.61 | 55.53 | 18.87 |
| 2 | $3p3d$... 70.16 | 11.43 | 18.41 |
| 3 | $3p4d$... 80.74 | 3.82 | 15.44 |
| 4 | $3p5d$... 83.21 | 1.83 | 14.95 |
| 5 | $3p6d$... 83.34 | 1.20 | 15.46 |
| 6 | $3p7d$... 86.36 | 0.97 | 12.67 |

Mean value of $r$ by $nd_{\mathrm{PRHF}}$ and by $d$-type NO of PRHF + PT (a.u.).

| | Solution 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| PRHF | 9.39 | 19.42 | 32.43 | 48.35 | 72.11 | 118.12 |
| PRHF + PT | 4.84 | 12.33 | 22.68 | 36.51 | 53.38 | 71.46 |

[a] The values of the diagonal elements are expressed by the difference from the energy of $3s3p^3$. The energy of $3s3p^3$ is −288.6004 a.u. which is obtained by the use of the $1s$, $2s$, $3s$, $2p$, and $3p$ RHF orbitals for ($3p3d$) $^3D^o$. Note that the energy of $3s3p^3$ is greater than the RHF value by 0.0193 a.u. (see Table II). The off-diagonal element is $\langle 3pnd_{\mathrm{PRHF}}|H|3s3p^3\rangle$.

[b] See Ref. 10.

most constant for the first four or five solutions. These solutions may be close to those of RHF. The $(3s3p^3)\,{}^3D^o$ given by RHF lies at the midpoint of $(3p3d_{\rm PRHF})\,{}^3D^o$ and $(3p4d_{\rm PRHF})\,{}^3D^o$, whereas $(3s3p^3)\,{}^3D^o$ is the lowest state in experiment. The calculated term values are far from the experimental ones for these three solutions.

Since the matrix elements between the $3s3p^3$ and $3pnd_{\rm PRHF}$'s are not zero, we have performed a CI calculation with $3s3p^3$ and ($3pnd_{\rm PRHF}$; $n=3-13$). We call this CI PRHF+ PT. The results are given in Table IV.

Experimentally, the lowest ${}^3D^o$ lies below ${}^2P^o$ by 2.56 eV. In the PRHF+ PT calculation, it lies below ${}^2P^o$ by 2.55 eV which is close to experiment. The lowest state was designated as $3p3d$ up to 1957 and was redesignated as $3s3p^3$ after 1958. Radziemski and Andrew[4] adopted the same designation although their semi empirical calculation indicates the first state to be $3p3d$. Contrary to the result of Radziemski and Andrew, the weight of $3s3p^3$ reaches 56% for the lowest ${}^3D^o$ and is greater than that of $\sum 3s^2 3pnd$ (44%) (see Table IV). It would be appropriate to designate the lowest state as $3s3p^3$, if the labeling has a meaning in a case of such a strong mixing.

The relative energies with respect to ${}^2P^o$ of the PRHF+ PT calculation are compared favorably with those of the PRHF calculation for the higher solutions. It should be noted that a fairly large mixing of $3pnd_{\rm PRHF}$'s occurs in these solutions. Since the matrix elements between $3pnd_{\rm PRHF}$'s are zero, the mixing arises from the interaction of $3pnd_{\rm PRHF}$'s with $3s3p^3$. The perturbation theory gives the following expression for the perturbed wave function $\psi_n$:

$$\psi_n = \Phi_n + a_{n,\rm PT}(1 - \tfrac{1}{2}a_{n,\rm PT})\Phi_{\rm PT} + a_{n,\rm PT} \sum_m{}' \frac{H_{m,\rm PT}}{E_n - E_m}\Phi_m + \cdots \,. \tag{2a}$$

Here

$$a_{n,\rm PT} = H_{{\rm PT},n}/(E_n - E_{\rm PT}),\quad H_{{\rm PT},n} = (\Phi_{\rm PT}\,|H|\,\Phi_n)\,, \tag{2b}$$

and $\Phi_n$ and $\Phi_{\rm PT}$ denote $3pnd_{\rm PHRF}$ and $3s3p^3$, respectively. Some of the matrix elements $H_{m,\rm PT}$ in the summation have the order of the magnitude of the corresponding energy spacings $E_n - E_m$ (see the first part of Table IV). Therefore the second- and higher-order effects of the mixing coefficients are as great as or greater than the first-order effect. In fact, we can see that, in the sixth solution, the weight of $3s3p^3$ is 1%, whereas the sum of the weights of the Rydberg configurations other than the main one amounts to 13%. The matrix element $H_{n,\rm PT}$ decreases gradually with the increase in $n$. Thus the effect of $3s3p^3$ is expected to be still large for the higher states with $n \geq 8$. We conclude that $(3s3p^3)\,{}^3D^o$ which is predominant in the first ${}^3D^o$ state acts as a strong perturber.

The present result shows a strong contrast with that of the aluminium $(3s^2nd)$ Rydberg series.[13] In this case $3s3p^2$ acts as a strong perturber and is smeared out over the entire series. The weight of $3s3p^2$ does not exceed 21% in any members of the series.

The weights of the Rydberg-type configurations amount to (89-99)% for the second to sixth solutions. The designation for these solutions will be $3p3d$, $3p4d$, $3p5d$, and $3p6d$.

In order to confirm the designation given above, we have performed a rather large CI calculation for the ${}^3D^o$ series. The atomic orbitals (AO's) for the CI calculation are given in Table V and are common for all the series under consideration. They mainly consist of the natural orbitals (NO's) which are obtained from the 498-dimensional CI calculation for the ionized state ${}^2P^o$ (see the Appendix). In these orbitals, the $4s_{\rm NO}$, $4p_{\rm NO}$, $3d_{\rm NO}$ and $4f_{\rm NO}-7f_{\rm NO}$ and in some cases $5p-7p$, $4d_{\rm NO}$, and $5d_{\rm NO}$ are chosen as the correlating orbitals.

In the CI calculation for the ${}^3D^o$ series, $3s3p^3$, $3s^2 3pnd$ ($n=3-13$) and $3s3p^2np$ ($n=4-7$) are treated as reference functions and the electronic correlations of the outer four electrons of these functions are considered. Two types of the correlations are taken into account. Firstly, pairwise excitations which represent the $3s$-$nd$ and $3p$-$nd$ correlations in the Rydberg configurations and those which represent the correlations in the other two types reference functions $3s3p^3$ and $3s3p^2np$'s are considered.[19] Secondly, in order to describe the correlation effects of the ion core in the Rydberg configurations we select 18 configuration-state functions (CSF's) from 498 CSF's for ${}^2P^o$ which have large coefficients ($|c_i| \geq 0.01$, see Table XIV) and make CSF's for the Rydberg series by adding a $d$ electron to these CSF's.

The truncated set of CSF's describes the correlation effects of the ion core almost fully, because the 18-dimensional CI calculation for ${}^2P^o$

TABLE V. Atomic orbitals for the Rydberg series.

| | | |
|---|---|---|
| $s$ type | $1-2s_{\rm HF}({}^3D^o)$ | $3-4s_{\rm NO}({}^2P^o)$ |
| $p$ type | $2p_{\rm HF}({}^3D^o)$ | $3-4p_{\rm NO}({}^2P^o)$ |
| | $3p$ 0.71 $3p$ 0.41 $3p$ 0.24 | |
| $d$ type | $3-13d_{\rm NO}({}^2P^o)$ | |
| $f$ type | $4-7f_{\rm NO}({}^2P^o)$ | |

TABLE VI. Reference configurations and results for $^3D^o$.

| | |
|---|---|
| Reference functions | $3s^23pnd$, $n=3$–$13$<br>$3s3p^3$<br>$3s3p^2np$, $n=4$–$7$ |
| Dimension of CI | 838 |

| | | Relative energy to $^2P^o$ (eV) | |
|---|---|---|---|
| Solution | Total energy (a.u.) | CI | Expt. [a] |
| 1 | −288.7317 | −2.630 | −2.558 |
| 2 | −288.6886 | −1.458 | −1.452 |
| 3 | −288.6663 | −0.851 | −0.851 |
| 4 | −288.6552 | −0.549 | −0.548 |
| 5 | −288.6490 | −0.380 | −0.375 |
| 6 | −288.6453 | −0.278 | −0.272 |
| $3s^23p$ | −288.6350 | 0.0 | 0.0 |

[a] See Ref. 10.

gives the total energy of −288.6350 a.u. which is only 0.001 a.u. above the result of the 498-dimensional CI. (The calculated *M*-*M* shell correlation energy by the 18-dimensional CI is −1.693 eV, which covers (90−94)% of the estimated experimental value for $^2P^o$.) The number of CSF's thus obtained is 838 for the $^3D^o$ series.

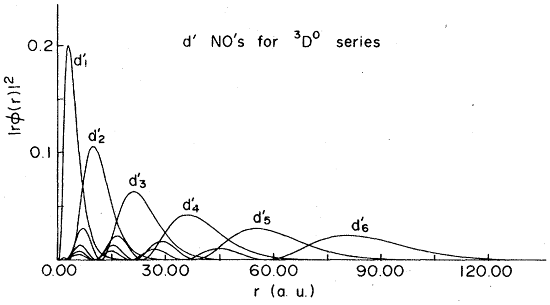

FIG. 2. Radial charge distribution of *d'* NO's for the $^3D^o$ Rydberg series. The suffix *i* which denotes the level is attached to *d'*.

The total energies and the relative energies to $^2P^o$ by these CI calculations are given in Table VI together with the experimental values. The agreement between the calculation and experiment is satisfactory in that the maximum error is only 0.006 eV except for the first solution.

The weights of the important configurations are given in the first part of the Table VII. The weights of $3s3p^3$ and $\sum 3s^2pnd$ for the first solution are 56% and 39%, respectively. The designation for the first state is $3s3p^3$. This is the same result as the PRHF+ PT calculation. In the rest of the solutions the weights of $3s3p^3$ in the table are

TABLE VII. Important configurations and results of NO analysis for $^3D^o$ series.

(a) Important configurations (%)

| Solution / CSF's | $\sum 3s^23pnd$ | $\sum 3p^3nd$ | $\sum' 3s3p3dnd$ [a] | $\sum 3s3d^2np$ | $3s3p^3$ [b] |
|---|---|---|---|---|---|
| 1 | 38.99 | 1.97 | 0.56 | 1.29 | 55.66 |
| 2 | 79.73 | 2.51 | 2.17 | 0.26 | 14.22 |
| 3 | 89.27 | 2.62 | 2.43 | 0.11 | 4.60 |
| 4 | 91.76 | 2.64 | 2.50 | 0.06 | 2.11 |
| 5 | 92.61 | 2.66 | 2.52 | 0.04 | 1.27 |
| 6 | 93.11 | 2.65 | 2.54 | 0.03 | 0.78 |
| $3s^23p$ | 93.92 | 2.66 | 2.57 | ··· | ··· |

(b) Occupation numbers for each NO.

| Solution, designation / NO | $3s_{NO}$ | $3p_{NO}$ | $d'$ | $d''$ | $\langle r_{d'}\rangle$ [c] (a.u.) |
|---|---|---|---|---|---|
| 1 ... $3s3p^3$ | 1.369 | 2.148 | 0.441 | 0.018 | 4.466 |
| 2 ... $3p3d$ | 1.767 | 1.327 | 0.849 | 0.035 | 11.554 |
| 3 ... $3p4d$ | 1.861 | 1.140 | 0.951 | 0.033 | 21.300 |
| 4 ... $3p5d$ | 1.886 | 1.093 | 0.977 | 0.032 | 34.392 |
| 5 ... $3p6d$ | 1.894 | 1.077 | 0.986 | 0.032 | 50.165 |
| 6 ... $3p7d$ | 1.899 | 1.067 | 0.992 | 0.032 | 71.715 |
| $3s^23p$ | 1.907 | 1.053 | 0.032 | ··· | ··· |

[a] The symbol $\sum'$ indicates that summation on $n$ is performed except for $n=3$.

[b] The contribution from $\sum' 3s3p^2np$ is also included. The weights of $\sum' 3s3p^2np$ are small compared with that of ($3s3p^3$): they are 2.96%, 1.57%, 0.52%, 0.28%, 0.19%, and 0.12% for the respective solutions.

[c] The symbol $\langle r_{d'}\rangle$ indicates $\langle d'|r|d'\rangle$.

also nearly equal to those given in Table IV. The NO analysis is performed and the results are shown in the second part of Table VII where the $d$-type NO's with the largest and next-largest occupation numbers are denoted by $d'$ and $d''$, respectively. The radial charge distribution of $d'$ orbital for each level is given in Fig. 2. The orbital $d'$ for the first state ($d_1'$) is rather contracted ($\langle r_{d'}\rangle = 4.5$ a.u.). Except for $d_1'$, the others show the typical shape of the Rydberg series. They are quite similar to the hydrogen $nd$ orbitals with $n = 3-7$. One of the examples is shown in Fig. 3. Since the occupation numbers for $d_i'$ ($i = 2-6$) are greater than 0.85, we assign the higher

TABLE VIII. Configuration interaction with $3pnd_{\text{PRHF}}$ and $3s3p^3$ for $^1D^o$ series. [a]

Configurations $3s^2 3pnd_{\text{PRHF}}$ and $3s3p^3$
Dimension of CI 12
Matrix element for the first five members of PRHF + PT [b]

| | $3d_{\text{PRHF}}$ | $4d_{\text{PRHF}}$ | $5d_{\text{PRHF}}$ | $6d_{\text{PRHF}}$ | $7d_{\text{PRHF}}$ |
|---|---|---|---|---|---|
| Diagonal | −0.2126 [c] | −0.1820 | −0.1683 | −0.1611 | −0.1566 |
| Off diagonal | 0.0383 | 0.0249 | 0.0173 | −0.0127 | −0.0089 |

| Solution | Total energy (a.u.) | Relative energy to $^2P^o$ (eV) PRHF | PRHF + PT | Expt. |
|---|---|---|---|---|
| 1 | −288.6495 | −1.821 | −2.087 | −2.305 |
| 2 | −288.6133 | −0.990 | −1.103 | −1.170 |
| 3 | −288.5974 | −0.616 | −0.671 | −0.699 |
| 4 | −288.5892 | −0.419 | −0.448 | −0.469 |
| 5 | −288.5843 | −0.298 | −0.313 | −0.339 |
| · | · | · | · | · |
| · | · | · | · | · |
| · | · | · | · | · |
| 9 | −288.5190 | 2.203 | 1.462 | ··· |
| 10 | −288.4009 | 10.020 | 4.675 | ··· |

Weight of configurations (%)

| Solution | The largest configuration in $3pnd_{\text{PRHF}}$ and its weight | $3s3p^3$ | Others |
|---|---|---|---|
| 1 | $3p3d$... 89.04 | 5.83 | 5.13 |
| 2 | $3p4d$... 87.26 | 2.43 | 10.30 |
| 3 | $3p5d$... 87.50 | 1.20 | 11.30 |
| 4 | $3p6d$... 88.88 | 0.65 | 10.47 |
| 5 | $3p7d$... 91.84 | 0.35 | 7.81 |
| · | · | · | · |
| · | · | · | · |
| · | · | · | · |
| 9 | $3p11d$... 71.69 | 16.00 | 12.31 |
| 10 | $3p11d$... 24.54 | 60.88 | 14.58 |

Mean value of $r$ by $nd_{\text{PRHF}}$ and by $d$-type NO of PRHF + PT (a.u.).

| Solution | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| PRHF | 7.80 | 17.41 | 30.05 | 46.40 | 72.14 |
| PRHF + PT | 6.28 | 15.54 | 27.69 | 44.07 | 69.60 |

[a] The $1s$, $2s$, $3s$, $2p$, and $3p$ orbitals are the RHF orbitals for $(3p3d)\ ^3D^o$. The $nd$ orbitals are determined by CI with the configurations $(3pnd)\ ^1D^o$, and they are denoted by $nd_{\text{PRHF}}$.

[b] The value of the diagonal element is expressed by the difference from $3s3p^3$. The energy of the term is −288.4271 a.u. Note that the position of $3s3p^3$ is pushed up by 0.0390 a.u. compared with the RHF value (see Table II), and this $3s3p^3$ situated above the ionized level by 3.96 eV. The off-diagonal element is $\langle 3pnd_{\text{PRHF}} | H | 3s3p^3 \rangle$.

[c] The value is higher than the value given in Table II by 0.0004 a.u. (RHF: −288.6401; PRHF: −288.6397).

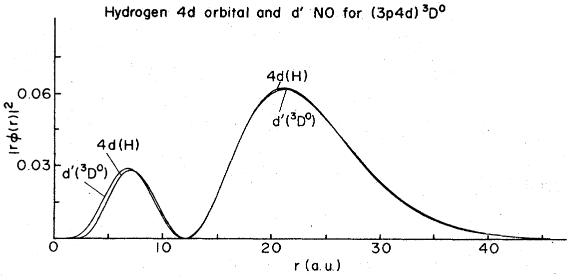

FIG. 3. Radial charge distributions of the hydrogen $4d$ orbital and $d'$ NO of $(3p4d)\ ^3D^o$.

states as $(3pnd,\ n=3-7)\,^3D^o$. It is found that the shapes of $d''$ orbitals are close to $d'$ NO for $^2P^o$. They are the correlating orbitals for the ion core and $3s3p^3$.

The weights of $\sum 3p^3nd$ and $\sum' 3s3p3dnd$ increase and approach to those of the ionized state as the state becomes higher. They express the correlation effects of the ion core.

### B. $^1D^0$ series and its perturber

The PRHF and PRHF+PT calculations are performed. The results are given in Table VIII. The contributions of $3s3p^3$ in the PRHF+PT wave functions are small in comparison with those of the $^3D^o$ series. Nevertheless we find that the relative energies to $^2P^o$ of the PRHF+PT calculation are much improved and that the small contribution of $3s3p^3$ gives rise to a considerable mixing of $3pnd_{\mathrm{PRHF}}$ configurations. The absolute value of the matrix element between $3pnd_{\mathrm{PRHF}}$ and $3s3p^3$ slowly decreases with the increase in the principal quantum number $n$. The effect of $(3s3p^3)\,^1D^o$ can be expected to extend to higher members of the Rydberg series. The term $(3s3p^3)\,^1D^o$, which is above the ionized state by ~4 eV (see footnote b in Table VIII), act as a strong perturber.

Radziemski and Andrew[4] showed by their calculation that $(3s3p^3)\,^1D^o$ is above the ionized level, whereas Brown, Tilford, Tousey, and Ginter[9] reported that $(3s3p^3)\,^1D^o$ probably lies below the ionized level. Table VIII shows that the state, which lies above $^2P^o$ by 4.68 eV, mainly consists of $(3s3p^3)\,^1D^o$. The result is in accord with that of Radziemski and Andrew.

The configuration $3s3p^3$ is valencelike and the electronic correlation is probably greater than those of the ion core.

TABLE IX. Reference functions and results for $^1D^o$ series.

| | | | |
|---|---|---|---|
| Reference functions | | $3s^23pnd$, $n=3-13$<br>$3s3p^3$<br>$3s3p^2np$, $n=4-7$ | |
| Dimension of CI | | 606 | |
| | | Relative energy to $^2P^o$ (eV) | |
| Solution | Total energy (a.u.) | CI | Expt. [a] |
| 1 | −288.7185 | −2.272 | −2.305 |
| 2 | −288.6775 | −1.156 | −1.170 |
| 3 | −288.6606 | −0.696 | −0.699 |
| 4 | −288.6520 | −0.462 | −0.469 |
| 5 | −288.6468 | −0.321 | −0.339 |
| • | • | • | • |
| • | • | • | • |
| • | • | • | • |
| $3s^23p$ | −288.6350 | 0.0 | 0.0 |
| • | • | • | • |
| • | • | • | • |
| • | • | • | • |
| 9 | −288.5949 | 1.103 | ⋯ |
| 10 | −288.5226 | 3.059 | ⋯ |

[a] See Ref. 10.

The correlation effect may bring the position of $3s3p^3$ below the ionized state $^2P^o$. Therefore we have performed a rather extensive CI calculation. The reference functions are $3s3p^3$, $3s3p^2np$ $(n=4-7)$, and $3s^23pnd$ $(n=3-13)$. The methods of the calculation are the same as those of the $^3D^o$ series. The dimension of CI is 606. The total energies and the energies relative to $^2P^o$ are given in Table IX. The first eight solutions are found below the ionized state, and they have a main configuration of $\sum 3s^23pnd$. The ninth and tenth solutions are situated at 1.10 and 3.06 eV above $^2P^o$. The sums of the contributions from $3s3p^3$ and $\sum 3s3p^2np$ are 27.6% and 44.5%, for the respective solutions (see the first part of Table X). We did not find a state in which $3s3p^3$ is a leading term below $^2P^o$. We feel that any further inclusion of the correlation effect does not bring the position of the state, where $3s3p^3$ is predominant, below the ionized state.

The relative energies with respect to $^2P^o$ for the first five solutions of 606-dimensional CI were already given in Table IX. The agreements between the calculation and experiment are reasonably good.

### C. $^3F^o$ and $^1F^o$ Rydberg series

The total energies and the relative energies with respect to $^2P^o$ by the PRHF and extensive CI calculations are collected in Tables XI and XII together with the experimental term energies. The differences between the PRHF and experimental values for $^3F^o$ and $^1F^o$ are less than 0.19 and 0.10 eV, respectively. The agreements of the PRHF results with experiment for the two series are as good as or sometimes better than those of the PRHF+PT results for the $^3D^o$ and $^1D^o$ series. This implies that the $^3F^o$ and $^1F^o$ series are pure Ryd-

TABLE X. Important configurations and results of NO analysis for ${}^1D^o$ series.

(a) Important configurations (%)

| Solutions / CSF's | $\sum 3s^23pnd$ | $\sum 3p^3nd$ | $\sum' 3s3p3dnd$ [a] | $\sum 3s3d^2np$ | $3s3p^3$ [b] |
|---|---|---|---|---|---|
| 1 | 85.47 | 2.79 | 1.42 | 0.82 | 7.70 |
| 2 | 90.45 | 2.74 | 2.28 | 0.17 | 3.28 |
| 3 | 92.07 | 2.71 | 2.45 | 0.06 | 1.76 |
| 4 | 92.85 | 2.69 | 2.51 | 0.03 | 1.02 |
| 5 | 93.26 | 2.69 | 2.53 | 0.02 | 0.63 |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| $3s^23p$ | 93.92 | 2.66 | 2.57 | ... | ... |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| 9 | 65.79 | 3.32 | 1.74 | 0.25 | 27.55 |
| 10 | 47.65 | 3.33 | 1.02 | 1.59 | 44.50 |

(b) Occupation numbers for each NO

| Solution, designation / NO | $3s_{NO}$ | $3p_{NO}$ | $d'$ | $d''$ | $\langle r_{d'} \rangle$ [c] (a.u.) |
|---|---|---|---|---|---|
| 1 ... $3p3d$ | 1.825 | 1.209 | 0.923 | 0.023 | 5.659 |
| 2 ... $3p4d$ | 1.872 | 1.119 | 0.965 | 0.031 | 14.827 |
| 3 ... $3p5d$ | 1.888 | 1.088 | 0.981 | 0.032 | 26.740 |
| 4 ... $3p6d$ | 1.896 | 1.073 | 0.989 | 0.032 | 42.862 |
| 5 ... $3p7d$ | 1.900 | 1.067 | 0.993 | 0.032 | 67.359 |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| $3s^23p$ | 1.907 | 1.053 | 0.032 | ... | ... |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| · | · | · | · | · | · |
| 9 ... ? | 1.621 | 1.595 | 0.700 | 0.045 | 17.886 |
| 10 ... ? | 1.436 | 1.911 | 0.534 | 0.041 | 8.772 |

[a] See footnote a in Table VII.

[b] The contribution from $\sum' 3s3p^2np$ is also included. The weights of $\sum' 3s3p^2np$ are 0.46%, 0.21%, 0.13%, 0.08%, 0.05%, 3.45%, and 10.06% for the respective solutions.

[c] See footnote c in Table VII.

TABLE XI. Results of PRHF and CI for ${}^3F^o$ series. [a]

| | Total energy (a.u.) | | Relative energy to ${}^2P^o$ (eV) | | |
|---|---|---|---|---|---|
| State | PRHF | CI | PRHF | CI | Expt. [b] |
| $3p3d$ | −288.6384 | −288.7051 | −1.786 | −1.907 | −1.980 |
| $3p4d$ | −288.6091 | −288.6729 | −0.990 | −1.029 | −1.048 |
| $3p5d$ | −288.5955 | −288.6584 | −0.617 | −0.635 | −0.643 |
| $3p6d$ | −288.5882 | −288.6508 | −0.420 | −0.429 | −0.434 |
| $3p7d$ | −288.5837 | −288.6462 | −0.299 | −0.303 | −0.312 |
| $3s^23p$ | −288.5728 | −288.6350 | 0.0 | 0.0 | 0.0 |

[a] The reference functions are ($3s^23pnd$, $n=3$–13) ${}^3F^o$ and ($3s3p^2np$, $n=4$–7) ${}^3F^o$ and the number of dimension for CI is 671.

[b] See Ref. 10.

TABLE XII. Results of PRHF and CI for ${}^1F^o$ series. [a]

| | Total energy (a.u.) | | Relative energy to ${}^2P^o$ (eV) | | |
|---|---|---|---|---|---|
| State | PRHF | CI | PRHF | CI | Expt. [b] |
| $3p3d$ | −288.6265 | −288.6909 | −1.463 | −1.521 | −1.559 |
| $3p4d$ | −288.6032 | −288.6665 | −0.828 | −0.855 | −0.874 |
| $3p5d$ | −288.5923 | −288.6551 | −0.531 | −0.546 | −0.560 |
| $3p6d$ | −288.5862 | −288.6489 | −0.367 | −0.377 | −0.389 |
| $3p7d$ | −288.5826 | −288.6452 | −0.268 | −0.275 | −0.285 |
| $3s^23p$ | −288.5728 | −288.6350 | 0.0 | 0.0 | 0.0 |

[a] The reference functions are ($3s^23pnd$, $n=3$–13) ${}^1F^o$ and ($3s3p^2np$, $n=4$–7) ${}^1F^o$ and the number of dimension for CI is 526.

[b] See Ref. 10.

berg series.

In fact, the weights of the main configuration $\sum 3s^2 3pnd$ are around 93.5% in the wave functions of the extensive CI calculation for the $^1F^o$ and $^3F^o$ series, and the occupation numbers of $d'$ orbitals (Rydberg ones) are always nearly 1 (occupation number $\geq 0.997$). Moreover the shapes of the resulted $3s_{\mathrm{NO}}$, $3p_{\mathrm{NO}}$, and the correlating $d$-type NO and the occupation numbers of these orbitals in each solution are close to those of the ionized state $^2P^o$ (occupation numbers: $3s_{\mathrm{NO}}$ 1.904–1.907 for $^3F^o$, 1.905–1.907 for $^1F^o$ and 1.907 for $^2P^o$; $3p_{\mathrm{NO}}$ 1.056–1.053 for $^3F^o$, 1.054–1053 for $^1F^o$ and 1.053 for $^2P^o$; $d''$ 0.026–0.031 for $^3F^o$, 0.031 for $^1F^o$ and $d'$ 0.032 for $^2P^o$). Tables XI and XII show that the results obtained by the extensive CI calculations are satisfactory.

## III. QUANTUM DEFECTS

The quantum defect ($\mu$) and the energy lowering from the ionized level ($\Delta E$) are related by

$$\Delta E = R_y/(n-\mu)^2 . \tag{3}$$

The calculated and experimental $\mu$'s for $^1F^o$ and $^3F^o$ are given in Fig. 4. The experimental results are denoted by $\mu_{\mathrm{EXPTL}}$. The quantities $\mu_{\mathrm{PRHF}}$ agree well with $\mu_{\mathrm{EXPTL}}$. The error is at most ~0.15. The quantum defects, $\mu_{\mathrm{PRHF}}$'s are smaller than $\mu_{\mathrm{EXPTL}}$'s. This indicates that the wave function obtained by PRHF is broader than the true one. It is a general tendency in RHF-level wave functions. The diffuseness of the wave function is reduced in the CI calculation as is shown in the figure.

The small decreases in $\mu_{\mathrm{PRHF}}$ and $\mu_{\mathrm{CI}}$ at $(3p6d)$ $^1F^o$ will be attributed partly to the deficiency of the $d$-type orbitals for the series.

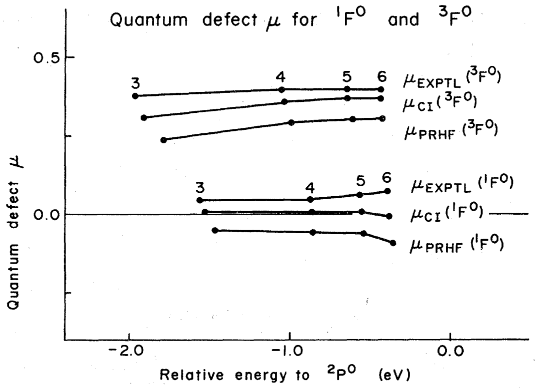

FIG. 4. Quantum defects $\mu$ for $^1F^o$ and $^3F^o$. The suffix CI indicates the 526- and 671-dimensional CI's for $^1F^o$ and $^3F^o$, respectively.

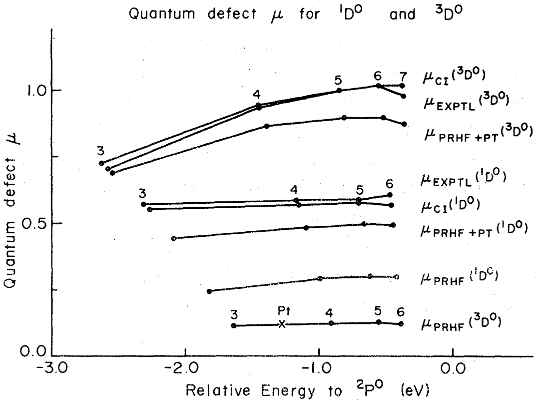

FIG. 5. Quantum defects $\mu$ for $^1D^o$ and $^3D^o$. The suffix CI indicates the 606- and 838-dimensional CI's for $^1D^o$ and $^3D^o$, respectively. The symbol PT indicates $(3s3p^3)^3D^o$.

The quantum defects for $^1D^o$ and $^3D^o$ are given in Fig. 5. A comparison of $\mu_{\mathrm{PRHF}}$ with $\mu_{\mathrm{PRHF+PT}}$ of the $^1D^o$ series clearly shows the large effect of the perturber. It should be noted that the PRHF calculation gives almost the same quantum defects for the $^3F^o$ and $^1D^o$ series and the PRHF+ PT calculation resolves these near degeneracies. For the $^3D^o$ series, we label all the levels by a running quantum numer $n$,[20] and take $n = 3$ for the lowest $^3D^o$ state. Reflecting the existence of the perturber, $\mu$'s for PRHF+ PT, CI and experiment increase as the quantum numer $n$ increases. The CI calculation almost reproduces the experimental results.

## IV. CONCLUDING REMARKS

We have performed CI calculations on the first five or six members of the $^1D^o$, $^3D^o$, $^1F^o$, and $^3F^o$ Rydberg series of the silicon atom. The magnetic terms are not included in the Hamiltonian. The calculated energies relative to the ionized level, $(3s^2 3p)\,^2P^o$, agree well with the experimental values.

Our rather large CI calculation shows that the weight of $3s3p^3$ exceeds 55% and that of the Rydberg-type configurations is 39% in the first $^3D^o$ state. The configurations $3s3p^3$ and $3pnd$ are so strongly mixed and perturbed with each other, that it will not be meaningful to designate the state by a single term. If it is necessary for the sake of convenience, the labeling for the first state is $3s3p^3$ and that for the higher states is $3pnd$, where $n$ begins with 3.

It is also found that the $^1D^o$ series is strongly perturbed by $3s3p^3$. For $^3D^o$, at any levels of approximation, a state which has the leading configuration of $3s3p^3$ is found below the ionized state, whereas a corresponding state is not found below the ionized level for ${}^1D^o$.

The common role of the strong perturber is as follows. The perturber mixes the unperturbed Rydgerg configurations which have zero matrix elements among them and it considerably deforms Rydberg configurations from the unperturbed ones, even though the contribution of the perturber itself is small in the wave functions.

The present result agrees with the conclusion of Radziemski and Andrew[4] as to the position of $(3s3p^3)\,{}^1D^o$ relative to ${}^2P^o$.

The ${}^1F^o$ and ${}^3F^o$ series are found to be pure Rydberg series.

## ACKNOWLEDGMENTS

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## APPENDIX: CONFIGURATION-INTERACTION CALCULATIONS FOR THE IONIZED STATE AND THE GROUND STATE

In this Appendix, we discuss the ground state ${}^3P$ and the ionized state ${}^2P^o$ to which all the Rydberg series under consideration converge. The correlation energies for both states will be investigated.

Iterative-natural-orbital–configuration-interaction (INO-CI) calculations are performed for the two states. The atomic orbitals for CI are common for the two states and are given in Table XIII. The correlation effects of the $M$-shell electrons are taken into account by exciting one or two electrons from the reference function ($3s^23p$ for ${}^2P^o$ and $3s^23p^2$ for ${}^3P$). For two electron excitations, the angular momentum conservation of the excited pair is taken into account. For example, let us consider $3s$-$3p$ pair excitations. Excitations of $(3s3p)^{1,3}P \rightarrow (\alpha k\alpha' k')^{1,3}P$ are taken into account, but excitations of $(3s3p)^{1,3}P \rightarrow (\alpha k\alpha' k')^{1,3}L$ $(L \neq P)$ are not included in CI. The dimension of CI amounts to 498 and 734 for ${}^2P^o$ and ${}^3P$, respectively. The results for ${}^2P^o$ and ${}^3P$ are given in Tables XIV and XV, respectively.

TABLE XIII. Atomic orbitals for CI of ${}^2P^o$ and ${}^3P$.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $s$ type | $1s_{HF}-8s_{HF}$ $[(3p3d)\ {}^3D^o]$ | | | | $3s$ | 0.79 | $3s$ | 0.53 |
| | $3s$ | 0.35 | $3s$ | 0.23 | $3s$ | 0.16 | | |
| $p$ type | $2p_{HF}-8p_{HF}$ $[(3p3d)\ {}^3D^o]$ | | | | | | | |
| $d$ type | Same as those given in Table I. | | | | | | | |
| $f$ type | $4f$ | 2.20 | $4f$ | 1.27 | $4f$ | 0.73 | $4f$ | 0.42 |

TABLE XIV. Results of CI for ${}^2P^o$.

| | |
|---|---|
| Reference function | $3s^23p$ |
| Dimension of CI | 498 |
| Total energy (CI) | −288.6363 a.u. |
| Total energy (RHF) | −288.5728 a.u. |
| Correlation energy | −1.728 eV |

Important configuration $\{|c| \geq 0.01\}$

| | Configurations | Number of CSF's | Weight (%) | |
|---|---|---|---|---|
| Main | $3s^23p$ | 1 | 93.97 | |
| Reorganization | $3s^24p$ | 1 | 0.02 | |
| $s$–$s$ correlation | $4s^23p$ | 1 | 0.05 | 2.91 |
| | $3p^3$ | 1 | 2.62 | |
| | $(4p^2)^1S3p$ | 1 | 0.03 | |
| | $(3d^2)^1S3p$ | 1 | 0.20 | |
| | $(4f^2)^1S3p$ | 1 | 0.01 | |
| $s$–$p$ correlation | $4p4s3s$ [a] | 2 | 0.11 | 3.06 |
| | $4p3p^2$ [a] | 3 | 0.26 | |
| | $3d3p3s$ [a] | 2 | 2.54 | |
| | $3d4p3s$ [a] | 2 | 0.08 | |
| | $4f3d3s$ [a] | 2 | 0.07 | |

[a] The sum of the weights of all CSF's is given.

We consider how much of the $M$-$M$ shell correlation energy is taken into account by the present CI. The sum of the $K$-$M$, $L$-$M$, and $M$-$M$ shell correlation energies is estimated to be −0.087 a.u. for silicon ${}^2P^o$ by Clementi[21] from the experimental data. A value of −0.007 a.u. is given by Clementi[21] for the sum of $K$-$M$ and $L$-$M$ correlation energies of Na($K^2L^83s$). Meyer and Losmos[22] have shown that the $L$-$M$ shell correlation energy per one $M$-shell electron is almost constant from Na to Al($K^2L^83s^23p$) (−0.005 to −0.006 a.u.). Since

TABLE XV. Results of CI for ${}^3P$ and ionization potential.

| | |
|---|---|
| Reference | $3s^23p^2$ |
| Dimension of CI | 734 |
| Total energy (CI) | −288.9293 a.u. |
| Total energy (RHF) | −288.8540 a.u. |
| Correlation energy | −2.049 eV |

Ionization potential

| | |
|---|---|
| RHF | 7.652 eV |
| CI | 7.973 |
| Expt. (BS) [a] | 8.175 |

[a] See Ref. 10.

the $L$-$M$ shell correlation energy is much greater than the $K$-$M$ shell correlation energy, we adopt $-0.006$ to $-0.007$ a.u. for the sum of the $K$-$M$ and $L$-$M$ shell correlation energies per one electron for silicon. By the use of these values, the experimental $M$-$M$ shell correlation energy for $^2P^o$ is estimated to be $-1.80$ to $-1.88$ eV. In the present CI, the $M$-$M$ shell correlation energy is calculated to be $-1.73$ eV for $^2P^o$ (see Table XIV), which corresponds to (92–96)% of the estimated experimental value. The $M$-$M$ shell correlation energy for $^3P$ is estimated to be $-2.10$ to $-2.20$ eV. The calculated value is $-2.05$ eV (see Table XV) which covers (93–98)% of the estimated experimental value. The present CI, thus, sufficiently describes the correlation effects among the $M$-shell electrons.

The ionization potential $P$ of the CI calculation is 7.97 eV, whereas the experimental value is 8.18 eV. The difference between the two is 0.21 eV ($=0.007$ a.u.), which is almost equal to the sum of the $K$-$M$ and $L$-$M$ correlation energies per one $M$-shell electron adopted for silicon. It is reasonable because the following relation holds for

$$P_{\mathrm{EXPTL}} - P_{\mathrm{CI}} \sim E_{\mathrm{corr}}^{\mathrm{K\text{-}M\ and\ L\text{-}M}}(^2P^o) - E_{\mathrm{corr}}^{\mathrm{K\text{-}M\ and\ L\text{-}M}}(^3P)\,, \tag{A1}$$

where we assume that the correlation energies among the inner shell electrons are equal in the two states and that the $M$-$M$ shell correlation effects are fully taken into account in the CI calculations.

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[1] A. Fowler, Proc. R. Soc. A 123, 422 (1929).

[2] C. C. Kiess, J. Res. Natl. Bur. Stand. 21, 185 (1938).

[3] *Atomic Energy Levels*, U. S. Natl. Bur. Stand. Circ. No. 467, edited by C. E. Moore (U. S. GPO, Washington, D. C. 1949), Vol 1, p. 144.

[4] L. J. Radziemski, Jr. and K. L. Andrew, J. Opt. Soc. Am. 55, 474 (1965).

[5] U. Litzen, Ark. Fys. 31, 453 (1966).

[6] V. Kaufman, L. J. Radziemski, Jr., and K. L. Andrew, J. Opt. Soc. Am. 56, 911 (1966).

[7] L. J. Radziemski, Jr., V. Kaufman, and U. Litzen, J. Opt. Soc. Am. 57, 336 (1967).

[8] D. L. Lambert and B. Warner, Mon. Not. R. Astr. Soc. 138, 213 (1968).

[9] C. M. Brown, S. G. Tilford, R. Tousey, and M. L. Ginter, J. Opt. Soc. Am. 64, 1665 (1974).

[10] S. Bashkin and J. O. Stoner, Jr., *Atomic Energy Levels and Grotrian Diagrams* (North-Holland, Amsterdam, 1975), Vol 1, p. 490.

[11] B. Warner, Mon. Not. R. Astr. Soc. 139, 1 (1968). The values of the coefficients are not given in the paper of Radziemski and Andrew (Ref. 5) but are given in this paper.

[12] *Atomic Energy Levels*, U. S. Natl. Bur. Stand. Circ. No. 467, edited by C. E. Moore (U. S. GPO, Washington, D. C., 1958), Vol. 3, p. 240.

[13] C. E. Moore, Selected Tables of Atomic Spectra, *Atomic Energy Levels and Multiplet Tables Si I*, NSRDS-NBS No. 3.

[14] C. E. Moore, C. M. Brown, G. D. Sadlin, S. G. Tilford, and R. Tousey, Astrophys. J. Suppl. 33, 393 (1977).

[15] A. W. Weiss, Phys. Rev. A 9, 1524 (1974).

[16] C. C. J. Roothaan and P. S. Bagus, *Method in Computational Physics* (Academic, New York, 1963), Vol. 2, p. 47.

[17] E. Clementi, IBM J. Res. Develop. Suppl. 9, 2 (1965).

[18] The present author and Fukashi Sasaki have developed a general CI program, called ATOMIC CI PROGRAM. The formulation of energy expressions has been given by Fukashi Sasaki: F. Sasaki, Int. J. Quantum Chem. 8, 605 (1974).

[19] We have not shown a list of configurations to save space. It is available upon request.

[20] M. J. Seaton, Proc. Phys. Soc. 88, 815 (1966).

[21] E. Clementi, J. Chem. Phys. 39, 175 (1963).

[22] W. Meyer and P. Rosmos, J. Chem. Phys. 63, 2356 (1975).