Theoretical Analysis on $3dnl\,J=1^e-5^e$ Autoionizing Levels in Ca

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Previous studies on the even parity $3dnl\,J=1-5$ autoionizing levels of calcium have been critically evaluated. These levels have been studied within the framework of the weakest bound electron potential model theory. 30 $3dnl$ series are treated and the results are listed here. In these calculations, the jj coupling scheme is used. It is remarkable that the perturbation approach that has been emphasized in our calculations so as to adequately consider the correlation between the two excited electrons is more important than in the case of singly excited states. Compared with the experimental results and the values from other theoretical methods, the present results are in concurrence with the experimental data, and showed comparative accuracy with other methods. Some levels, which have not been reported previously, are predicted here. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1707042]

Key words: calcium; critical evaluation; doubly excited states; WBEPM theory

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1. Introduction

The autoionization state of an atom plays an important role in many aspects. It relates to the research of astrophysics and controlled fusion, and has been proposed as an efficient way to the realization of vacuum ultraviolet laser. The study of autoionization is of great significance in the research of electron correlation, the many-body problem, and so on. Considerable interest has been devoted to doubly excited atoms by various scientists over the past years. The alkaline earth atoms are the most ideal atomic systems to study doubly excited autoionizing states, both experimentally and theoretically. Their two s valence electrons can be easily excited using a conventional dye laser system, while the closed inner shells are more difficult to excite.

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TABLE 1. Parameters obtained from Eqs. (6) and (9) of series $3dnl$ of Ca[a]

	J	a_1	a_2	a_3	a_4	b_1	b_2	b_3	b_4
$3d_{3/2}ns_{1/2}$	1	2.229 14	−44.655	6 183.44	−453 180	−0.002 16	0.000 01		
$3d_{3/2}ns_{1/2}$	2	2.304 20	−22.193	3 881.08	−161 340				
$3d_{5/2}ns_{1/2}$	2	2.438 93	−137.90	29 395.1	−1.708E6				
$3d_{5/2}ns_{1/2}$	3	2.254 34	13.567 63	−1 808.96	58 610.94				
$3d_{3/2}nd_{3/2}$	0	0.643 63	−11.821 41	296.941 9	−2 625.723				
$3d_{5/2}nd_{5/2}$	0	0.614 81	−18.365 88	772.518 6	−15 019.16				
$3d_{5/2}nd_{5/2}$	1	0.887 43	−5.362 36	260.903 6	−3 497.415	0.000 07	0.000 01		
$3d_{3/2}nd_{3/2}$	1	0.830 97	8.084 67	−392.484	5 640.048	0.000 05	0.00 005		
$3d_{5/2}nd_{3/2}$	1	0.980 81	−41.751 5	1 383.681	−16 402.0	0.000 00	0.000 00		
$3d_{3/2}nd_{5/2}$	1	0.992 23	−41.618 33	4 118.194	−91 096.26	0.002 26	0.000 34	0.000 05	0.000 01
$3d_{3/2}nd_{3/2}$	2	0.577 47	−8.669 73	506.533 5	−10 087.85				
$3d_{5/2}nd_{5/2}$	2	0.617 02	−8.901 21	239.844 4	−2 327.42				
$3d_{5/2}nd_{3/2}$	2	0.973 81	−42.615 02	1 486.888	−16 750.08	0.000 36	0.000 01		
$3d_{3/2}nd_{5/2}$	2	0.964 14	−47.948 95	3 487.218	−63 110.98	0.000 78	0.000 44	−0.000 29	
$3d_{5/2}nd_{5/2}$	3	0.750 27	19.627 10	−872.184	11 823.47				
$3d_{3/2}nd_{3/2}$	3	0.845 49	0.872 33	−2.076 35	19.423 6				
$3d_{5/2}nd_{3/2}$	3	−0.955 96	779.216	−111 124.4	4 824E6				
$3d_{3/2}nd_{5/2}$	3	0.501 68	38.018 5	−1 412.584	17 366.91				
$3d_{5/2}nd_{3/2}$	4	0.750 50	−16.864 70	−30.288 1	7 991.917				
$3d_{3/2}nd_{5/2}$	4	0.356 08	59.876 87	−2 508.993	33 426.72	0.000 07	0.000 02		
$3d_{5/2}nd_{5/2}$	4	0.555 90	−16.621 12	1 191.236	−21 375.39				
$3d_{5/2}nd_{5/2}$	5	0.848 26	0.045 13	14.737 88	−176.665 1				
$3d_{5/2}ng_{7/2}$	1	0.021 93	−0.653 07	7.049 93	−48.183 48				
$3d_{5/2}ng_{9/2}$	2	0.016 34	0.030 66	−20.387 4	298.293 4				
$3d_{5/2}ng_{7/2}$	2	0.028 54	−1.162 78	27.967 21	−284.791 3				
$3d_{3/2}ng_{7/2}$	2	0.022 61	−0.624 07	7.634 55	−43.596 00				
$3d_{3/2}ng_{7/2}$	3	0.026 07	−1.178 30	48.464 18	−664.713 9				
$3d_{3/2}ng_{9/2}$	3	0.021 35	−0.380 22	−4.372 10	124.077 1				
$3d_{5/2}ng_{9/2}$	3	0.028 59	−1.207 17	30.707 32	−326.506 4				
$3d_{5/2}ng_{7/2}$	3	0.026 62	−1.081 37	38.142 78	−486.693 9				

[a]The perturb levels are listed with the corresponding tables of results.

The studies on doubly excited states of calcium trace back to 1960.[1] The earlier research was focused on the odd parity $J=1$ states, which can be obtained in absorption from the ground state. Later, a wealth of data of both odd parity and even parity was obtained, being made possible by the development of laser techniques. A review of the correlated work done on this topic has been written by Aymar *et al.*[2] in 1996.

Researchers began to investigate the even parity $3dnl$ series of calcium in 1991. Although theoretical methods were employed to obtain the energy values of some low-lying odd parity autoionizing levels, to our knowledge, only two methods have been reported to treat the even parity autoionizing levels:

(1) the combination of eigenchannel R-matrix and multichannel quantum defect theory (MQDT) method which is the most commonly used method; and
(2) the Coulomb Green's function analysis.

Aymar and Telmini[3] studied the $J=0$ and $J=2$ spectra of calcium below $3d_{3/2}$ threshold for $n\leqslant 15$ through a combination of eigenchannel R matrix and MQDT method. This work was followed by Bolovinos *et al.*[4] using two-step laser optogalvanis technique in a Ca DC discharge. They measured the energies of the even $3dnd$ $J=0,2$ and $3dng$ $J=2$ autoionizing states of calcium below 62 500 cm^{-1}, and detected the perturbers of $4p^2\,{}^1S_0$ and $4p5p\,{}^3D_2$. The experimental energies, measured by Bolovinos *et al.*,[4] showed good

TABLE 2. [Ar] $3d_{3/2}ns_{1/2}$ $J=1$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
11	61 501.3	61 501.3	61 506.8	40		62 878.8	
12	61 802.0	61 802.0	61 805.4	41		62 882.7	
13	62 001.7	62 001.5	62 003.4	42		62 886.4	
14	62 156.0	62 156.5	62 158.4	43		62 889.8	
15	62 277.8	62 277.2	62 278.4	44		62 892.9	
16	62 372.3	62 372.5	62 373.4	45		62 895.9	
17	62 449.0	62 449.1	62 449.8	46		62 898.6	
18	62 511.6	62 511.5	62 512.2	47		62 901.1	
19	62 563.2	62 563.1	62 563.6	48		62 903.5	
20	62 606.0	62 606.1	62 606.7	49		62 905.7	
21	62 642.3	62 642.4	62 642.8	50		62 907.8	
22		62 673.4		51		62 909.8	
23	62 700.2	62 700.0	62 700.6	52		62 911.6	
24	62 723.4	62 723.0	62 723.6	53		62 913.4	
25	62 743.3	62 743.0	62 743.6	54		62 915.0	
26	62 761.3	62 760.6	62 761.1	55		62 916.6	
27	62 776.5	62 776.1	62 776.6	56		62 918.0	
28	62 790.1	62 789.8	62 790.3	57		62 919.4	
29	62 802.2	62 802.0	62 802.4	58		62 920.7	
30	62 813.3	62 812.9	62 813.3	59		62 922.0	
31	62 823.0	62 822.7	62 823.1	60		62 923.1	
32	62 831.9	62 831.5	62 831.9	65		62 928.2	
33	62 840.0	62 839.5	62 839.9	70		62 932.2	
34	62 847.1	62 846.8	62 847.1	75		62 935.4	
35	62 853.7	62 853.3	62 853.6	80		62 937.9	
36	62 859.7	62 859.3	62 859.7	85		62 940.1	
37		62 864.8		90		62 941.9	
38		62 869.9		95		62 943.4	
39		62 874.5		100		62 944.6	

[a]The perturb levels are: $4p5p\ ^1P_1$ (61 132.1 cm^{-1}) and $^3D_1$ (61 728.9 cm^{-1}).
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 3. [Ar] $3d_{3/2}ns_{1/2}$ $J=2$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
11		61 500.8		40		62 879.0	
12		61 786.8		41		62 882.9	
13		61 997.9		42		62 886.6	
14	62 156.4	62 156.4	61 157.1	43		62 889.9	
15		62 278.2		44		62 893.1	
16		62 373.9		45		62 896.0	
17	62 450.5	62 450.5	62 449.6	46		62 898.7	
18	62 512.8	62 512.8	62 511.8	47		62 901.2	
19		62 564.2		48		62 903.6	
20		62 607.2		49		62 905.8	
21		62 643.4		50		62 907.9	
22		62 674.2		51		62 909.9	
23		62 700.8		52		62 911.7	
24		62 723.7		53		62 913.5	
25		62 743.7		54		62 915.1	
26		62 761.2	62 761.2	55		62 916.6	
27		62 776.6		56		62 918.1	
28	62 790.2	62 790.3	62 790.3	57		62 919.5	
29		62 802.4		58		62 920.8	
30		62 813.3		59		62 922.0	
31	62 823.2	62 823.1	62 823.0	60		62 923.2	
32		62 831.9		65		62 928.2	
33		62 839.8		70		62 932.2	
34	62 847.0	62 847.0	62 847.2	75		62 935.4	
35		62 853.6		80		62 938.0	
36	62 859.9	62 859.6	62 859.7	85		62 940.1	
37		62 865.1		90		62 941.9	
38		62 870.1		95		62 943.4	
39		62 874.7		100		62 944.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

agreement with the experimental and theoretical results reported in Aymar and Talmini.[3] Most of the deviations between the experimental and theoretical results are less than 10 cm^{-1} for $n \geqslant 8$, however the deviations are relatively large for $n<8$.

Assimopoulos *et al.*[5] presented additional experimental and theoretical results from the same method for $J=0^e$, 1^e, and 2^e autoionizing spectra below $3d$ threshold of calcium. The spectra were explored by a two-step laser excitation from the $3d4s$ metastable states through the $3d4p\ ^3P_{0,1,2}$ intermediate states. Several perturbers were assigned to $4p^2$ and $4p5p$ configurations. The experimental data were measured with an accuracy of no more than 0.2 cm^{-1}. In this paper,[5] the experimental data and theoretical energy levels were in good agreement.

Subsequently the same authors reported results for the $J=3^e$ series[6] in the same year (1994), and the results for $3dnd$ $J=4$, 5 series[7] in 1998. In the former paper, the perturber was assigned to $4p5p\ ^3D_3$. It was found that there was strong mixing between $3d_{3/2}nd_{5/2}$ and $3d_{5/2}nd_{3/2}$ for both the $J=3$ and $J=4$ cases. The results of the theoretical method mentioned above, namely, the combination of eigenchannel R-matrix and MQDT, are very accurate in highly excited states concerning the deviations with experimental

TABLE 4. $[\mathrm{Ar}]\,3d_{5/2}ns_{1/2}\,J=2$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
12	61 862.0	61 862.0	61 858.4	41		62 943.3	
13		62 051.2		42		62 947.0	
14		62 210.6		43		62 950.4	
15	62 335.9	62 335.9	62 337.6	44		62 953.5	
16		62 433.9		45		62 956.5	
17		62 511.7		46		62 959.2	
18		62 574.5		47		62 961.7	
19		62 626.0		48		62 964.1	
20		62 668.8		49		62 966.3	
21		62 704.9		50		62 968.4	
22		62 735.5	62 733.8	51		62 970.4	
23		62 761.8	62 760.7	52		62 972.3	
24	62 784.6	62 784.6	62 783.5	53		62 974.0	
25		62 804.4		54		62 975.6	
26		62 821.8		55		62 977.2	
27		62 837.2	62 837.1	56		62 978.7	
28	62 850.8	62 850.8	62 850.7	57		62 980.0	
29		62 862.9	62 863.0	58		62 981.3	
30		62 873.8		59		62 982.6	
31		62 883.5		60		62 983.8	
32		62 892.3		61		62 984.9	
33		62 900.2		62		62 985.9	
34		62 907.4		63		62 987.0	
35		62 914.0		64		62 987.9	
36		62 920.0		65		62 988.8	
37		62 925.5		70		62 992.8	
38		62 930.5		80		62 998.6	
39		62 935.1		90		63 002.5	
40		62 939.4		100		63 005.3	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.* [5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.* [5]

TABLE 5. $[\mathrm{Ar}]\,3d_{5/2}ns_{1/2}\,J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
9	60 566.5	60 566.5	60 577.8	38		62 930.9	
10		61 189.9	61 167.0	39		62 935.5	
11		61 582.6	61 570.6	40		62 939.8	
12	61 831.8	61 859.0	61 838.7	41		62 943.7	
13	62 063.3	62 063.0	62 065.5	42		62 947.3	
14	62 217.5	62 218.0	62 219.2	43		62 950.7	
15		62 338.3		44		62 953.8	
16	62 433.8	62 433.5	62 434.2	45		62 956.8	
17	62 510.1	62 510.1	62 510.1	46		62 959.5	
18	62 572.5	62 572.6	62 572.5	47		62 962.0	
19	62 623.5	62 624.2	62 623.5	48		62 964.4	
20	62 667.2	62 667.3	62 667.2	49		62 966.6	
21	62 703.5	62 703.7	62 703.5	50		62 968.7	
22	62 734.5	62 734.7	62 734.5	51		62 970.6	
23	62 761.5	62 761.3	62 761.5	52		62 972.5	
24	62 784.6	62 784.3	62 784.6	53		62 974.2	
25	62 804.4	62 804.4	62 804.4	54		62 975.8	
26	62 821.6	62 821.9	62 821.6	55		62 977.4	
27		62 837.4		56		62 978.8	
28	62 850.8	62 851.1	62 850.8	57		62 980.2	
29		62 863.3		58		62 981.5	
30	62 874.1	62 874.1	62 874.1	59		62 982.8	
31		62 883.9		60		62 983.9	
32	62 883.9	62 892.7	62 883.9	65		62 989.0	
33	62 892.7	62 900.7	62 892.7	70		62 992.9	
34		62 907.9		75		62 996.1	
35		62 914.4		80		62 998.7	
36		62 920.4		90		63 002.6	
37		62 925.9		100		63 005.4	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

data mainly less than 1 cm^{-1}. The inaccuracy in low excited states is relatively large. For example, in the series $3d_{5/2}nd_{3/2}$, the deviation for $n=5$, 6, 7, and 8 are 99.3, 33.2, 21.8, and 12.1 cm^{-1}, respectively.

Another method, called the Sturmian expansion of the Coulomb Green's function, was applied to analyze the low doubly excited states of alkaline earth atoms[8] including $3dng$ in Ca. The results of Ca are slightly more accurate than those from the R-matrix method. Later, these authors carried out the Coulomb Green's function analysis for polarization effects in autoionization process of alkaline–earth–metal atoms.[9]

The above mentioned studies are those that dealt with the even parity doubly excited states of Ca up to now. Only the MQDT plus R-matrix theory and Coulomb Green's function analysis are employed to investigate the properties of the even parity doubly excited states of Ca, and they have only little overlap. Furthermore, there is still an obvious lack of experimental data. It is necessary to confirm the exiting data, as well as provide for ''missing'' levels (by prediction).

Recently, the weakest bound electron potential model theory (WBEPM theory)[10–22] has been employed to study the singly excited levels of many-valence-electron atoms including Al,[23] rare gas Kr,[24] IVA atoms,[25] and heavy metal IB atoms.[26] After comparing both calculations based on the WBEPM theory and the calculations obtained using other methods against experimental data, it is apparent that the

TABLE 6. [Ar] $3d_{3/2}nd_{3/2}$ $J=0$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	57 611.1	57 611.2	57 691.4	34	62 855.3	62 857.6	62 855.6
6	59 351.6	59 351.1	59 385.8	35	62 863.0	62 863.2	62 862.9
7	60 361.4	60 362.1	60 377.3	36	62 867.1	62 868.4	62 866.9
8	60 998.6	60 998.4	61 006.4	37	62 870.4	62 873.2	62 870.5
9	61 426.7	61 426.4	61 430.6	38	62 876.5	62 877.5	62 876.4
10	61 728.2	61 728.4	61 730.2	39	62 879.8	62 881.6	62 879.7
11	61 948.5	61 949.5	61 949.8	40		62 885.3	
12	62 114.5	62 116.1	62 115.6	41		62 888.8	
13	62 242.9	62 244.8	62 244.3	42		62 892.0	
14	62 345.0	62 346.1	62 346.6	43		62 895.0	
15	62 428.5	62 427.4	62 430.1	44		62 897.8	
16	62 480.8	62 493.5	62 481.9	45		62 900.4	
17	62 539.7	62 547.9	62 540.8	46		62 902.8	
18	62 587.3	62 593.4	62 588.8	47		62 905.1	
19	62 627.8	62 631.6	62 629.5	48		62 907.2	
20	62 663.9	62 664.1	62 664.9	49		62 909.2	
21	62 686.3	62 692.0	62 685.6	50		62 911.1	
22	62 711.8	62 716.1	62 712.4	51		62 912.9	
23	62 734.9	62 737.0	62 735.8	52		62 914.6	
24	62 748.5	62 755.3	62 749.4	53		62 916.1	
25	62 767.5	62 771.5	62 768.2	54		62 917.6	
26	62 784.1	62 785.7	62 784.8	55		62 919.0	
27	62 793.0	62 798.4	62 794.3	60		62 925.0	
28	62 807.5	62 809.7	62 807.7	65		62 929.7	
29	62 814.9	62 819.8	62 815.2	70		62 933.3	
30	62 826.9	62 828.9	62 826.6	75		62 936.3	
31	62 836.9	62 837.2	62 836.9	80		62 938.7	
32	62 842.7	62 844.6	62 842.4	90		62 942.4	
33	62 850.9	62 851.4	62 850.9	100		62 945.0	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 7. [Ar] $3d_{5/2}nd_{5/2}$ $J=0$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 535	58 726.7	58 762	34		62 918.5	
6	59 594.0	59 594.1	59 702.7	35		62 924.1	
7	60 481.6	60 481.2	60 518.8	36		62 929.3	
8	61 090.3	61 090.8	61 107.9	37		62 934.0	
9	61 508.0	61 508.1	61 517.9	38		62 938.4	
10	61 804.3	61 803.9	61 810.1	39		62 942.4	
11	62 020.8	62 021.0	62 024.7	40		62 946.1	
12	62 183.7	62 184.8	62 186.2	41		62 949.6	
13	62 308.7	62 311.5	62 310.4	42		62 952.8	
14	62 405.4	62 411.5	62 407.0	43		62 955.8	
15	62 498.8	62 491.7	62 500.6	44		62 958.6	
16	62 559.2	62 557.0	62 560.8	45		62 961.2	
17	62 609.8	62 610.9	62 611.4	46		62 963.6	
18	62 651.1	62 655.9	62 652.6	47		62 965.9	
19		62 693.8	62 697.3	48		62 968.0	
20	62 725.4	62 726.1	62 726.0	49		62 970.0	
21	62 756.0	62 753.8	62 757.6	50		62 971.9	
22	62 777.3	62 777.7	62 777.8	51		62 973.6	
23	62 799.6	62 798.5	62 800.8	52		62 975.3	
24	62 819.6	62 816.7	62 820.3	53		62 976.9	
25	62 832.6	62 832.7	62 832.6	54		62 978.3	
26	62 847.0	62 846.9	62 847.3	55		62 979.7	
27	62 859.9	62 859.5	62 859.8	60		62 985.7	
28	62 873.4	62 870.8	62 873.2	65		62 990.4	
29		62 880.8		70		62 997.0	
30		62 889.9		75		62 999.4	
31		62 898.1		80		63 001.4	
32		62 905.6		90		63 003.1	
33		62 912.3		100		63 005.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of *R*-matrix/MQDT are selected from Assimopoulos *et al.*[5]

present calculations are as good as any theoretical method known to date. In previous studies, only the singly excited states are treated. For the doubly excited states, the correlation between the two excited electrons significantly increases. Can the WBEPM theory be extended to the case of doubly excited states? How would the correlation be included adequately? An investigation of these questions will be explored in this paper.

In this study, even parity $3dnl$ autoionization levels of Ca have been treated within the framework of the WBEPM theory. Section 2 presents the theory and principle of calculation. The parameters in the calculation are listed in Table 1. In Tables 2–32 the calculated results are compared with experimental data and the results from other theoretical methods.

2. Theory and Principle of Calculation

The WBEPM theory was suggested by Zheng.[10] As the details of the theory have been introduced in our previous work,[10–26] we describe it only briefly here. The concept of weakest bound electron (WBE) was first represented when defining the concept of the ionization potential of a free

TABLE 8. [Ar] $3d_{5/2}nd_{5/2}$ $J=1$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	58 843.8	58 843.6	58 835.6	35		62 922.6	
7	60 094.3	60 095.2	60 089.7	36		62 927.9	
8	60 850.3	60 849.7	60 847.6	37		62 932.7	
9	61 375.0	61 374.5	61 377.8	38		62 937.2	
10	61 693.8	61 693.9	61 697.7	39		62 941.3	
11	61 953.0	61 953.5	61 953.0	40		62 945.1	
12	62 134.4	62 134.4	62 134.2	41		62 948.7	
13	62 273.3	62 273.1	62 273.1	42		62 951.9	
14	62 382.2	62 381.6	62 381.8	43		62 955.0	
15	62 468.4	62 468.0	62 468.4	44		62 957.8	
16	62 538.5	62 538.0	62 538.4	45		62 960.5	
17	62 595.7	62 595.4	62 595.8	46		62 962.9	
18		62 643.1	62 643.6	47		62 965.2	
19		62 683.1	62 683.5	48		62 967.4	
20		62 717.0	62 717.4	49		62 969.4	
21		62 746.0	62 746.3	50		62 971.4	
22	62 771.3	62 771.0	62 771.4	51		62 973.2	
23	62 792.9	62 792.7	62 793.0	52		62 974.8	
24		62 811.7	62 811.9	53		62 976.4	
25		62 828.3	62 828.6	54		62 977.9	
26		62 843.0	62 843.3	55		62 979.4	
27		62 856.1		60		62 985.4	
28	62 868.0	62 867.7	62 867.9	65		62 990.1	
29		62 878.1		70		62 993.9	
30		62 887.5		75		62 996.9	
31		62 895.9		80		62 999.3	
32		62 903.6		85		63 001.3	
33		62 910.5		90		63 003.0	
34		62 916.8		100		63 005.7	

[a]The perturb levels are: $4p5p\ ^1P_1$ and $^3D_1$.
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 9. [Ar] $3d_{3/2}nd_{3/2}$ $J=1$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	58 761.4	58 761.0	58 757.6	35		62 862.2	62 862.0
7	60 022.6	60 024.2	60 020.0	36		62 867.4	62 867.3
8	60 779.6	60 778.2	60 777.9	37		62 872.3	62 872.1
9	61 300.0	61 299.3	61 301.0	38	62 876.2	62 876.7	62 876.6
10	61 622.5	61 623.1	61 627.0	39	62 880.3	62 880.8	62 880.7
11	61 892.9	61 893.7	61 892.9	40		62 884.6	
12	62 073.5	62 073.1	62 073.5	41		62 888.1	
13	62 212.4	62 212.3	62 212.4	42		62 891.4	
14	62 321.1	62 321.3	62 321.1	43		62 894.4	
15	62 407.7	62 408.0	62 407.6	44		62 897.3	
16	62 477.6	62 478.1	62 477.7	45		62 899.9	
17	62 535.0	62 535.6	62 535.0	46		62 902.4	
18	62 582.8	62 583.3	62 582.7	47		62 904.7	
19	62 622.8	62 623.3	62 622.8	48		62 906.8	
20		62 657.2	62 656.6	49		62 908.9	
21		62 686.2	62 685.6	50		62 910.8	
22		62 711.1	62 710.6	51		62 912.6	
23		62 732.7	62 732.3	52		62 914.2	
24		62 751.6	62 751.3	53		62 915.8	
25	62 767.9	62 768.2	62 767.9	54		62 917.3	
26		62 782.9	62 782.5	55		62 918.8	
27		62 795.9	62 795.6	60		62 924.8	
28	62 807.6	62 807.5	62 807.2	65		62 929.5	
29		62 817.8	62 817.2	70		62 933.2	
30	62 826.9	62 827.2	62 826.9	75		62 936.2	
31	62 835.5	62 835.6	62 835.4	80		62 938.6	
32	62 843.2	62 843.2	62 842.9	85		62 940.7	
33	62 850.1	62 850.1	62 879.9	90		62 942.4	
34	62 856.0	62 856.4	62 856.2	100		62 945.0	

[a]The perturb levels are: $4p5p\ ^1P_1$ and $^3D_1$.
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

particle.[27] The WBE in a given system is different from all the other electrons in the system. Those are called nonweakest bound electrons (NWBEs) in behavior. From the viewpoint of excitation and ionization process, the WBE is the most active one of the electrons in the system, and also the one that can be excited or ionized the most easily. So, many properties of the many-electron systems are concerned with the WBE, and thus it is very useful treating WBE accurately. Since the WBE is different from NWBEs in behavior, it can be treated separately. By the separation of WBE and NWBEs, the problem of a many-electron system can be simplified to be a single-electron problem of WBE. The Schrödinger equation of the WBE is

$$[-\tfrac{1}{2}\nabla_i^2+V(r_i)]\varphi_i=\epsilon_i\varphi_i\,. \tag{1}$$

The potential is suggested in WBEPM theory as

$$V=-\frac{Z'}{r_i}+\frac{2dl+d(d+1)}{2r_i^2}, \tag{2}$$

in which Z' is the effective nuclear charge, l is the azimuthal quantum number, and d is a parameter. The first term on the

TABLE 10. [Ar] $3d_{5/2}nd_{3/2}$ $J=1$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	59 363.5	59 363.5	59 363.5	35		62 922.2	
7	60 379.1	60 379.1	60 379.1	36		62 927.5	
8	61 021.0	61 021.0	61 021.0	37		62 932.4	
9	61 452.6	61 452.7	61 452.6	38		62 936.9	
10	61 758.3	61 758.3	61 758.3	39		62 941.0	
11	61 982.2	61 982.0	61 982.2	40		62 944.9	
12	62 151.8	62 151.9	62 151.8	41		62 948.4	
13	62 283.8	62 283.8	62 283.8	42		62 951.7	
14	62 387.9	62 388.0	62 387.9	43		62 954.8	
15	62 471.1	62 471.8	62 471.1	44		62 957.6	
16	62 542.8	62 540.0	62 542.8	45		62 960.3	
17	62 597.2	62 596.4	62 597.2	46		62 962.7	
18	62 643.8	62 643.4	62 643.8	47		62 965.1	
19	62 683.4	62 683.0	62 683.4	48		62 967.2	
20	62 716.8	62 716.7	62 716.8	49		62 969.3	
21	62 745.7	62 745.5	62 745.7	50		62 971.2	
22	62 770.8	62 770.4	62 770.8	51		62 973.0	
23	62 792.4	62 792.1	62 792.4	52		62 974.7	
24	62 811.2	62 811.0	62 811.2	53		62 976.3	
25	62 828.2	62 827.7	62 828.2	54		62 977.8	
26		62 842.4		55		62 979.3	
27	62 855.3	62 855.5	62 855.3	60		62 985.3	
28		62 867.1		65		62 990.1	
29		62 877.6		70		62 993.8	
30		62 886.9		75		62 996.8	
31		62 895.4		80		62 999.3	
32		62 903.1		85		63 001.3	
33		62 910.1		90		63 003.0	
34		62 916.4		100		63 005.6	

[a]The perturb levels are: $4p5p\ ^1P_1$ and $^3D_1$.
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 11. [Ar] $3d_{3/2}nd_{5/2}$ $J=1$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	58 807.9	58 807.9	58 801.5	35	62 861.7	62 861.9	62 861.7
7	60 062.6	60 062.6	60 059.2	36	62 866.7	62 867.2	62 867.0
8	60 820.4	60 820.4	60 819.0	37		62 872.1	
9	61 328.2	61 328.2	61 328.0	38		62 876.5	
10	61 661.5	61 661.5	61 661.4	39		62 880.6	
11	61 910.7	61 910.7	61 910.7	40		62 884.5	
12	62 088.6	62 088.6	62 088.6	41		62 888.0	
13	62 224.3	62 224.2	62 224.4	42		62 891.3	
14	62 329.9	62 330.0	62 330.2	43		62 894.3	
15	62 414.3	62 414.3	62 414.7	44		62 897.1	
16	62 483.1	62 482.5	62 483.6	45		62 899.8	
17	62 535.8	62 538.7	62 535.9	46		62 902.2	
18	62 583.5	62 585.4	62 584.2	47		62 904.5	
19	62 623.5	62 624.7	62 623.8	48		62 906.7	
20	62 656.6	62 658.1	62 657.4	49		62 908.7	
21	62 685.4	62 686.7	62 686.4	50		62 910.7	
22	62 710.3	62 711.4	62 710.8	51		62 912.5	
23	62 731.8	62 732.9	62 732.4	52		62 914.1	
24	62 750.7	62 751.7	62 751.2	53		62 915.7	
25	62 767.5	62 768.2	62 767.7	54		62 917.2	
26	62 781.9	62 782.7	62 782.3	55		62 918.7	
27	62 795.0	62 795.7	62 795.4	60		62 924.7	
28	62 806.5	62 807.3	62 806.9	65		62 929.4	
29	62 817.0	62 817.6	62 817.3	70		62 933.2	
30	62 826.2	62 826.9	62 826.6	75		62 936.2	
31	62 834.8	62 835.3	62 835.1	80		62 938.6	
32	62 842.2	62 843.0	62 842.6	85		62 940.6	
33	62 849.5	62 849.9	62 849.7	90		62 942.3	
34		62 856.2		100		62 945.0	

[a]Perturbers are: $4p5p\ ^1P_1$ and $^3D_1$, $3d_{5/2}6d_{3/2}$ (59 363.5 cm^{-1}), $3d_{5/2}7d_{3/2}$ (60 379.1 cm^{-1}).
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

right of Eq. (2) represents the Coulomb potential, and the second term the dipole potential owing to the polarization effect.

The solution of Eq. (1) is[10]

$$\epsilon = -\frac{Z'^2}{2n'^2}, \tag{3}$$

$$R = A \exp\left(-\frac{Z'r}{n'}\right) r^{l'} L_{n-l-1}^{2l'+1}\left(\frac{2Z'r}{n'}\right), \tag{4}$$

$$A = \left(\frac{2Z'}{n'}\right)^{l'+3/2}\left[\frac{2n'}{(n-l-1)!}\Gamma(n'+l'+1)\right]^{-1/2}, \tag{5}$$

$$n'-n = l'-l = d, \tag{6}$$

where n' and l' are the effective principal quantum number and effective azimuthal quantum number, respectively, and R is the radial function of WBE with the generalized Laguerre polynomial L.

In order to explore the regularities of energy levels of many-valence-electron systems, the authors have defined

TABLE 12. $[\mathrm{Ar}]\,3d_{3/2}nd_{3/2}\,J=2$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	59 352.6	59 352.4	59 353.6	35		62 863.6	
7	60 340.0	60 340.8	60 373.2	36		62 868.7	62 869.2
8	60 992.1	60 991.3	61 012.8	37		62 873.5	
9	61 427.5	61 427.3	61 440.3	38	62 877.8	62 877.8	62 877.8
10	61 732.0	61 732.5	61 741.6	39		62 881.8	
11		61 954.5	61 961.7	40		62 885.6	
12	62 121.2	62 121.1	62 126.7	41		62 889.0	
13	62 249.9	62 249.3	62 254.0	42		62 892.2	
14	62 350.4	62 350.1	62 354.2	43		62 895.2	
15	62 432.3	62 430.8	62 434.8	44		62 898.0	
16		62 496.5		45		62 900.6	
17	62 552.0	62 550.5	62 553.7	46		62 903.0	
18	62 597.2	62 595.6	62 596.5	47		62 905.2	
19		62 633.6		48		62 907.4	
20		62 665.8		49		62 909.4	
21		62 693.5		50		62 911.2	
22	62 716.8	62 717.4	62 717.4	51		62 913.0	
23	62 739.2	62 738.2	62 739.3	52		62 914.7	
24		62 756.4		53		62 916.2	
25	62 773.4	62 772.4	62 773.9	54		62 917.7	
26	62 787.1	62 786.5	62 787.3	55		62 919.1	
27		62 799.1		60		62 925.1	
28	62 811.2	62 810.3	62 810.6	65		62 929.7	
29		62 820.4		70		62 933.4	
30		62 829.5	62 830.2	75		62 936.3	
31	62 838.4	62 837.7	62 838.2	80		62 938.8	
32		62 845.1		85		62 940.8	
33		62 851.8		90		62 942.4	
34		62 858.0		100		62 945.0	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 13. $[\mathrm{Ar}]\,3d_{5/2}nd_{5/2}\,J=2$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	57 638.4	57 638.7	57 723.4	34		62 918.4	
6	59 389.4	59 388.0	59 431.6	35		62 924.1	
7	60 410.0	60 411.5	60 434.7	36		62 929.2	
8	61 054.3	61 054.6	61 070.1	37		62 934.0	
9	61 486.5	61 485.8	61 497.3	38		62 938.3	
10	61 791.5	61 791.5	61 795.0	39		62 942.4	
11	62 011.4	62 011.1	62 016.2	40		62 946.1	
12	62 177.7	62 178.0	62 181.0	41		62 949.6	
13	62 305.6	62 306.7	62 307.8	42		62 952.8	
14	62 405.4	62 408.0	62 406.4	43		62 955.8	
15		62 489.1		44		62 958.5	
16		62 555.1	62 558.6	45		62 961.1	
17	62 609.6	62 609.5	62 610.3	46		62 963.6	
18	62 652.7	62 654.8	62 653.5	47		62 965.8	
19		62 693.0		48		62 968.0	
20	62 725.5	62 725.4	62 725.7	49		62 970.0	
21		62 753.2		50		62 971.8	
22	62 777.6	62 777.2	62 777.6	51		62 973.6	
23		62 798.1		52		62 975.3	
24	62 815.4	62 816.4	62 815.8	53		62 976.9	
25	62 832.6	62 832.5	62 832.6	54		62 978.3	
26		62 846.7		55		62 979.7	
27		62 859.3		60		62 985.7	
28	62 870.4	62 870.6	62 870.4	65		62 990.4	
29		62 880.7		70		62 994.0	
30		62 889.8		75		62 997.0	
31		62 898.0		80		62 999.4	
32		62 905.5		90		63 003.1	
33		62 912.2		100		63 005.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

the concept of spectrum-level-like series to classify the energy levels.[25] A spectrum-level-like series is a series composed of energy levels with the same spectral level symbols in a given electron configuration series of a system. According to the definition, for example, the series of energy levels Ca $[\mathrm{Ar}]3d(^2D_{3/2})nd_{3/2}\,J=2$ is a spectrum-level-like series.

As for the $3dnl$ doubly excited states of Ca, nl electron lies in a higher orbital than $3d$ and can be assigned as the weakest bound electron. The $3dnl$ series converge on two ionization limits $^2D_{3/2}$ and $^2D_{5/2}$, respectively, corresponding to the fine structure splitting. The jj coupling scheme is used in this paper to study the even parity $J=1-5$ series of Ca. In a given series, energy levels depend on the principal quantum number of the weakest bound electron only

$$T(n)=E(n)+T_{\mathrm{limit}}\approx T_{\mathrm{limit}}-\frac{Z'^2}{2n'^2}. \tag{7}$$

In order to simplify the equation that has two various parameters, we employed the representation of energy in quantum defect theory (QDT) to do a transformation

$$\frac{Z'}{n'}=\frac{Z_{\mathrm{net}}}{n-\delta_n}, \tag{8}$$

TABLE 14. [Ar] $3d_{5/2}nd_{3/2}$ $J=2$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
5	57 578.9	57 578.9	57 678.2	34		62 916.5	
6	59 363.5	59 363.7	59 396.7	35		62 922.3	
7	60 378.0	60 376.7	60 399.8	36		62 927.6	
8	61 023.7	61 025.6	61 035.8	37		62 932.5	
9	61 457.0	61 456.3	61 464.0	38		62 937.0	
10		61 687.5		39		62 941.1	
11	61 986.9	61 986.8	61 989.0	40		62 944.9	
12		62 155.3		41		62 948.5	
13	62 286.6	62 286.3	62 287.2	42		62 951.8	
14	62 389.8	62 390.0	62 390.0	43		62 954.8	
15	62 472.1	62 473.4	62 471.8	44		62 957.7	
16	62 544.5	62 541.3	62 545.4	45		62 960.3	
17	62 600.5	62 597.4	62 601.3	46		62 962.8	
18	62 645.5	62 644.3	62 646.2	47		62 965.1	
19	62 684.3	62 683.7	62 684.2	48		62 967.3	
20		62 717.3		49		62 969.3	
21	62 746.5	62 746.1	62 747.2	50		62 971.2	
22	62 771.0	62 770.9	62 771.4	51		62 973.0	
23	62 793.0	62 792.5	62 793.3	52		62 974.7	
24	62 812.1	62 811.4	62 812.5	53		62 976.3	
25	62 828.0	62 828.0	62 828.4	54		62 977.8	
26		62 842.6	62 843.1	55		62 979.3	
27		62 855.7	62 856.1	60		62 985.4	
28		62 867.3	62 867.7	65		62 990.1	
29		62 877.7		70		62 993.8	
30		62 887.1		75		62 996.8	
31		62 895.6		80		62 999.3	
32		62 903.2		90		63 003.0	
33		62 910.2		100		63 005.7	

[a]The perturb levels are: $4p5p\ ^3D_2$ (61 804.2 cm^{-1}), $3d_{3/2}6d_{5/2}$ (58 787.4 cm^{-1}).
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 15. [Ar] $3d_{3/2}nd_{5/2}$ $J=2$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	58 787.4	58 787.6	58 785.2	33		62 849.8	
7	60 051.6	60 053.3	60 050.7	34	62 856.0	62 856.1	62 856.2
8	60 816.7	60 810.2	60 816.6	35	62 862.5	62 861.9	62 862.6
9	61 313.9	61 318.2	61 314.1	36	62 867.1	62 867.1	62 867.3
10	61 752.7	61 621.4	61 762.6	37	62 872.7	62 872.0	62 872.8
11	61 919.7	61 919.2	61 922.0	38		62 876.5	
12	62 092.9	62 097.0	62 094.2	39		62 880.6	
13	62 228.8	62 228.7	62 230.2	40		62 884.4	
14		62 332.4	62 335.4	41		62 887.9	
15	62 421.4	62 415.6	62 423.0	42		62 891.2	
16		62 483.2		43		62 894.2	
17	62 536.3	62 539.0	62 536.2	44		62 897.1	
18	62 585.8	62 585.5	62 586.2	45		62 899.7	
19	62 626.4	62 624.7	62 627.0	46		62 902.2	
20	62 661.5	62 658.0	62 662.0	47		62 904.5	
21	62 686.3	62 686.6	62 687.1	48		62 906.7	
22	62 712.4	62 711.3	62 712.0	49		62 908.7	
23	62 734.5	62 732.7	62 734.8	50		62 910.6	
24	62 750.2	62 751.5	62 750.6	55		62 918.6	
25	62 768.2	62 768.0	62 768.5	60		62 924.7	
26		62 782.6		65		62 929.4	
27	62 795.1	62 795.5	62 795.3	70		62 933.2	
28	62 807.6	62 807.1	62 807.8	75		62 936.2	
29	62 819.6	62 817.5	62 819.2	80		62 938.6	
30	62 826.9	62 826.8	62 827.2	85		62 940.6	
31	62 836.9	62 835.2	62 836.4	90		62 942.3	
32	62 842.7	62 842.8	62 843.0	100		62 945.0	

[a]The perturbers are: $4p5p\ ^3D_2$ (61 804.2 cm^{-1}), mix of $3d10d$ and $4p5p$ (61 767.3 cm^{-1}), and $3d_{5/2}6d_{3/2}$(59 363.5 cm^{-1}).
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

where Z_{net} is the net nuclear charge and $Z_{net}=1$ for atoms, δ_n is the quantum defect number in QDT. Then Eq. (7) turns out to be

$$T(n)=T_{limit}-\frac{Z_{net}^2}{2(n-\delta_n)^2}. \tag{9}$$

By exploring the regularity of $\delta_n \sim n$, Risberg once suggested the following formula, that can be solved through iteration, for a series not been perturbed:

$$\delta_n(\epsilon_n)=\sum_{i=0}^{\infty} a_i(n-\delta_n)^{-i}. \tag{10}$$

To simplify this equation, Martin[28] cut the polynomial to its first four even power terms and takes δ_0, the quantum defect of the leader in a series, instead of δ_n in the polynomial

$$\delta_n(\epsilon_n)=\sum_{i=0}^{3} a_i(n-\delta_0)^{-2i}. \tag{11}$$

TABLE 16. [Ar] $3d_{5/2}nd_{5/2}$ $J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	58 821.1	58 820.0	58 819.6	35		62 923.2	
7	60 084.8	60 089.4	60 084.3	36		62 928.4	
8	60 851.3	60 846.8	60 851.2	37		62 933.3	
9	61 351.2	61 349.0	61 351.4	38		62 937.7	
10	61 693.2	61 697.3	61 693.4	39		62 941.8	
11	61 939.7	61 947.5	61 963.5	40		62 945.6	
12	62 133.7	62 132.9	62 133.9	41		62 949.1	
13	62 272.3	62 273.8	62 272.4	42		62 952.3	
14	62 380.9	62 383.5	62 381.1	43		62 955.3	
15	62 467.9	62 470.4	62 467.8	44		62 958.1	
16	62 538.1	62 540.6	62 538.0	45		62 960.8	
17	62 595.1	62 598.0	62 595.4	46		62 963.2	
18	62 643.1	62 645.6	62 643.2	47		62 965.5	
19	62 683.2	62 685.5	62 683.2	48		62 967.7	
20	62 716.8	62 719.2	62 717.2	49		62 969.7	
21	62 746.0	62 748.1	62 746.2	50		62 971.6	
22	62 771.0	62 772.9	62 771.2	51		62 973.4	
23	62 793.0	62 794.4	62 792.9	52		62 975.0	
24	62 811.6	62 813.2	62 811.8	53		62 976.6	
25	62 828.0	62 829.7	62 828.4	54		62 978.1	
26	62 843.1	62 844.3	62 843.2	55		62 979.5	
27	62 856.0	62 857.3	62 856.2	60		62 985.6	
28		62 868.8	62 867.8	65		62 990.3	
29	62 877.8	62 879.1	62 878.2	70		62 994.0	
30	62 887.2	62 888.4	62 887.6	75		62 996.9	
31	62 895.7	62 896.8	62 896.0	80		62 999.4	
32		62 904.3		85		63 001.4	
33		62 911.2		90		63 003.1	
34		62 917.5		100		63 005.7	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

TABLE 17. [Ar] $3d_{3/2}nd_{3/2}$ $J=3$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	58 775.2	58 775.3	58 775.2	35		62 862.1	
7	60 038.4	60 038.1	60 038.2	36		62 867.4	
8	60 802.2	60 802.4	60 802.0	37		62 872.2	
9	61 300.2	61 300.7	61 300.0	38		62 876.7	
10	61 644.3	61 643.8	61 642.9	39		62 880.8	
11		61 890.2		40		62 884.6	
12	62 073.0	62 073.1	62 072.8	41		62 888.1	
13	62 212.5	62 212.6	62 212.4	42		62 891.4	
14	62 321.2	62 321.5	62 321.1	43		62 894.4	
15	62 407.8	62 408.1	62 407.8	44		62 897.2	
16	62 477.9	62 478.1	62 477.8	45		62 899.9	
17	62 535.2	62 535.5	62 535.0	46		62 902.3	
18	62 582.9	62 583.1	62 583.0	47		62 904.6	
19		62 623.1	62 622.8	48		62 906.8	
20		62 657.0	62 656.8	49		62 908.8	
21		62 685.9	62 685.8	50		62 910.7	
22	62 710.3	62 710.9	62 710.8	51		62 912.5	
23	62 731.8	62 732.5	62 732.4	52		62 914.2	
24	62 750.7	62 751.4	62 751.3	53		62 915.8	
25	62 768.2	62 768.0	62 767.9	54		62 917.3	
26	62 781.9	62 782.7	62 782.6	55		62 918.7	
27		62 795.7	62 795.6	60		62 924.8	
28	62 807.6	62 807.3	62 807.2	65		62 929.5	
29	62 817.0	62 817.7	62 817.6	70		62 933.2	
30		62 827.0	62 827.0	75		62 936.2	
31		62 835.5	62 835.4	80		62 938.6	
32		62 843.1	62 843.1	85		62 940.7	
33	62 849.8	62 850.0	62 850.0	90		62 942.3	
34		62 856.3	62 856.3	100		62 945.0	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

Martin[28] treated atomic Na with this equation and got very good results.

While many series are perturbed by foreign levels, we suggested adding the perturbation terms to Eq. (11) enlightened by Langer[29]

$$\delta_n(\epsilon_n)=\sum_{i=0}^{3} a_i m^{-2i}+\sum_{j=1}^{N}\frac{b_j}{m^{-2}-\epsilon_j}, \qquad (12)$$

with $m=n-\delta_0$ and $\epsilon_j=(T_{\text{limit}}-T_{j,\ \text{perturber}})/Z_{\text{net}}^2$; N is the number of perturbing foreign levels.[24,25] Then combining Eqs. (9) and (12), we can calculate the parameters a_i and b_j by the least square method using the first $(6+N)$ data of a given series, and then predict the higher levels with these parameters.

3. Results and Analysis

Using the method mentioned above, 30 series of $3dnl$ ($l=0,2,4$) $J=0^e-3^e$ and $3dnd$ $J=4$, 5 autoionizing energy levels of Ca are calculated. The jj coupling frame is used. The experimental values of energy levels are taken from Assimopoulos *et al.*,[5] Luc-koenig *et al.*,[6] and Assimopoulos *et al.*[7]

TABLE 18. [Ar] $3d_{5/2}nd_{3/2}$ $J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
10	61 766.9	61 766.6	61 777.6	39		62 946.4	
11	61 993.5	62 010.0	62 000.4	40		62 949.9	
12	62 161.2	62 164.2	62 165.2	41		62 953.2	
13	62 290.6	62 287.1	62 292.9	42		62 956.2	
14	62 391.9	62 389.9	62 393.0	43		62 959.0	
15	62 472.2	62 475.7	62 472.4	44		62 961.6	
16		62 547.0	62 557.4	45		62 964.0	
17	62 606.8	62 606.1	62 607.3	46		62 966.3	
18	62 648.9	62 655.2	62 649.4	47		62 968.4	
19	62 684.3	62 696.1	62 684.4	48		62 970.4	
20	62 723.8	62 730.5	62 724.2	49		62 972.3	
21	62 749.0	62 759.6	62 748.8	50		62 974.1	
22	62 776.8	62 784.5	62 776.7	51		62 975.7	
23	62 794.5	62 805.8	62 794.4	52		62 977.3	
24	62 814.7	62 824.3	62 814.8	53		62 978.8	
25	62 831.9	62 840.4	62 832.0	54		62 980.2	
26	62 846.6	62 854.5	62 846.8	55		62 981.5	
27		62 866.9	62 859.4	56		62 982.7	
28		62 877.9	62 870.3	57		62 983.9	
29		62 887.7	62 879.7	58		62 985.0	
30		62 896.5	62 889.9	59		62 986.1	
31		62 904.4		60		62 987.1	
32		62 911.5		65		62 991.5	
33		62 917.9		70		62 994.9	
34		62 923.8		75		62 997.8	
35		62 929.1		80		63 000.0	
36		62 934.0		85		63 002.0	
37		62 938.5		90		63 003.5	
38		62 942.6		100		63 006.1	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

TABLE 19. [Ar] $3d_{3/2}nd_{5/2}$ $J=3$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	58 805.8	58 804.9	58 803.2	35	62 863.2	62 863.8	62 863.3
7	60 060.1	60 063.9	60 059.4	36	62 867.1	62 868.9	62 867.4
8	60 822.6	60 818.6	60 822.8	37		62 873.6	62 873.4
9	61 319.9	61 318.8	61 321.0	38		62 878.0	62 877.0
10	61 661.3	61 664.1	61 662.8	39		62 882.0	62 882.1
11	61 918.9	61 910.9	61 922.0	40		62 885.7	62 885.1
12	62 093.5	62 092.9	62 095.8	41		62 889.2	62 887.9
13	62 231.1	62 230.8	62 233.8	42		62 892.4	62 892.1
14	62 339.3	62 337.8	62 342.0	43		62 895.3	62 894.7
15	62 425.6	62 422.6	62 428.2	44		62 898.1	
16		62 490.9	62 498.6	45		62 900.7	
17	62 536.3	62 546.8	62 536.2	46		62 903.1	
18	62 587.1	62 593.1	62 587.4	47		62 905.4	
19	62 628.5	62 631.9	62 629.6	48		62 907.5	
20	62 664.0	62 664.7	62 665.0	49		62 909.5	
21		62 692.8	62 696.1	50		62 911.3	
22	62 713.1	62 717.0	62 712.9	51		62 913.1	
23	62 736.1	62 738.0	62 736.4	52		62 914.7	
24		62 756.3	62 757.2	53		62 916.3	
25	62 769.2	62 772.4	62 769.0	54		62 917.8	
26	62 785.5	62 786.6	62 785.4	55		62 919.2	
27		62 799.2	62 800.2	60		62 925.1	
28		62 810.5	62 808.5	65		62 929.8	
29		62 820.6	62 820.4	70		62 933.4	
30	62 827.2	62 829.7	62 827.4	75		62 936.4	
31	62 837.1	62 837.9	62 837.3	80		62 938.8	
32		62 845.3	62 842.9	85		62 940.8	
33		62 852.0	62 851.4	90		62 942.4	
34		62 858.2		100		62 945.1	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

As mentioned above in Sec. 1, the correlation between the two excited electrons is important for the doubly excited states. For the $3dnl$ states the correlation is more important when n is relatively small because the true potential field is more similar to the central potential when n is large. To evaluate the correlation adequately, we emphasize that the perturbations come from foreign levels in our calculation. The parameters are determined by fitting the first several experimental values of energy levels in the calculation of the WBEPM theory, so the correlation and relaxation effects are partly included, but this is not enough. By emphasizing the consideration of perturbation, the mix between different spectra or different configurations is introduced into the calculation, and thus one can supplement much of the undervaluation for the correlation. The details of treatment are amplified as follows.

In the following we present the results of various $3dnl$ series. The corresponding parameters can be found in Table 1.

$4p5p$ levels were observed to perturb $3dnd$ and $3dns$ levels extremely:[5,6] $^1P_1$ (61 132.1 cm^{-1}) and $^3D_1$ (61 728.9 cm^{-1}) perturbs the $J=1$ series, $^3D_2$ (61 804.2 cm^{-1}) perturbs the $J=2$ series, and $^3D_3$ perturbs the $J=3$ series. In our calculation the $4p5p$ $^3D_3$ perturber has not been counted in, because it shows a very broad peak that is not fit for our perturber model.

TABLE 20. [Ar] $3d_{5/2}nd_{3/2}$ $J=4$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	59 463.5	59 462.0	59 488.9	35		62 923.4	
7	60 457.2	60 464.9	60 473.4	36		62 928.6	
8	61 084.7	61 071.8	61 095.6	37		62 933.4	
9	61 477.8	61 485.4	61 486.3	38		62 937.8	
10	61 781.8	61 782.1	61 787.6	39		62 941.9	
11	62 002.9	62 001.8	62 006.4	40		62 945.6	
12	62 168.0	62 168.6	62 170.4	41		62 949.1	
13	62 295.0	62 298.0	62 296.5	42		62 952.4	
14	62 394.5	62 400.3	62 395.3	43		62 955.4	
15	62 473.6	62 482.4	62 474.0	44		62 958.2	
16		62 549.2		45		62 960.8	
17	62 608.2	62 604.4	62 609.1	46		62 963.3	
18	62 650.2	62 650.4	62 650.6	47		62 965.6	
19	62 684.9	62 689.1	62 685.1	48		62 967.7	
20	62 724.6	62 722.0	62 725.2	49		62 969.7	
21	62 749.2	62 750.3	62 749.4	50		62 971.6	
22	62 776.9	62 774.6	62 777.4	51		62 973.4	
23	62 794.6	62 795.8	62 794.8	52		62 975.1	
24	62 815.1	62 814.4	62 815.3	53		62 976.7	
25	62 832.3	62 830.7	62 832.5	54		62 978.1	
26	62 846.9	62 845.1	62 847.2	55		62 979.6	
27	62 859.2	62 857.9	62 859.7	60		62 985.6	
28		62 869.3		65		62 990.3	
29		62 879.5		70		62 994.0	
30		62 888.7		75		62 996.9	
31		62 897.1		80		62 999.4	
32		62 904.6		85		63 001.4	
33		62 911.4		90		63 003.1	
34		62 917.7		100		63 005.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.* [7]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[7]

TABLE 21. [Ar] $3d_{3/2}nd_{5/2}$ $J=4$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})[a]

		Theoretical results				Theoretical results	
n	T_{expt}[b]	This work	R/MQDT[c]	n	T_{expt}[b]	This work	R/MQDT[c]
6	58 829.6	58 829.6	58 834.0	35	62 863.3	62 864.5	62 863.6
7	60 077.8	60 077.9	60 080.7	36		62 869.6	
8	60 836.1	60 836.2	60 838.2	37		62 874.2	
9	61 331.1	61 331.3	61 332.9	38		62 878.6	
10	61 672.0	61 671.2	61 673.8	39		62 882.5	
11	61 916.8	61 917.2	61 918.5	40		62 886.2	
12	62 098.7	62 099	62 100.0	41		62 889.6	
13	62 236.9	62 236.7	62 238.5	42		62 892.8	
14	62 344.8	62 343.3	62 346.6	43		62 895.7	
15	62 431.2	62 427.6	62 433.0	44		62 898.5	
16	62 502.1	62 495.5	62 503.5	45		62 901	
17		62 550.9		46		62 903.4	
18		62 596.7		47		62 905.7	
19	62 630.5	62 635.2	62 631.0	48		62 907.8	
20	62 666.4	62 667.7	62 667.0	49		62 909.7	
21	62 698.0	62 695.4	62 698.7	50		62 911.6	
22	62 713.3	62 719.4	62 713.6	51		62 913.3	
23	62 737.0	62 740.1	62 737.5	52		62 915	
24	62 758.2	62 758.2	62 758.7	53		62 916.5	
25	62 769.2	62 774.1	62 769.4	54		62 918	
26	62 785.8	62 788.2	62 786.2	55		62 919.4	
27	62 801.2	62 800.7	62 801.5	60		62 925.3	
28	62 808.8	62 811.8	62 808.9	65		62 929.9	
29	62 820.8	62 821.8	62 821.1	70		62 933.5	
30	62 828.0	62 830.7	62 827.6	75		62 936.5	
31	62 837.6	62 838.8	62 837.8	80		62 938.8	
32	62 843.0	62 846.2	62 843.2	85		62 940.8	
33	62 851.6	62 852.8	62 851.8	90		62 942.5	
34	62 856.3	62 858.9	62 856.4	100		62 945.1	

[a]The perturb levels are: $3d_{5/2}7d_{3/2}$ (60 457.2 cm^{-1}) and $3d_{5/2}8d_{3/2}$ (61 084.7 cm^{-1}).
[b]The experimental values T_{expt} are selected from Assimopoulos *et al.*[7]
[c]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[7]

There are four $3dns$ series. Two of them ($3d_{3/2}ns$ $J=1,2$) converge to the $3d_{3/2}$ limit and the other two ($3d_{5/2}ns$ $J=2,3$) converge to the $3d_{5/2}$ limit. The results of these four series are listed in Tables 2 to 5. As for the series $3d_{3/2}ns$ $J=1$, two perturbers $4p5p$ $^1P_1$ and $^3D_1$ are included in the calculation. As for the series $3d_{5/2}ns$ $J=2$, there are only four experimental values to fit the parameters. As for the series $3d_{5/2}ns$ $J=3$, the data of $n=12$ is not involved in the fitting of parameters because of the serious overlap with $4p5p$ there. It can be observed from these tables that all of the present results have the same accuracy of less than 1 cm^{-1}. For the low excited $3dns$ states, there are no experimental values, so the parameters are determined by the first few experimental data. We calculated the energy levels from where the experimental data started to appear.

There are 18 $3dnd$ series. Ten of them converge to the $3d_{5/2}$ limit: $3d_{5/2}nd_{5/2}$ $J=0$, 1, 2, 3, 4, 5 and $3d_{5/2}nd_{3/2}$ $J=1$, 2, 3, 4. The other eight converge to the $3d_{3/2}$ limit: $3d_{3/2}nd_{3/2}$ $J=0$, 1, 2, 3 and $3d_{3/2}nd_{5/2}$ $J=1$, 2, 3, 4.

$J=0$. The series $3d_{3/2}nd_{3/2}$ and $3d_{5/2}nd_{5/2}$ mixed in most parts of the spectrum. It can be seen from Table 6 that, for

TABLE 22. [Ar] $3d_{5/2}nd_{5/2}$ $J=4$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	59 344.1	59 345.8	59 375.2	35		62 924.4	
7	60 389.7	60 381.3	60 408.7	36		62 929.6	
8	61 042.9	61 056.7	61 055.4	37		62 934.3	
9	61 506.5	61 498.8	61 514.4	38		62 938.6	
10	61 804.2	61 803.7	61 810.2	39		62 942.6	
11	62 022.7	62 023.9	62 027.0	40		62 946.3	
12	62 187.0	62 188.7	62 190.4	41		62 949.8	
13	62 313.8	62 315.4	62 316.6	42		62 953.0	
14	62 413.5	62 415.0	62 415.9	43		62 956.0	
15	62 493.3	62 494.8	62 495.2	44		62 958.7	
16	62 561.7	62 559.7	62 563.1	45		62 961.3	
17	62 613.8	62 613.3	62 615.0	46		62 963.7	
18	62 658.0	62 658.0	62 659.1	47		62 966.0	
19	62 694.8	62 695.6	62 696.0	48		62 968.1	
20		62 727.7		49		62 970.1	
21	62 755.2	62 755.1	62 755.9	50		62 972.0	
22	62 779.3	62 778.9	62 780.0	51		62 973.7	
23	62 799.4	62 799.5	62 800.0	52		62 975.4	
24	62 818.0	62 817.6	62 818.4	53		62 977.0	
25	62 834.0	62 833.6	62 834.3	54		62 978.4	
26	62 848.0	62 847.6	62 848.4	55		62 979.8	
27	62 860.5	62 860.2	62 860.9	60		62 985.8	
28		62 871.4		65		62 990.4	
29		62 881.4		70		62 994.1	
30		62 890.4		75		62 997.0	
31		62 898.6		80		62 999.5	
32		62 906.0		85		63 001.5	
33		62 912.7		90		63 003.1	
34		62 918.8		100		63 005.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[7]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[7]

TABLE 23. [Ar] $3d_{5/2}nd_{5/2}$ $J=5$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
6	58 860.8	58 860.8	58 865.2	35	62 922.8	62 922.8	62 922.8
7	60 109.3	60 109.3	60 112.1	36	62 928.1	62 928.0	62 928.1
8	60 868.2	60 868.2	60 870.0	37	62 933.0	62 932.9	62 932.9
9	61 364.1	61 364.1	61 365.4	38	62 937.5	62 937.3	62 937.4
10	61 705.9	61 705.9	61 706.9	39	62 941.5	62 941.4	62 941.5
11	61 951.7	61 951.7	61 952.5	40	62 945.4	62 945.3	62 945.3
12	62 134.2	62 134.2	62 134.9	41		62 948.8	
13	62 273.6	62 273.6	62 274.1	42		62 952.0	
14	62 382.3	62 382.3	62 382.8	43		62 955.1	
15	62 468.9	62 468.9	62 469.2	44		62 957.9	
16	62 538.7	62 538.8	62 539.1	45		62 960.5	
17	62 596.2	62 596.2	62 596.4	46		62 963.0	
18	62 643.9	62 643.8	62 644.0	47		62 965.3	
19	62 683.7	62 683.8	62 684.0	48		62 967.5	
20	62 717.7	62 717.7	62 717.8	49		62 969.5	
21	62 746.6	62 746.6	62 746.7	50		62 971.4	
22	62 771.5	62 771.6	62 771.7	51		62 973.2	
23	62 793.2	62 793.2	62 793.3	52		62 974.9	
24	62 812.1	62 812.1	62 812.2	53		62 976.5	
25	62 828.7	62 828.7	62 828.8	54		62 978.0	
26	62 843.2	62 843.4	62 843.4	55		62 979.4	
27	62 856.3	62 856.4	62 856.4	60		62 985.5	
28	62 868.1	62 868.0	62 868.0	65		62 990.2	
29	62 878.4	62 878.4	62 878.4	70		62 993.9	
30	62 887.6	62 887.7	62 887.8	75		62 996.9	
31	62 896.2	62 896.1	62 896.2	80		62 999.3	
32	62 903.8	62 903.8	62 903.8	85		63 001.3	
33	62 910.7	62 910.7	62 910.7	90		63 003.0	
34	62 917.2	62 917.0	62 917.1	100		63 005.7	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[7]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[7]

series $3d_{3/2}nd_{3/2}$, the errors are relatively large when $n=12-27$. This comes from the overlap between the two $3dnl$ $J=0$ series that causes all the peaks to be impure and the overlap in this area is very strong. As for the series $3d_{5/2}nd_{5/2}$ listed in Table 7, the data of $n=5$ have not been taken into the fitting of parameters because of the strong overlap with $4p^2\,{}^1S_0$.

$J=1$. The series $3d_{3/2}nd_{3/2}$ and $3d_{5/2}nd_{5/2}$ are relatively simple. There is almost no mix between them. These two series are perturbed by $4p5p\,{}^1P_1$ and ${}^3D_1$. Our results for these two series agree with the experimental data very well. It can be seen from Tables 8 and 9 that all but two of the deviations are less than 1 cm^{-1}, while the series $3d_{3/2}nd_{5/2}$ and $3d_{5/2}n'd_{3/2}$ mix strongly for $n=n'=6-10$ and $n=32-34$ ($n'=26-27$). So for example, in the calculation of series $3d_{3/2}nd_{5/2}$, not only the perturbers $4p5p\,{}^1P_1$ and ${}^3D_1$ are accounted, but also the levels of $3d_{5/2}6d_{3/2}$ (59 363.5 cm^{-1}) and $3d_{5/2}7d_{3/2}$ (60 379.1 cm^{-1}) are involved as perturbers. The corresponding results are listed in Table 11. Most of the results have errors of less than 1 cm^{-1} compared with the experimental data.

$J=2$. The experiment shows that the $3dnd$ $J=2$ series is much more mixed than $3dnd$ $J=1$. So the errors of the results of these two series are a bit larger with the biggest around 9 cm^{-1}. But it is small when compared with the energy interval between neighboring levels. The series

TABLE 24. [Ar] $3d_{5/2}ng_{7/2}$ $J=1$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 620.3	58 620.4	58 620.3	34		62 921.8	
6	59 960.4	59 960.3	59 958.9	35		62 927.1	
7	60 770.3	60 770.2	60 768.8	36		62 932.1	
8	61 296.6	61 296.5	61 295.1	37		62 936.6	
9	61 656.6	61 657.6	61 655.8	38		62 940.8	
10	61 916.7	61 915.9	61 916.2	39		62 944.6	
11		62 107.1		40		62 948.2	
12		62 252.5		41		62 951.5	
13		62 365.7		42		62 954.6	
14	62 455.4	62 455.5	62 455.5	43		62 957.4	
15	62 528.0	62 527.9	62 528.0	44		62 960.1	
16		62 587.1		45		62 962.6	
17		62 636.2		46		62 964.9	
18		62 677.4		47		62 967.1	
19		62 712.2		48		62 969.2	
20		62 741.9		49		62 971.1	
21		62 767.5		50		62 972.9	
22		62 789.7		51		62 974.6	
23		62 809.0		52		62 976.2	
24		62 826.0		53		62 977.7	
25		62 841.0		54		62 979.2	
26		62 854.2		55		62 980.5	
27		62 866.1		60		62 986.3	
28		62 876.7		65		62 990.8	
29		62 886.2		70		62 994.4	
30		62 894.7		75		62 997.3	
31		62 902.5		80		62 999.7	
32		62 909.5		90		63 003.3	
33		62 915.9		100		63 005.9	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 25. [Ar] $3d_{5/2}ng_{9/2}$ $J=2$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 620.3	58 620.3	58 620.4	34		62 921.8	
6	59 960.6	59 960.6	59 959.0	35		62 927.2	
7	60 770.3	60 770.3	60 768.9	36		62 932.1	
8	61 296.6	61 296.6	61 295.5	37		62 936.6	
9	61 657.8	61 657.8	61 657.3	38		62 940.8	
10		61 916.2	61 915.4	39		62 944.6	
11		62 107.4		40		62 948.2	
12		62 252.8		41		62 951.5	
13		62 365.9		42		62 954.6	
14		62 455.7		43		62 957.4	
15		62 528.1		44		62 960.1	
16		62 587.3		45		62 962.6	
17		62 636.4		46		62 964.9	
18		62 677.5		47		62 967.1	
19		62 712.3		48		62 969.2	
20		62 742.1		49		62 971.1	
21		62 767.6		50		62 972.9	
22		62 789.8		51		62 974.6	
23		62 809.1		52		62 976.2	
24		62 826.1		53		62 977.7	
25		62 841.0		54		62 979.2	
26		62 854.3		55		62 980.5	
27		62 866.1		60		62 986.3	
28		62 876.7		65		62 990.9	
29		62 886.2		70		62 994.4	
30		62 894.8		75		62 997.3	
31		62 902.5		80		62 999.7	
32		62 909.6		90		63 003.3	
33		62 916.0		100		63 005.9	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

$3d_{3/2}nd_{3/2}$ and $3d_{5/2}nd_{5/2}$ are not perturbed by the $4p5p\ ^3D_2$ level (61 804.2 cm^{-1}). The results of the series $3d_{5/2}nd_{3/2}$ are listed in Table 14. Besides $4p5p\ ^3D_2$, the level $3d_{3/2}6d_{5/2}$ (58 787.4 cm^{-1}) is taken into calculation as a perturber. The results of series $3d_{3/2}nd_{5/2}$ are listed in Table 15. Three levels are taken into the calculation as perturbers: $4p5p\ ^3D_2$, a level assigned as a mix of $3d10d$ and $4p5p$ (61 767.3 cm^{-1}), and $3d_{5/2}6d_{3/2}$ (59 363.5 cm^{-1}).

$J=3$. These series are perturbed by the level $4p5p\ ^3D_3$. In our model of calculation, the perturber is located to a point. The peak of $4p5p\ ^3D_3$ in the spectrum is so broad that it is difficult to decide in which point it lies. Our model is not fit for this case so that we did not conclude the perturber $4p5p\ ^3D_3$ in our calculation for the $J=3$ series. The results of these four series are listed in Tables 16–19. Because $3d11d$ $J=3$ levels are situated in the range of the perturber $4p5p\ ^3D_3$ and are mixed with it strongly (about 61 800–62 000 cm^{-1}), the levels $3d_{3/2}11d_{3/2}$, $3d_{3/2}11d_{5/2}$, $3d_{5/2}11d_{3/2}$, and $3d_{5/2}11d_{5/2}$ are not included in the fit for parameters.

$J=4$. The $3d_{3/2}nd_{5/2}$ and $3d_{5/2}nd_{3/2}$ series mixed strongly among themselves, especially in the low excited states where $3d_{3/2}nd_{5/2}$ and $3d_{5/2}nd_{3/2}$ components appear coinstantaneously with almost the same weight. The results of series

TABLE 26. [Ar] $3d_{5/2}ng_{7/2}$ $J=2$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 612.4	58 612.4	58 614.0	34		62 921.8	
6	59 956.7	59 956.7	59 956.0	35		62 927.1	
7	60 768.3	60 768.3	60 767.6	36		62 932.0	
8	61 295.3	61 295.3	61 294.8	37		62 936.6	
9		61 656.7		38		62 940.7	
10	61 915.2	61 915.2	61 914.9	39		62 944.6	
11		62 106.5		40		62 948.2	
12		62 252.0		41		62 951.5	
13		62 365.3		42		62 954.5	
14		62 455.1		43		62 957.4	
15		62 527.6		44		62 960.1	
16		62 586.9		45		62 962.6	
17		62 636.0		46		62 964.9	
18		62 677.2		47		62 967.1	
19		62 712.0		48		62 969.2	
20		62 741.8		49		62 971.1	
21		62 767.4		50		62 972.9	
22		62 789.6		51		62 974.6	
23		62 808.9		52		62 976.2	
24		62 825.9		53		62 977.7	
25		62 840.9		54		62 979.2	
26		62 854.2		55		62 980.5	
27		62 866.0		60		62 986.3	
28		62 876.6		65		62 990.8	
29		62 886.1		70		62 994.4	
30		62 894.7		75		62 997.3	
31		62 902.4		80		62 999.7	
32		62 909.5		90		63 003.3	
33		62 915.9		100		63 005.9	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

TABLE 27. [Ar] $3d_{3/2}ng_{7/2}$ $J=2$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 554.3	58 554.3	58 555.5	34		62 861.1	
6	59 897.4	59 897.5	59 896.4	35		62 866.5	
7	60 708.7	60 708.5	60 707.2	36		62 871.4	
8	61 235.1	61 235.3	61 234.4	37		62 875.9	
9	61 596.6	61 596.6	61 595.7	38		62 880.1	
10		61 855.0		39		62 883.9	
11		62 046.3		40		62 887.5	
12		62 191.7		41		62 890.8	
13		62 304.9		42		62 893.9	
14		62 394.7		43		62 896.7	
15		62 467.1		44		62 899.4	
16		62 526.4		45		62 901.9	
17		62 575.5		46		62 904.2	
18		62 616.7		47		62 906.4	
19		62 651.5		48		62 908.5	
20		62 681.2		49		62 910.4	
21		62 706.8		50		62 912.2	
22		62 729.0		51		62 913.9	
23		62 748.3		52		62 915.5	
24		62 765.3		53		62 917.1	
25		62 780.3		54		62 918.5	
26		62 793.5		55		62 919.8	
27		62 805.4		60		62 925.6	
28		62 816.0		65		62 930.2	
29		62 825.5		70		62 933.7	
30		62 834.0		75		62 936.6	
31		62 841.8		80		62 939.0	
32		62 848.8		90		62 942.6	
33		62 855.2		100		62 945.2	

[a]The experimental values T_{expt} are selected from Assimopoulos *et al.*[5]
[b]The results of R-matrix/MQDT are selected from Assimopoulos *et al.*[5]

$3d_{5/2}nd_{3/2}$ and $3d_{3/2}nd_{5/2}$ are listed in Tables 20 and 21. It can be observed from the table that the deviations in low excited states are much larger and those in higher excited states are relatively small. As for the levels assigned to series $3d_{3/2}nd_{5/2}$, the component of $3d_{5/2}nd_{3/2}$ is almost as much as $3d_{3/2}nd_{5/2}$ when n is small. So the levels $3d_{5/2}7d_{3/2}$ and $3d_{5/2}8d_{3/2}$ are counted in the calculation as peturbers.

$J=5$. There's only one $J=5$ $3dnd$ series, $3d_{5/2}nd_{5/2}$. This series is simple and pure with no perturbation and mix. We listed the results of this series in Table 23 with the experimental data and results of QMDT for comparison.

We studied eight $3dng$ series: $3d_{5/2}ng_{9/2}$ $J=2-3$, $3d_{5/2}ng_{7/2}$ $J=1-3$, $3d_{3/2}ng_{9/2}$ $J=3$, and $3d_{3/2}ng_{7/2}$ $J=2$, 3. The first five series converge to the limit $3d_{5/2}$ and the later three to $3d_{3/2}$. The perturber levels $4p5p$ even have no effect on the $3dng$ series, and the mix among these series can be ignored. Therefore, the $3dng$ series are relatively simpler and purer than the $3dnd$ series. The results of these eight series are listed in Tables 24–31. It can be seen from the tables that almost all the deviations are less than 1 cm^{-1}. As for all the $3dng$ series we calculated, 95% of the results have such accuracy.

The results of Poirrer and Semaoune with Coulomb

TABLE 28. $[\mathrm{Ar}]\,3d_{3/2}ng_{7/2}\,J=3$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 542.1	58 542.3	58 545.7	34		62 861.1	
6	59 892.0	59 891.1	59 892.4	35		62 866.4	
7	60 704.9	60 706.0	60 705.7	36		62 871.4	
8		61 234.2	61 233.7	37		62 875.9	
9	61 596.6	61 596.0	61 595.6	38		62 880.1	
10	61 854.6	61 854.7	61 854.4	39		62 883.9	
11		62 046.1	62 045.9	40		62 887.5	
12	62 191.5	62 191.5	62 191.5	41		62 890.8	
13		62 304.8	62 304.7	42		62 893.9	
14		62 394.6	62 394.6	43		62 896.7	
15		62 467.0	62 467.1	44		62 899.4	
16		62 526.3	62 526.4	45		62 901.9	
17	62 575.5	62 575.4	62 575.4	46		62 904.2	
18	62 616.6	62 616.6	62 616.7	47		62 906.4	
19		62 651.4		48		62 908.5	
20		62 681.2		49		62 910.4	
21		62 706.8		50		62 912.2	
22		62 728.9		51		62 913.9	
23		62 748.3		52		62 915.5	
24		62 765.3		53		62 917.0	
25		62 780.2		54		62 918.5	
26		62 793.5		55		62 919.8	
27		62 805.3		60		62 925.6	
28		62 815.9		65		62 930.2	
29		62 825.4		70		62 933.7	
30		62 834.0		75		62 936.6	
31		62 841.8		80		62 939.0	
32		62 848.8		90		62 942.6	
33		62 855.2		100		62 945.2	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

TABLE 29. $[\mathrm{Ar}]\,3d_{3/2}ng_{9/2}\,J=3$ series of Ca I (limit is 62 956.15 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 554.3	58 554.2	58 555.5	34		62 861.1	
6	59 897.4	59 897.7	59 896.4	35		62 866.5	
7	60 708.7	60 708.4	60 707.3	36		62 871.4	
8	61 235.1	61 235.2	61 234.2	37		62 875.9	
9	61 596.6	61 596.5	61 595.6	38		62 880.1	
10	61 854.7	61 855.0	61 854.3	39		62 883.9	
11	62 046.4	62 046.3	62 046.2	40		62 887.5	
12	62 191.5	62 191.7	62 191.6	41		62 890.8	
13		62 304.9	62 304.8	42		62 893.9	
14		62 394.7	62 394.6	43		62 896.7	
15		62 467.2	62 467.0	44		62 899.4	
16		62 526.4	62 526.4	45		62 901.9	
17	62 575.5	62 575.5	62 575.4	46		62 904.2	
18	62 616.6	62 616.7	62 616.7	47		62 906.4	
19		62 651.5		48		62 908.5	
20		62 681.2		49		62 910.4	
21		62 706.8		50		62 912.2	
22		62 729.0		51		62 913.9	
23		62 748.3		52		62 915.5	
24		62 765.3		53		62 917.1	
25		62 780.3		54		62 918.5	
26		62 793.6		55		62 919.8	
27		62 805.4		60		62 925.6	
28		62 816.0		65		62 930.2	
29		62 825.5		70		62 933.7	
30		62 834.1		75		62 936.6	
31		62 841.8		80		62 939.0	
32		62 848.8		90		62 942.6	
33		62 855.3		100		62 945.2	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

Green's function listed in Table 32 are computed in the jk coupling scheme. The transformation between jk and jj coupling schemes is[8]

$$|d_{5/2}g[k=\tfrac{5}{2}]J=3\rangle=-(\tfrac{8}{63})^{1/2}|d_{5/2}g_{7/2}J=3\rangle+(\tfrac{55}{63})^{1/2}|d_{5/2}g_{9/2}J=3\rangle. \quad (13)$$

Studying all the tables carefully, one will find that the deviations between R-matrix/MQDT results and experimental data are larger in low excited state and less in higher excited states. It agrees with the approximation to central potential when n is large. As for the present results, it can be observed that the deviations are obviously generally very small in low excited states as well as in higher excited states, except for where the mix is too strong. Compared with the results from the R-matrix/MQDT, it can be observed that the present results are almost as accurate as those of the combination method in high excited states but much better than theirs in low excited states. The essential of multichannel quantum defect theory is to treat excited electrons in different ways according to the distance between the electron and nuclear. The correlation between electrons is taken as a local effect when the electron is very near to the nuclear. In contrast, when the electron is far from this range it is treated as

TABLE 30. $[\mathrm{Ar}]\,3d_{5/2}ng_{9/2}\,J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 612.4	58 612.4	58 614.0	34		62 921.8	
6	59 956.7	59 956.6	59 956.0	35		62 927.1	
7	60 768.3	60 768.4	60 767.6	36		62 932.0	
8	61 295.3	61 295.3	61 294.8	37		62 936.6	
9	61 656.8	61 656.7	61 656.3	38		62 940.7	
10	61 915.2	61 915.2	61 915.0	39		62 944.6	
11	62 106.6	62 106.5	62 106.7	40		62 948.2	
12	62 252.3	62 252.0	62 252.2	41		62 951.5	
13	62 365.6	62 365.3	62 365.4	42		62 954.5	
14	62 455.4	62 455.1	62 455.3	43		62 957.4	
15	62 527.7	62 527.6	62 527.8	44		62 960.1	
16		62 586.9	62 587.0	45		62 962.6	
17	62 636.3	62 636.0	62 636.2	46		62 964.9	
18	62 677.3	62 677.2	62 677.3	47		62 967.1	
19		62 712.0		48		62 969.2	
20		62 741.8		49		62 971.1	
21		62 767.4		50		62 972.9	
22		62 789.6		51		62 974.6	
23		62 808.9		52		62 976.2	
24		62 825.9		53		62 977.7	
25		62 840.9		54		62 979.2	
26		62 854.2		55		62 980.5	
27		62 866.0		60		62 986.3	
28		62 876.6		65		62 990.8	
29		62 886.1		70		62 994.4	
30		62 894.7		75		62 997.3	
31		62 902.4		80		62 999.7	
32		62 909.5		90		63 003.3	
33		62 915.9		100		63 005.9	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

TABLE 31. $[\mathrm{Ar}]\,3d_{5/2}ng_{7/2}\,J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results				Theoretical results	
n	T_{expt}[a]	This work	R/MQDT[b]	n	T_{expt}[a]	This work	R/MQDT[b]
5	58 604.1	58 604.2	58 607.5	34		62 921.8	
6	59 953.0	59 952.7	59 953.5	35		62 927.1	
7	60 766.5	60 766.9	60 766.6	36		62 932.0	
8		61 294.8	61 294.5	37		62 936.6	
9	61 656.8	61 656.6	61 656.3	38		62 940.7	
10	61 915.2	61 915.3	61 915.0	39		62 944.6	
11		62 106.6	62 106.7	40		62 948.2	
12	62 252.3	62 252.1	62 252.2	41		62 951.5	
13	62 365.6	62 365.4	62 365.4	42		62 954.6	
14	62 455.4	62 455.2	62 455.3	43		62 957.4	
15	62 527.7	62 527.7	62 527.8	44		62 960.1	
16		62 586.9	62 587.0	45		62 962.6	
17	62 636.3	62 636.1	62 636.2	46		62 964.9	
18	62 677.3	62 677.3	62 677.3	47		62 967.1	
19		62 712.1	62 636.3	48		62 969.2	
20		62 741.8	62 677.3	49		62 971.1	
21		62 767.4		50		62 972.9	
22		62 789.6		51		62 974.6	
23		62 809.0		52		62 976.2	
24		62 825.9		53		62 977.7	
25		62 840.9		54		62 979.2	
26		62 854.2		55		62 980.5	
27		62 866.0		60		62 986.3	
28		62 876.6		65		62 990.8	
29		62 886.1		70		62 994.4	
30		62 894.7		75		62 997.3	
31		62 902.5		80		62 999.7	
32		62 909.5		90		63 003.3	
33		62 915.9		100		63 005.9	

[a]The experimental values T_{expt} are selected from Luc-koenig *et al.*[6]
[b]The results of R-matrix/MQDT are selected from Luc-koenig *et al.*[6]

a single electron. So the higher the electron was excited, the closer to the true situation the model is, and the more accurate the results are, while in low excited states it cannot usually give very precise results. One advantage of WBEPM theory is better results in low excited states. Another is the WBEPM theory is much simpler. In the theoretical method of R-matrix/MQDT, more channels would be taken into the computation and a larger box of radius would be introduced in the R-matrix calculation in order to get more accurate results. The calculation would then be more complex. As for the calculation within the framework of WBEPM theory, the computation is much simpler because the problem of a many-valence-electron system can be transformed to a single electron problem by separating the weakest bound electron from the nonweakest bound electron.

4. Conclusions

In this paper, the even parity $J=0-5$ $3dnl$ $(l=s,d,g)$ autoionizing levels of calcium have been calculated via the WBEPM theory. By emphasizing the treatment of perturbation, the correlation between electrons is considered

TABLE 32. [Ar] $3d_{5/2}ng[k=5/2]$ $J=3$ series of Ca I (limit is 63 016.84 cm^{-1})—Comparison between calculated results and experimental values (cm^{-1})

		Theoretical results		
n	T_{expt}[a]	This work[b]	R/MQDT[c]	Coulomb Green's function[d]
5	58 612.4	58 611.4	58 614.0	58 611.86
6	59 956.7	59 956.1	59 956.0	59 956.58
7	60 768.3	60 768.2	60 767.4	60 768.43
8	61 295.3	61 295.3	61 294.8	61 295.62
9	61 656.8	61 656.7	61 656.3	61 657.11
10	61 915.2	61 915.2	61 915.0	61 915.68
11	62 106.6	62 106.5	62 106.7	62 106.97
12	62 252.3	62 252.0	62 252.2	62 252.44
13	62 365.6	62 365.3	62 365.4	62 365.63
14	62 455.4	62 455.1	62 455.3	62 455.43
15	62 527.7	62 527.6	62 527.8	62 527.86
16		62 586.9	62 587.0	
17	62 636.3	62 636.0	62 636.2	
18	62 677.3	62 677.2	62 677.3	
19		62 712.1		
20		62 741.8		
30		62 894.7		
40		62 948.2		
50		62 972.9		
60		62 986.3		
70		62 994.4		
80		62 999.7		
90		63 003.3		
100		63 005.9		

[a]The experimental values T_{expt} are calculated from Eq. (13) using the values from Luc-koenig *et al.*[6]
[b]These values are calculated from Eq. (13), using the data in Tables 30 and 31.
[c]The results of R-matrix/MQDT are calculated from Eq. (13), using the values from Luc-koenig *et al.*[6]
[d]The results of Coulomb Green's function are selected from Poirier and Semaoune.[8]

relatively complete. Part of the results are listed herein compar-ing the experimental data and the results obtained from other methods. This shows a high correlation between our calculated results and the exiting data.

There are several levels in the experimental and theoretical data concerning the even parity autoionization states of calcium that have not been reported. These levels are predicted here. We hope that the present work will stimulate further experimental exploration on the even parity autoionization states of Ca to confirm our calculations.

5. References

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