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Dynamic polarizabilities and Rydberg states of the sodium isoelectronic sequence

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The frequency-dependent dipole polarizabilities $\alpha_d(\omega)$ of the sodium isoelectronic sequence ($Z=11,\ldots,18$) have been calculated within linear-response theory using the time-dependent coupled Hartree-Fock scheme. The excitation energies for the transitions $3\,^2S \rightarrow n\,^2P$ ($n=3,\ldots,7$) have been estimated from the position of the poles of a frequency-dependent functional, and analytic representations of the excited Rydberg p-state wave functions have been obtained. The extrapolated polarizability values $\alpha_d(\omega)_{\omega\rightarrow 0}$ are compared with the available static data. The transition energies compared well with spectroscopic data. The oscillator strengths have been estimated in length form and the quantum defect values have been calculated using complete screening. They all compare favorably with data currently available.

I. INTRODUCTION

Rydberg states of atoms are of considerable interest today because of their importance when investigating superradiance, laser isotope separation, microwave detectors, and various other physical processes.[1,2] The recent development of tunable lasers has made the study of such states very effective and exciting from both the theoretical and experimental points of view.[3–13] The effects of electric and magnetic fields[14–21] on such states have been extensively investigated while the collisional aspects of such states are under current investigation.[22–25] Recently very interesting experiments have been performed for the measurements of atomic dimensions by transmitting a beam of Rydberg atoms through very narrow slits.[26] The dephasing of Rydberg state atoms may be studied by using quantum beat echoes in a collection of coherently excited high Rydberg states of atoms.[27]

Theoretical investigations of Rydberg states very often use the improved virtual orbital method,[28] the frozen-core method,[29–31] and iterative and noniterative numerical methods using model potentials[32–36] and semiempirical model potentials.[37] Quantum-defect theory[1,38–40] has provided extremely valuable information on this matter. A recent calculation of such states for He has been performed by Drachman[41] using an optical potential analysis and for the lithium atom, the Schwinger T-matrix method has been applied.[42] Several good reviews on the subject are now available.[1,2,43,44]

For single excitations we have demonstrated that the time-dependent coupled Hartree-Fock (TDCHF) theory furnishes accurate excitation energies and excited-state wave functions.[45–47] These are obtained as a by-product in a dynamic polarizability calculation.[48,49] The method proper and several applications have been reviewed by Oddershede[50] and McCurdy *et al.*[51] In this paper we have studied the response of sodiumlike atomic systems ($Z=11,\ldots,18$) in the presence of a frequency-dependent dipolar field. The dynamic polarizabilities have been calculated and the excitation energies have been estimated from the position of the poles of the dynamic polarizability values for the first five transitions $3s\rightarrow np$ ($n=3,\ldots,7$). The details of the theory were given earlier.[45–49] In Sec. II, however, we present very briefly the salient features of the method used. The results are discussed in Sec. III.

II. METHOD

We consider the ground ^2S state of sodiumlike atoms to be described by the usual nonrelativistic Hamiltonian. A time-dependent external perturbation of the form

$$H'(\mathbf{r},t)=\sum_i h_i'(\mathbf{r})e^{-i\omega t}+\text{c.c.}\,, \tag{1}$$

is applied to the system, where

$$h'(\mathbf{r})=\lambda r\cos\theta \tag{2}$$

indicating a dipolar excitation of the system. This admixes a first-order correction $\delta\psi_i^{\pm}$ to each ground orbital ψ_i each of which is subsequently determined from a functional[52–54]

$$J(\Phi)=\frac{1}{T}\int_0^T dt\frac{\langle\Phi(\mathbf{r},t)[H-i\partial/\partial t]\Phi(\mathbf{r},t)\rangle}{\langle\Phi(\mathbf{r},t)\,|\,\Phi(\mathbf{r},t)\rangle} \tag{3}$$

subject to the variation

$$\delta J(\Phi)=0\,. \tag{4}$$

Here H is the total Hamiltonian including the external field and $\Phi(\mathbf{r},t)$ is the total wave function represented by

$$\Phi(\mathbf{r},t)=e^{-iE_0t}A\prod_i(\psi_i+\delta\psi_i^- e^{-i\omega t}+\delta\psi_i^+ e^{i\omega t})\,, \tag{5}$$

where E_0 is the HF ground-state energy. The excitation energies are obtained from the position of the poles of the dynamic polarizability

$$\alpha_d(\omega)=\sum_k(\langle\delta\psi_k^-\,|\,r\cos\theta\,|\,\psi_k\rangle+\langle\delta\psi_k^+\,|\,r\cos\theta\,|\,\psi_k\rangle)\,. \tag{6}$$

Renormalized first-order perturbed functions $\delta\psi_k$ at resonance give a reasonably accurate representation of the excited-state wave functions of the system. These may be utilized to estimate the dipolar oscillator strength values and matrix elements of different operators. These are also useful in collision calculations, where singly excited states are required which are otherwise difficult to calculate. In the next section we discuss the results.

III. RESULTS AND DISCUSSION

In this calculation we studied the isoelectronic sequence Na,Mg^+,Al^{2+},Si^{3+},P^{4+},S^{5+},Cl^{6+},Ar^{7+} for the transitions $3\,^2S \rightarrow n\,^2P$ ($n=3,\ldots,7$). The ground-state wave functions are those of Clementi.[55] The radial parts of the perturbed functions are of the form

$$\delta\psi_i^{\pm}(r) = \sum_p C_{ip}^{\pm} \chi_{ip}(r)\,, \tag{7}$$

where the χ_{ip}'s are appropriate Slater bases and the linear coefficients are obtained variationally. Presently we have used a 12-parameter representation for all the excited states. The dynamic polarizability values $\alpha_d(\omega)$ have been determined using Eq. (6). The static limit $\alpha_d(\omega)_{\omega\rightarrow 0}$ has been evaluated and compared with the available static results in Table I. For sodium the static limit is larger than the experimental value. However, it compares favorably with the finite perturbation calculation of Reinsch and Meyer[56] without full correlation and with the HF values estimated by Cohen and Drake[57] using the Z-expansion technique. For the isoelectronic series Mg^+—Cl^{6+}, our results, although slightly lower, are in good agreement with those of Cohen and Drake.[57] The dynamic polarizabilities of Na are plotted against frequency in Fig. 1 for the five transitions concerned. The pattern clearly shows the positions of the poles of $\alpha_d(\omega)$. In Fig. 2 we plotted the static limit $\alpha_d(\omega)_{\omega\rightarrow 0}$ versus the atomic number Z. Very regular behavior is observed.

TABLE I. Static limit $\alpha_d(\omega)_{\omega\rightarrow 0}$ for the dynamic polarizabilities.

	Dipole polarizability (Å^3)	
Ion	Static limit (Å^3)	Static values
Na	28.34	24.4±1.7,[a] 24.74,[b] 27.2,[c] 27.1,[d] 28.56,[e] 24.45,[f] 26.78,[g] 24.12,[h] 24.93[i]
Mg^+	5.764	7.41,[g] 6.75[h]
Al^{2+}	2.2896	3.05,[g] 2.80[h]
Si^{3+}	1.1753	1.55,[g] 1.43[h]
P^{4+}	0.6960	
S^{5+}	0.4490	
Cl^{6+}	0.3080	0.376,[g] 0.352[h]
Ar^{7+}	0.2211	

[a] W. D. Hall and J. C. Zorn, Phys. Rev. A 10, 1141 (1974).

[b] R. M. Sternheimer, Phys. Rev. 183, A112 (1969).

[c] P. W. Langhoff and R. P. Hurst, Phys. Rev. 139, A1415 (1965).

[d] M. Yoshimine and R. P. Hurst, Phys. Rev. 135, A612 (1964).

[e] Reference 56.

[f] Coupled electron pair approximation results obtained in Ref. 56.

[g] Reference 57.

[h] Results obtained by a modified formula in Ref. 57.

[i] P. K. Mukherjee, R. K. Moitra, and A. Mukherji, Int. J. Quantum Chem. 5, 637 (1971).

The transition energies as obtained from the position of the poles of the dynamic polarizability values are displayed in Table II. The results are compared with the spectroscopic values of Moore,[58] and those of Bashkin and Stoner.[59] For the $3s \rightarrow 3p$ transition of sodium the transition energy is off by 7.6% and it goes down to about 1% for the higher-order transitions for the heavier

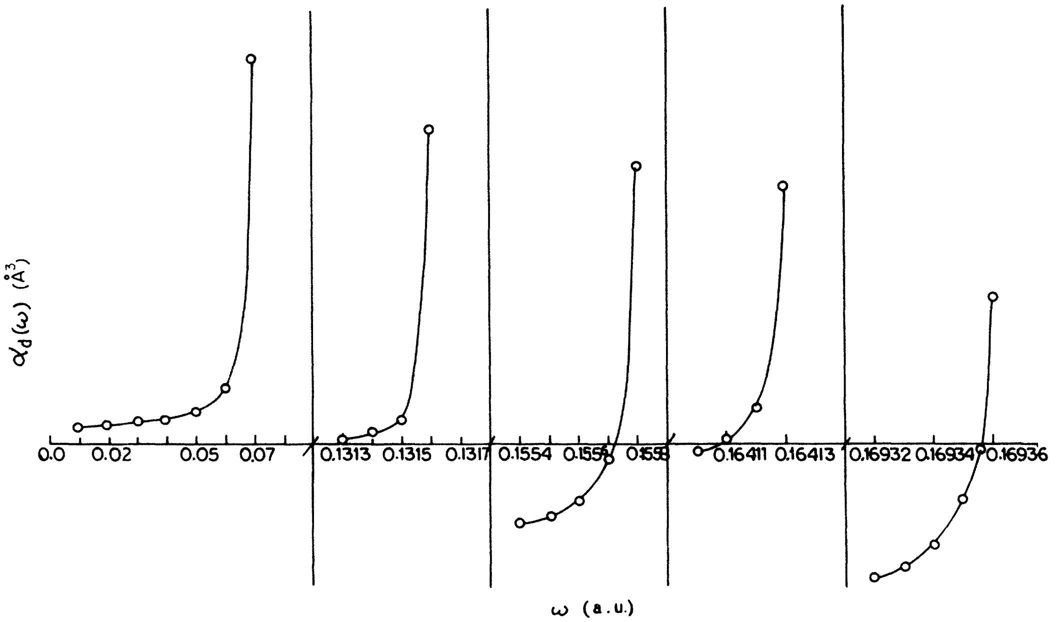

FIG. 1. Plot of $\alpha_d(\omega)$ (in arbitrary scale) vs ω for the first five transitions of sodium near resonance.

TABLE II. Transition energies (a.u., 1 a.u. = 219 474.62 cm^{-1}), oscillator strength values, and effective quantum number as obtained from frequency-dependent calculations.

		Excitation energies				Oscillator strength values		Effective quantum number		
Ion	Transition Scheme	Calc.	Expt. values[a]	Other values	% dev.	Calc.	Other values	Calc.	Expt. value[a]	Other values[h]
Na	$3\,^2S \rightarrow 3\,^2P$	0.0714	0.0773	0.0715[b] 0.073[c] 0.0774[d] 0.0723[e]	7.6	0.9688	0.982[f] 0.968[b] 0.987[c] 0.980[d] 0.9694[g] 0.9468[h] 0.965[i]	2.1265	2.1167	2.117
	$\rightarrow 4\,^2P$	0.1316	0.1379	0.132[b] 0.132[c] 0.1387[d] 0.1315[e]	4.6	0.0121	0.0142[f] 0.0103[b] 0.013[c] 0.0133[d] 0.0138[g] 0.0154[h] 0.0127[i]	3.1506	3.1326	3.133
	$\rightarrow 5\,^2P$	0.1558	0.1597	0.153[b] 0.1606[d] 0.1528[e]	2.4	0.0020	0.002 21[f] 0.001 32[b] 0.0020[d] 0.0021[g] 0.0026[h]	4.3710	4.1378	4.139
	$\rightarrow 6\,^2P$	0.1641	0.1699	0.1709[d] 0.1630[e]	3.4	0.0004	0.00073[f] 0.0006[d] 0.000 65[g] 0.000 84[h]	5.2940	5.1403	5.141
	$\rightarrow 7\,^2P$	0.1694	0.1756		3.6	0.0001	0.000 36[f] 0.000 28[g] 0.000 38[h]	6.2970	6.1417	6.142
Mg^+	$3\,^2S \rightarrow 3\,^2P$	0.1544	0.1627	0.158[c] 0.1622[d]	5.1	0.928	0.940[f] 0.955[c] 0.943[d] 0.8993[h] 0.913[i]	2.2985	2.2645	2.266
	$\rightarrow 4\,^2P$	0.3573	0.3674	0.358[c] 0.3687[d]	2.8	0.0014	0.000 23[f] 0.000[c] 0.0006[d] 0.000 103[h] 0.00097[i]	3.2971	3.2862	3.287
	$\rightarrow 5\,^2P$	0.4334	0.4441	0.4458[d]	2.4	0.0018	0.0010[f] 0.0013[d] 0.000 775[h]	4.3057	4.2934	4.295
	$\rightarrow 6\,^2P$	0.4702	0.4813	0.4832[d]	2.3	0.0012	0.0009[d] 0.0006[h]	5.3045	5.2970	5.298
	$\rightarrow 7\,^2P$	0.4973	0.5021[j]		1.0	0.0007	0.000 41[h]	6.7435	6.2987[j]	6.300
Al^{2+}	$3\,^2S \rightarrow 3\,^2P$	0.2355	0.2452	0.2434[d]	4.0	0.816	0.875[f] 0.869[d] 0.831[h] 0.836[i]	2.3786	2.3704	2.372
	$\rightarrow 4\,^2P$	0.6422	0.6546	0.6560[d]	1.9	0.018	0.011[f] 0.0133[d] 0.009 96[h]	3.4025	3.3923	3.394
	$\rightarrow 5\,^2P$	0.7996	0.8131	0.8151[d]	1.7	0.0084	0.0068[f] 0.0076[d] 0.005 99[h]	4.4108	4.3996	4.402
	$\rightarrow 6\,^2P$	0.8775	0.8914	0.8935[d]	1.6	0.0051	0.0042[d] 0.003 33[h]	5.4162	5.4029	5.405
	$\rightarrow 7\,^2P$	0.9318	0.9357		0.4	0.0056	0.001 99[h]	6.7390	6.4024	6.407

TABLE II. (*Continued*).

Ion	Transition Scheme	Excitation energies			% dev.	Oscillator strength values		Effective quantum number		
		Calc.	Expt. values^{a}	Other values		Calc.	Other values	Calc.	Expt. value^{a}	Other values^{h}
Si^{3+}	$3\,^2S \rightarrow 3\,^2P$	0.3148	0.3259		3.4	0.774	0.803^{f} 0.766^{h} 0.765^{i}	2.4558	2.4488	2.451
	$\rightarrow 4\,^2P$	0.9804	0.9949		1.5	0.035	0.033^{f} 0.0278^{h}	3.4793	3.4699	3.472
	$\rightarrow 5\,^2P$	1.2439	1.2600		1.3	0.018	0.012 76^{h}	4.4871	4.4772	4.479
	$\rightarrow 6\,^2P$	1.3760	1.3929		1.2	0.0094	0.006 59^{h}	5.4919	5.4807	5.483
	$\rightarrow 7\,^2P$	1.4520	1.4687		1.1	0.0046	0.003 83^{h}	6.5019	6.4849	6.485
P^{4+}	$3\,^2S \rightarrow 3\,^2P$	0.3930	0.4057		3.1	0.665	0.67^{f} 0.707^{h} 0.702^{i}	2.5155	2.5090	2.511
	$\rightarrow 4\,^2P$	1.3696	1.3865		1.2	0.053	0.055^{f} 0.0479^{h}	3.5375	3.5289	3.531
	$\rightarrow 5\,^2P$	1.7636	1.7823		1.1	0.0245	0.22^{f} 0.019 58^{h}	4.5458	4.5356	4.538
	$\rightarrow 6\,^2P$	1.9626	1.9825		1.0	0.014	0.009 78^{h}	5.5494	5.5408	5.541
	$\rightarrow 7\,^2P$	2.0781	2.0976		0.9	0.0055	0.0056^{h}	6.5608	6.5421	6.543
S^{5+}	$3\,^2S \rightarrow 3\,^2P$	0.4708	0.4853	0.4835^{c}	3.0	0.644	0.64^{f} 0.689^{c} 0.658^{h} 0.651^{i}	2.5630	2.5568	2.559
	$\rightarrow 4\,^2P$	1.8093	1.8289	1.817^{c}	1.1	0.084	0.071^{f} 0.073^{c} 0.068^{h}	3.5836	3.5754	3.578
	$\rightarrow 5\,^2P$	2.3569	2.3790		0.9	0.030	0.028^{f} 0.026^{h}	4.5909	4.5821	4.585
	$\rightarrow 6\,^2P$	2.6373	2.6594		0.8	0.0114	0.0127^{h}	5.6017	5.5880	5.588
	$\rightarrow 7\,^2P$	2.7984				0.0109	0.0072^{h}	6.6055		6.590
Cl^{6+}	$3\,^2S \rightarrow 3\,^2P$	0.5480	0.5647	0.5569^{d}	3.0	0.631	0.63^{f} 0.626^{d} 0.6135^{h} 0.604^{i}	2.6019	2.5944	2.599
	$\rightarrow 4\,^{2P}$	2.2989	2.3216	2.3167^{d}	1.0	0.105	0.102^{f} 0.0987^{d} 0.0876^{h}	3.6214	3.6096	3.616
	$\rightarrow 5\,^2P$	3.0230	3.0498^{j}	3.0446^{d}	0.9	0.036	0.0357^{d} 0.0338^{h}	4.6277	4.6208^{j}	4.616
	$\rightarrow 6\,^2P$	3.3939	3.4230^{j}	3.4174^{d}	0.9	0.015	0.0172^{d} 0.0166^{h}	5.6294	5.6275^{j}	5.616
	$\rightarrow 7\,^2P$	3.6094				0.0049	0.0094^{h}	6.6285		6.616
Ar^{7+}	$3\,^2S \rightarrow 3\,^2P$	0.6248	0.6443		3.0	0.565	0.57^{f} 0.575^{h} 0.566^{i}	2.6342	2.6275	2.631
	$\rightarrow 4\,^2P$	2.8377	2.8647		0.9	0.134	0.12^{f} 0.106^{h}	3.6525	3.6431	3.648
	$\rightarrow 5\,^2P$	3.7617	3.7930		0.8	0.041	0.039^{f} 0.373^{h}	4.6583	4.6475	4.653
	$\rightarrow 6\,^2P$	4.2379	4.2748^{j}		0.9	0.024	0.0188^{h}	5.6612	5.6645^{j}	5.649
	$\rightarrow 7\,^2P$	4.6997				0.0089	0.0106^{h}	7.7219		6.649

[a] Reference 58.
[b] Reference 60.
[c] Reference 61.
[d] Reference 62.
[e] Reference 63.
[f] Reference 64.
[g] Reference 65.
[h] Reference 66.
[i] Reference 67.
[j] Reference 59.

TABLE III. Excited-state wave functions as obtained from frequency-dependent calculations ($[\pm n]=10^{\pm n}$).

Na

			C				C			C
n	ρ	3p	4p	5p	n	ρ	6p	n	ρ	7p
1	7.0	1.941 50	5.986 24	1.542 80[+1]	1	5.0	1.190 20	1	4.0	9.848 57[-1]
1	4.5	9.925 46[-1]	3.494 70[+1]	1.024 29[+2]	2	3.0	5.747 52[-1]	2	3.5	-8.144 83[-1]
2	4.5	1.219 17	4.431 24[+1]	1.297 22[+2]	3	2.0	-1.709 01	2	1.8	3.843 31[-1]
1	3.0	8.630 46[-1]	-3.862 51[+1]	-1.154 47[+2]	3	1.5	1.379 38	3	1.8	-3.710 80[-1]
2	3.0	-4.699 83[-1]	2.925 53[+1]	8.733 79[+1]	4	1.5	-6.545 76[-1]	3	1.0	5.232 90[-2]
2	1.8	2.326 89[-1]	-3.783 98	-1.152 91[+1]	4	1.0	7.272 29[-2]	4	1.0	-2.482 79[-2]
3	1.8	-2.204 52[-1]	1.693 49	5.308 93	5	1.0	-4.799 19[-2]	4	0.6	3.646 61[-3]
3	1.0	-4.022 92[-2]	-1.485 53[-1]	-3.976 91[-1]	4	0.7	7.113 79[-2]	5	0.6	-5.389 15[-4]
4	1.0	-1.983 34[-3]	5.652 42[-2]	1.701 78[-1]	5	0.7	-5.726 38[-3]	5	0.4	8.141 21[-5]
3	0.6	-6.408 07[-3]	-4.991 78[-2]	-1.375 85[-1]	5	0.4	9.527 17[-5]	6	0.4	-4.831 03[-6]
4	0.6	-9.015 13[-6]	4.806 86[-3]	1.322 98[-2]	6	0.4	-5.629 39[-6]	6	0.2	2.509 48[-8]
4	0.3	-1.272 07[-7]	1.664 12[-5]	-4.643 52[-5]	6	0.25	3.545 20[-8]	7	0.2	-5.754 28[-10]

Mg^+

				C		
n	ρ	3p	4p	5p	6p	7p
1	5.0	8.981 89	-5.344 75	-3.569 29	-2.584 88	-2.607 55
2	4.0	-3.689 20	1.666 89	7.783 60[-1]	1.846 64[-1]	-3.295 08
2	2.5	3.492 98	-1.665 08	-8.671 04[-1]	-3.541 30[-1]	2.161 82
3	2.5	-3.240 40	1.465 29	7.110 17[-1]	2.000 67[-1]	-2.816 76
3	1.5	-6.096 34[-2]	1.881 16[-1]	1.943 95[-1]	2.178 63[-1]	9.686 15[-1]
4	1.5	-1.467 97[-1]	2.427 83[-2]	-9.300 30[-3]	-3.883 98[-2]	-3.797 31[-1]
4	1.0	-1.567 07[-4]	6.886 94[-3]	6.159 23[-3]	8.136 23[-3]	5.927 86[-2]
5	1.0	-7.482 49[-4]	-3.266 57[-3]	-3.053 41[-3]	-2.950 61[-3]	-1.083 47[-2]
5	0.6	2.341 78[-5]	-1.764 91[-4]	-1.638 36[-4]	-1.374 39[-4]	-1.353 91[-4]
6	0.6	-1.826 77[-6]	1.023 25[-5]	2.562 36[-5]	3.081 13[-5]	6.354 49[-5]
6	0.4	3.270 49[-8]	-1.322 85[-7]	8.628 01[-8]	-8.405 35[-7]	-7.487 63[-6]
7	0.4	-1.026 69[-9]	4.161 58[-9]	-1.162 99[-9]	-1.014 78[-8]	3.037 50[-7]

Al^{2+}

				C		
n	ρ	3p	4p	5p	6p	7p
1	6.0	1.519 47[+1]	-9.550 48	-6.562 26	-4.840 70	-4.922 47
2	4.5	1.174 28[+2]	-1.568 20[+1]	-3.373 92	1.099 42[-1]	-1.000 78[+2]
2	3.5	-1.069 18[+2]	1.276 72[+1]	1.689 17	-1.221 90	9.200 38[+1]
3	3.5	1.652 16[+2]	-3.045 51[+1]	-8.351 68	-1.823 26	-1.109 48[+2]
3	2.8	-7.434 91[+1]	1.876 25[+1]	6.667 30	2.764 21	3.670 20[+1]
4	2.8	2.345 73[+1]	-6.410 08	-1.850 58	-4.481 42[-1]	-6.444 81
4	1.8	-1.299 67	8.195 20[-1]	4.022 23[-1]	2.259 70[-1]	-6.555 84[-1]
5	1.8	2.061 50[-1]	-2.020 71[-1]	-1.004 28[-1]	-5.392 76[-2]	3.018 53[-1]
5	1.0	-2.008 53[-3]	-5.372 10[-3]	-8.765 20[-3]	-9.064 92[-3]	-3.058 50[-2]
6	1.0	2.462 81[-4]	2.981 60[-4]	1.289 61[-3]	1.597 77[-3]	6.009 94[-3]
6	0.6	-1.753 35[-6]	-5.461 55[-7]	1.540 47[-5]	1.011 02[-5]	-1.483 10[-4]
7	0.6	9.227 73[-8]	2.479 99[-8]	-6.660 38[-7]	-1.894 01[-6]	9.060 26[-6]

Si^{3+}

			C				C			C
n	ρ	3p	4p	5p	n	ρ	6p	n	ρ	7p
1	7.0	2.469 55[+1]	-1.488 72[+1]	-1.035 41[+1]	1	7.0	-7.706 25	1	7.0	-4.737 03
2	4.0	1.405 01[+1]	-8.146 22	-4.955 98	2	4.0	-3.534 88	2	4.0	-5.449 44
3	4.0	-1.534 65[+1]	8.947 71	3.466 41	3	4.0	1.943 14	3	4.0	1.568 40[+1]
3	2.5	-2.802 99	2.371 58	2.934 62	3	2.5	2.535 62	3	2.5	-4.451 22
4	2.5	-1.364 52	7.213 37[-1]	-4.020 60[-1]	4	2.5	-5.690 99[-1]	4	2.5	4.565 16
4	1.5	-1.030 54[-1]	-3.966 86[-2]	5.215 84[-2]	4	1.5	7.200 43[-2]	4	1.5	-6.232 65[-1]
5	1.5	1.960 73[-2]	-4.699 74[-2]	-8.814 31[-2]	5	1.5	-9.328 99[-2]	5	1.5	1.624 76[-1]
5	1.0	-7.050 42[-4]	-7.681 67[-4]	6.546 42[-3]	5	1.0	1.032 24[-2]	5	1.0	-1.211 02[-2]
6	1.0	7.762 89[-5]	4.373 04[-5]	-3.802 08[-5]	6	1.0	-2.592 97[-5]	6	1.0	2.472 74[-3]
6	0.6	-5.542 25[-7]	2.051 76[-7]	4.433 73[-6]	5	0.6	-4.382 07[-4]	6	0.6	-1.157 97[-4]
7	0.6	3.243 36[-8]	-1.382 77[-8]	-2.659 18[-7]	6	0.6	1.517 08[-5]	7	0.6	8.417 39[-6]
7	0.4	-7.220 54[-11]	4.299 07[-11]	6.450 01[-10]	7	0.4	-4.665 48[-11]	7	0.4	-1.252 27[-8]

TABLE III. (*Continued*).

P^{4+}

n	ρ	C $3p$	C $4p$	n	ρ	C $5p$	n	ρ	C $6p$	n	ρ	C $7p$
1	9.0	3.501 58[+1]	−2.116 38[+1]	1	10.0	3.372 47[+1]	1	9.0	−1.018 46[+1]	1	7.5	−8.937 90
2	6.0	1.218 05[+2]	−8.222 27[+1]	1	7.0	−4.809 74[+1]	2	6.0	−8.882 01[+1]	2	4.5	−3.170 38
2	4.0	−6.070 16[+1]	4.437 45[+1]	2	7.0	2.977 13[+2]	2	4.0	6.362 90[+1]	3	4.5	−5.684 08
3	4.0	1.379 13[+2]	−1.048 05[+2]	2	5.0	−2.004 34[+2]	3	4.0	−1.887 92[+2]	3	3.0	8.902 53
3	3.2	−7.228 98[+1]	5.569 83[+1]	3	5.0	4.115 55[+2]	3	3.2	1.023 09[+2]	4	3.0	−4.722 68
4	3.2	2.010 03[+1]	−1.573 32[+1]	3	3.5	−3.675 18[+1]	4	3.2	−3.792 92[+1]	4	1.8	6.590 41[−1]
4	2.2	−1.497 16	7.029 95[−1]	4	3.5	1.853 91[+2]	4	2.2	7.669 99[−1]	5	1.8	−5.320 84[−1]
5	2.2	9.404 16[−2]	−2.158 57[−1]	3	2.5	−1.012 08[+2]	5	2.2	3.043 33[−1]	5	1.2	6.830 88[−2]
5	1.6	3.560 71[−2]	−1.364 54[−1]	4	2.5	3.190 15[+1]	5	1.6	−3.415 67[−1]	6	1.2	−5.524 48[−3]
6	1.6	−6.650 96[−3]	1.412 28[−2]	4	1.5	−1.182 97	6	1.6	7.754 95[−2]	6	0.8	−7.575 12[−4]
6	1.0	5.866 51[−5]	−9.449 17[−5]	5	1.5	2.270 41[−1]	6	1.0	8.382 28[−4]	7	0.8	7.167 50[−5]
7	1.0	−4.908 17[−6]	7.865 74[−6]	5	1.0	2.589 85[−3]	7	1.0	−1.900 97[−4]	7	0.5	1.585 52[−8]

S^{5+}

n	ρ	C $3p$	C $4p$	C $5p$	C $6p$	n	ρ	C $7p$
1	10.5	4.780 12[+1]	−2.923 57[+1]	−2.023 10[+1]	−1.561 30[+1]	1	8.0	−1.159 95[+1]
2	7.0	1.574 67[+2]	−1.020 88[+2]	−7.834 79[+1]	−4.178 68[+1]	2	4.8	−5.838 54
2	4.5	−4.798 92[+1]	3.474 67[+1]	3.098 69[+1]	7.445 27	3	4.8	3.932 91
3	4.5	8.546 03[+1]	−7.123 24[+1]	−8.355 56[+1]	2.150 29[+1]	3	3.4	8.543 71
3	3.5	−4.299 78[+1]	3.930 64[+1]	4.897 89[+1]	−1.504 18[+1]	4	3.4	−1.969 11
4	3.5	2.080 85	−7.269 36	−1.847 85[+1]	1.965 55[+1]	4	2.2	4.065 39[−1]
4	2.5	−5.009 89[−1]	5.853 08[−1]	1.596 87	−1.950 96	5	2.2	−8.390 85[−1]
5	2.5	−4.064 01[−1]	−5.588 08[−1]	−5.605 24[−1]	−6.892 65[−1]	5	1.4	4.780 98[−2]
5	1.9	9.355 57[−2]	−3.080 51[−1]	−5.618 42[−1]	6.869 28[−2]	6	1.4	1.975 94[−2]
6	1.9	−1.646 22[−2]	2.654 55[−2]	1.289 30[−1]	−5.353 02[−2]	6	1.0	−6.859 93[−3]
6	1.3	1.527 71[−4]	−3.001 05[−4]	5.591 48[−3]	2.464 98[−2]	7	1.0	6.935 97[−4]
7	1.3	−1.340 25[−5]	2.816 20[−5]	−3.390 23[−4]	−3.976 01[−3]	7	0.6	1.339 18[−7]

Cl^{6+}

n	ρ	C $3p$	C $4p$	C $5p$	C $6p$	n	ρ	C $7p$
1	8.5	−5.70391[+1]	3.536 80[+1]	2.472 46[+1]	1.876 86[+1]	1	8.5	1.318 69[+1]
2	5.2	−3.762 63[+1]	2.143 78[+1]	1.409 16[+1]	8.783 07	2	5.2	1.648 05[+1]
3	5.2	8.384 54[+1]	−4.574 14[+1]	−2.677 59[+1]	−3.840 97	3	4.2	−4.110 73[+1]
3	3.6	1.291 01	−9.095 60	−1.078 81[+1]	−1.844 92[+1]	4	3.6	4.360 24[+1]
4	3.6	2.997 60[+1]	−1.447 42[+1]	−6.626 51	6.138 39	4	2.5	−2.080 99[+1]
4	2.5	−4.399 73	3.401 06	2.171 07	−3.941 90[−1]	5	2.5	1.330 38[+1]
5	2.5	2.140 87	−4.183 99[−3]	8.204 98[−1]	1.731 12	5	1.7	−1.390 21
5	1.7	−1.703 66[−1]	1.560 45[−1]	3.130 65[−2]	−3.448 87[−2]	6	1.7	2.362 82[−1]
6	1.7	3.772 84[−2]	−3.077 71[−2]	−5.175 79[−2]	−7.485 33[−2]	6	1.2	2.810 66[−3]
6	1.2	−1.301 71[−3]	9.344 53[−4]	7.144 24[−4]	8.223 88[−3]	7	1.2	2.246 98[−4]
7	1.2	1.268 19[−4]	−9.057 12[−5]	−7.387 80[−5]	−4.472 37[−4]	6	0.8	−4.454 48[−4]
7	0.8	−1.619 75[−7]	1.151 05[−7]	1.129 87[−7]	3.592 86[−7]	7	0.8	2.139 06[−5]

Ar^{7+}

n	ρ	C $3p$	C $4p$	C $5p$	C $6p$	n	ρ	C $7p$
1	9.0	−7.172 06[+1]	4.472 78[+1]	3.118 89[+1]	2.367 20[+1]	1	9.0	1.417 87[+1]
2	5.5	−4.128 91[+1]	2.335 23[+1]	1.635 77[+1]	9.989 83	2	5.5	3.501 15
3	5.5	6.351 21[+1]	−3.353 70[+1]	−2.631 52[+1]	9.113 62[−1]	3	4.5	−1.458 24[+1]
3	3.8	3.891 92[+1]	−3.535 76[+1]	−2.590 46[+1]	−3.238 95[+1]	4	3.8	−7.490 99
4	3.8	−1.525 11	4.976 75	3.770 77	1.529 06[+1]	4	2.7	1.454 06
4	2.7	1.680 79	1.826 29	1.746 68	3.057 00[−1]	5	2.7	4.140 66
5	2.7	−4.928 26[−1]	1.784 96	2.805 27	2.307 25	5	1.9	−1.346 63
5	1.9	5.763 50[−3]	1.120 57[−1]	−2.483 13[−1]	3.513 33[−2]	6	1.9	2.893 66[−1]
6	1.9	1.092 34[−3]	−2.663 16[−2]	−4.170 60[−2]	−2.403 41[−1]	6	1.4	−8.400 95[−3]
6	1.4	−3.323 61[−4]	1.632 98[−3]	−1.515 39[−3]	3.202 08[−2]	7	1.4	6.605 54[−3]
7	1.4	4.211 58[−5]	−1.905 11[−4]	1.781 56[−4]	−2.081 21[−3]	6	0.9	−3.719 73[−3]
7	1.0	−1.650 60[−7]	6.307 84[−7]	−6.645 73[−7]	5.727 33[−6]	7	0.9	3.386 32[−4]

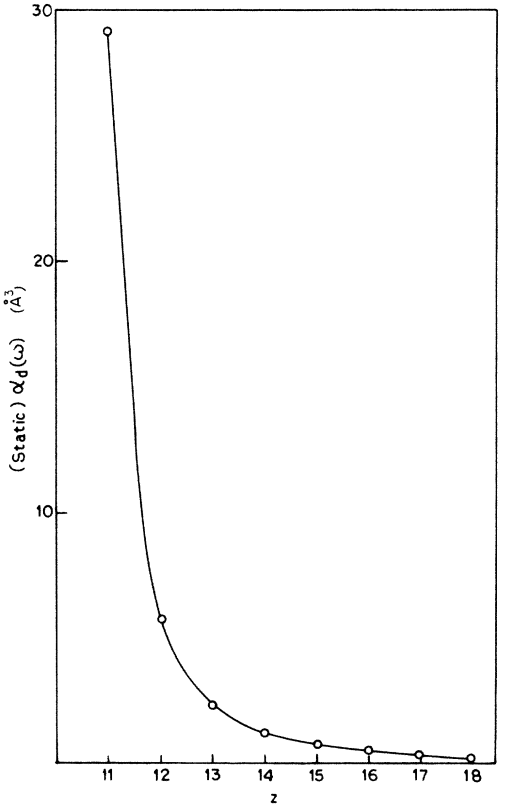

FIG. 2. Static limit of $\alpha_d(\omega)_{\omega\to0}$ vs Z for the isoelectronic members.

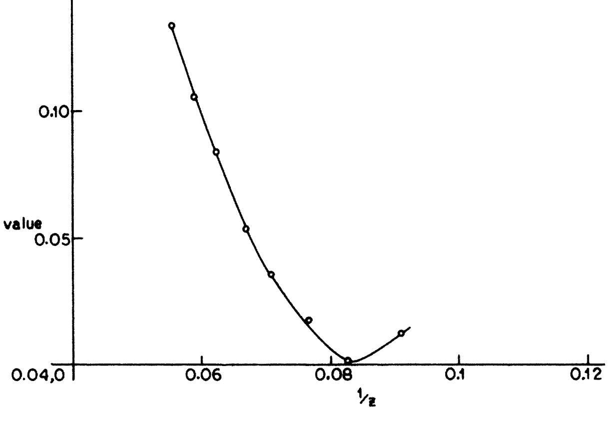

FIG. 3. $3s\to4p$ oscillator strength values vs $1/Z$ for the sodium isoelectronic sequence.

isoelectronic members. For comparison we have also listed the random-phase-approximation–exchange (RPAE) results of Amusia *et al.*,[60] relativistic HF results of Karwowski and Szulkin,[61] the frozen core with nonempirical polarization potential calculation of McEachran and Cohen[62] and the frozen-core-model calculation of Havriliak and King.[63] Our results tally almost exactly with those of Amusia *et al.*[60] which are similar in nature to our calculation but differ in procedural details. We have also evaluated the dipolar oscillator strengths in the length form and the values are listed in Table II. These are compared with the compilation of Wiese *et al.*,[64] the RPAE results of Amusia *et al.*,[60] the semiempirical model-potential calculation of Weisheit and Dalgarno,[65] the numerical Coulomb-potential calculation of Lindgard and Nielsen,[66] and with the frozen-core multiconfiguration self-consistent-field (MCSCF) calculation of Froese Fischer.[67] The relativistic results of Karwowski and Szulkin[61] and those of McEachran and Cohen[62] are also listed. In general our results agree well with the existing data. For the transitions $3s\to6p$ or $7p$ we observe substantial disagreement with the existing values. Although for higher transitions the other values listed show considerable deviation among themselves, better agreement is expected if we use a more extended and proper diffuse basis set for describing the higher Rydberg orbitals. In Figs. 3 and 4 we plotted the oscillator strength values for the $3s\to4p$ and $3s\to5p$ transitions, respectively, against $1/Z$ for the entire sequence studied here. In both cases we get a dip which corresponds to the position of the Mg$^+$ ion. This peculiarity is observed also by Wiese *et al.*[64] This is not a basis-set effect and is probably due to the peculiar distribution of the node positions of the $3s$, $4p$, and $5p$ orbitals of Mg$^+$ such that the dipolar matrix elements of $3s$ with $4p$ and $5p$ are quite small. Lastly we have evaluated the effective quantum numbers of the Rydberg orbitals using complete screening from the formula $n^*=1/\sqrt{2\epsilon}$ where ϵ is the ionization potential of the orbital concerned. These are also listed in Table II and are compared with the results obtained from the spectroscopic data of Moore[58] and Bashkin and Stoner[59] and also with the results of Lindgard and Nielsen.[66] Very good agreement is

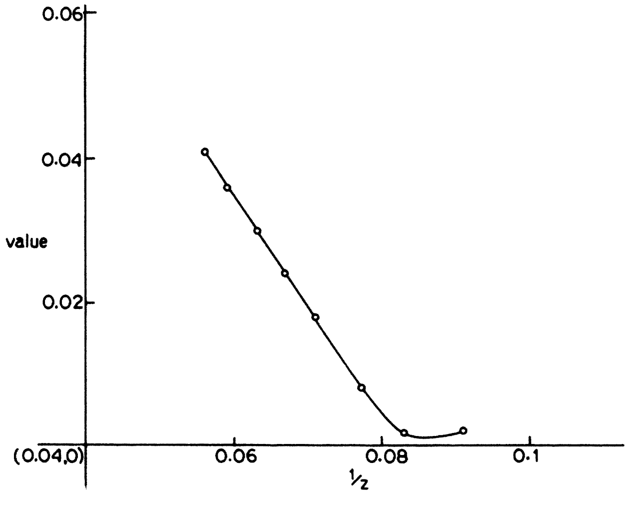

FIG. 4. $3s\to5p$ oscillator strength values vs $1/Z$ for the sodium isoelectronic sequence.

observed for small principal quantum numbers. This general trend is observed for all the isoelectronic ions studied here.

Some general observations may be obtained from the host of transition data calculated here. First of all, we notice that the transition energies are more accurate for the higher members of the isoelectronic sequence. This is due to two reasons. Firstly we have used a limited basis set for representing the excited states and secondly we have taken only that correlation into account which is embedded in an RPA-type calculation. The effective quantum numbers n^* calculated by us are somewhat larger than those found from spectroscopic values. The error probably lies in the incomplete description of the highly diffuse Rydberg states by the limited basis we used. To describe the response of the Rydberg electron in the long-range Coulomb potential properly, a very diffuse set of functions is necessary. An additional approximation is the use of Clementi orbital energies which are not correlated in order to calculate ϵ theoretically. The transition energies found by the TDCHF method do not have a specific bound and hence may contribute to the error.

In Table III we display the exponents and the coefficients for the Rydberg states of all the systems studied. The exponents are chosen from physical considerations. We tried to fit as many poles as possible properly with a given basis set. Whenever this was not possible we chose a new set. However, we restrict ourselves to 12-parameter representations for all the excited states. This sets a limit to our accuracy as far as higher-order transitions are concerned.

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