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Dynamic polarizabilities and Rydberg states of the sodium isoelectronic sequence. II

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Dynamic quadrupolar polarizabilities $\alpha_q(\omega)$ for the sodium isoelectronic sequence up to $Z=18$ have been calculated, and analytic representations of Rydberg *d*- and *s*-state wave functions have been obtained using time-dependent coupled Hartree-Fock theory. The excitation energies are obtained from the position of the poles of a frequency-dependent functional. The estimated static limit $\alpha_q(\omega)_{\omega\to 0}$ compares well with existing static results, and the transition energies are in good agreement with the spectroscopic values. The accuracy of the excited-state wave functions is checked indirectly by evaluating quadrupolar oscillator and multiplet strengths which compare favorably with other results wherever available. Furthermore, the quantum-defect values are estimated using complete screening and compared with those obtained spectroscopically. Excellent agreement is observed.

I. INTRODUCTION

The alkali-metal atoms are a topic of extensive study and interest today mainly because of their structural similarity to that of the hydrogen atom and as such various properties like polarizabilities and radiative lifetimes can be calculated using hydrogenic wave functions.[1] However, because of the presence of a tightly bound core, finer details of many of their spectral properties cannot be explained properly from a simple hydrogenic model and one has to go over to a many-electron problem. The Rydberg states of alkali-metal atoms and polarizability of these states have been extensively studied very recently[2–13] and the collisional aspects of these states are a topic of current investigation.[14,15] On the theoretical side, the quantum-defect theory,[7–9,12] the frozen-core Hartree-Fock approximation,[16,17] the random-phase-approximation with exchange (RPAE) calculations of Amusia *et al.*,[18] the frozen-core multiconfiguration self-consistent-field (MCSCF) calculation of Froese Fischer,[19] and the relativistic calculations of Karwowski and Szulkin[20] have lent substantial information.

It has been demonstrated that the time-dependent coupled Hartree-Fock (TDCHF) theory yields accurate results for properties connected with single excitations[21–26] and furnishes reasonably accurate excited-state wave functions.[26–28] The theory and procedural details are well reviewed by Oddershede[29] and McCurdy *et al.*[30] In a recent paper[26] (hereafter referred to as I) we have performed a detailed study of the dynamic dipolar polarizabilities and Rydberg *p* states of the sodium isoelectronic sequence and obtained accurate transition properties of such systems. In the present paper a similar study has been performed for the dynamic quadrupolar polarizabilities and excited *s* and *d* states of sodium and sodiumlike ions up to argon. The theory in detail is given earlier.[21–28] In Sec. II, however, we very briefly give the salient features of the method involved and the results are discussed in Sec. III.

II. METHOD

The ground state of sodiumlike ions is described by the usual nonrelativistic Hamiltonian and an 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. For multipolar excitations we may choose

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

Presently we study both quadrupolar excitation for which $l=2$ and monopolar excitation for which we may assume

$$h'(\mathbf{r})=\lambda f(r)Y_{00}(\theta,\varphi)\ . \tag{3}$$

As shown earlier,[31] the excitation properties do not depend on the choice of $f(r)$ and as such we choose $f(r)\sim r$. The first-order perturbed functions are obtained by optimizing a variational functional[26,32–34]

$$J(\Phi)=\frac{1}{T}\int_0^T \frac{\langle \Phi(\mathbf{r},t)\,|\,H-i\partial/\partial t\,|\,\Phi(\mathbf{r},t)\rangle}{\langle \Phi(\mathbf{r},t)\,|\,\Phi(\mathbf{r},t)\rangle}dt\ , \tag{4}$$

where Φ denotes the total wave function and H the total Hamiltonian in the presence of the external perturbation. The dynamic quadrupolar polarizability is estimated from

$$\alpha_q(\omega)=\sum_k[\langle \delta\psi_k^-\,|\,r^2P_2(\cos\theta)\,|\,\psi_k\rangle + \langle \delta\psi_k^+\,|\,r^2P_2(\cos\theta)\,|\,\psi_k\rangle]\ , \tag{5}$$

where $\delta\psi_k^{\pm}$ denote the first-order admixtures to the ground orbital ψ_k due to the two components of the external perturbation [Eq. (1)]. The quadrupolar polarizability values show a monotonic increase with the frequency ω and at certain values of ω discontinuities are observed. These values of ω correspond to the transition frequencies. The excited-state wave functions are obtained by re-

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

Ion	Quadrupole polarizabilities (Å^5) Static limit	Static values
Na	92.93	89.79,[a] 92.11,[b] 74.64,[b] 90.91,[c–e] 72.45,[f] 74.77,[g,h] 74.81,[i] 89.91,[j] 90.04,[k] 91.64,[k] 89.85,[k] 90.24,[k] 80.66[l]
Mg^+	7.1689	5.684,[m] 7.774[k]
Al^{2+}	1.5898	1.278,[m] 1.625[k]
Si^{3+}	0.5264	0.4315,[m] 0.5192[k]
P^{4+}	0.2216	0.1809,[m] 0.2085[k]
S^{5+}	0.1068	0.0880,[m] 0.0974[k]
Cl^{6+}	0.0567	0.0473[m]
Ar^{7+}	0.0324	0.0269[m]

[a] G. Figari, G. F. Musso and V. Magnasco, Mol. Phys. **50**, 1173 (1983).
[b] Reference 37.
[c] Reference 38.
[d] Reference 39.
[e] Reference 40.
[f] Reference 41.
[g] S. A. Adelman and A. Szabo, J. Chem. Phys. **58**, 687 (1973).
[h] G. Lamm and A. Szabo, J. Chem. Phys. **67**, 5942 (1977).
[i] R. M. Sternheimer, Phys. Rev. **138**, 112 (1969).
[j] J. J. C. Teixeira-Dias and L. M. C. Simões, Mol. Phys. **32**, 1191 (1976).
[k] Reference 43 (different values correspond to different starting functions).
[l] Reference 42.
[m] Reference 36.

normalizing $\delta\psi_k^-$ at the pole positions and may be used to calculate other properties associated with the transitions.

III. RESULTS AND DISCUSSIONS

Presently we have studied the transitions $3\,{}^2S \to n\,{}^2S$ ($n=4,5,\ldots,8$) and $3\,{}^2s \to n\,{}^2D$ ($n=3,\ldots,7$) for the ions Na, Mg^+, Al^{2+}, Si^{3+}, P^{4+}, S^{5+}, Cl^{6+}, Ar^{7+}. The ground ${}^2S$ wave functions have been taken from Clementi and Roetti,[35] while the radial part of the perturbed functions are of the form

$$\delta\psi_i^{\pm}(r)=\sum_p C_{ip}^{\pm}\chi_{ip}(r)\ , \tag{6}$$

where χ_{ip}'s are suitable Slater bases, preassigned from physical considerations. C_{ip}'s are coefficients to be determined variationally. In accordance with paper I we have chosen 12 parameter representations for all possible exci-

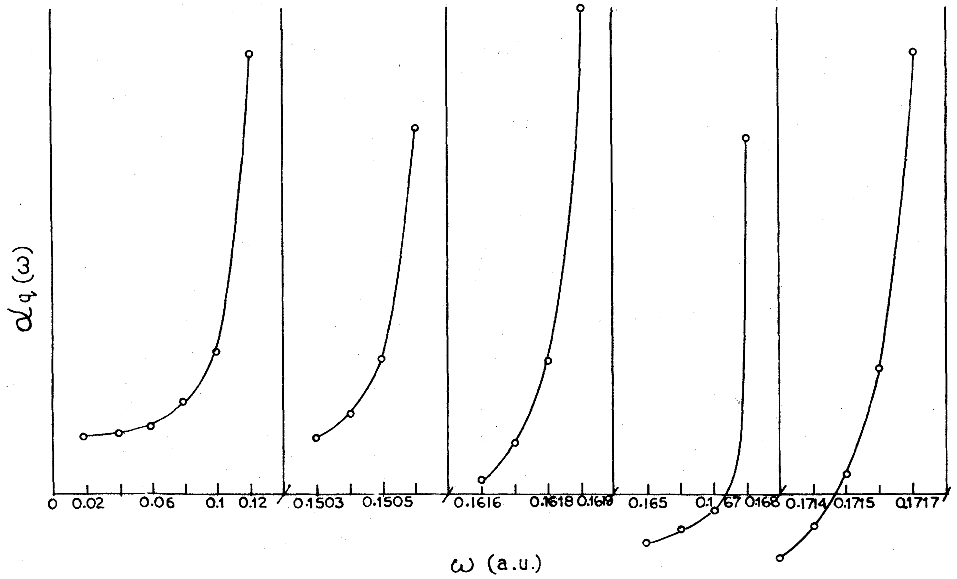

FIG. 1. Plot of $\alpha_q(\omega)$ (in arbitrary scale) vs ω for the first five transitions of sodium near resonance.

TABLE II. Transition energies (a.u.) (1 a.u.$=219\,474.62$ cm^{-1}) effective quantum number, quadrupolar multiplet strength, and oscillator strength as obtained from frequency-dependent calculations. Numbers in square brackets represent powers of ten.

Ion	Transition scheme	Excitation energies Calc.	Excitation energies Other values	% Deviation with respect to Ref. 44	Effective quantum number Calc.	Effective quantum number Expt.^{a}	Quadrupole multiplet strength Calc.	Quadrupole multiplet strength Other value^{b}	Quadrupole oscillator strength (wf) Calc.	Quadrupole oscillator strength (wf) Other values
Na	$3\,^2S\to4\,^2S$	0.1078	0.1173^{a} 0.1117^{b}	8.10	2.5964	2.6430				
	$\to5\,^2S$	0.1439	0.1513^{a} 0.1448^{b}	4.89	3.6240	3.6474				
	$\to6\,^2S$	0.1588	0.1657^{a} 0.1589^{b}	4.16	4.6454	4.6492				
	$\to7\,^2S$	0.1664	0.1732^{a} 0.1663^{b}	3.93	5.6668	5.6502				
	$\to8\,^2S$	0.1750	0.1776^{a} 0.1706^{b}	1.46	8.4697	6.6505				
	$\to3\,^2D$	0.1263	0.1329^{a} 0.1261^{b}	5.00	2.9969	2.9892	7.48[2]	7.59[2]	4.01[−6]	4.05[−6]^{b} 3.97[−6]^{c}
	$\to4\,^2D$	0.1506	0.1574^{a} 0.1505^{b}	4.32	3.9923	3.9869	1.13[2]	1.10[2]	1.03[−6]	9.97[−7]^{b} 1.02[−6]^{c}
	$\to5\,^2D$	0.1619	0.1688^{a} 0.1618^{b}	4.09	4.9913	4.9928	3.35[1]	3.53[1]	3.78[−7]	3.98[−7]^{b} 4.14[−7]^{c}
	$\to6\,^2D$	0.1680	0.1749^{a} 0.1679^{b}	3.95	5.9826	5.9852	1.24[1]	1.59[1]	1.56[−7]	2.01[−7]^{b} 2.12[−7]^{c}
	$\to7\,^2D$	0.1717	0.1786^{a} 0.1716^{b}	3.86	6.9775	6.9817	3.50	8.66	4.72[−8]	1.17[−7]^{b} 1.23[−7]^{c}
Mg^+	$3\,^2S\to4\,^2S$	0.3036	0.3181^{a} 0.3091^{b}	4.56	2.9008	2.9205				
	$\to5\,^2S$	0.4114	0.4228^{a} 0.4120^{b}	2.70	3.9241	3.9261				
	$\to6\,^2S$	0.4590	0.4702^{a} 0.4588^{b}	2.38	4.9302	4.9285				
	$\to7\,^2S$	0.4850	0.4957^{a} 0.4840^{b}	2.16	5.9613	5.9298				
	$\to8\,^2S$	0.5029	0.5109^{a} 0.4992^{b}	1.57	7.2188	6.9306				
	$\to3\,^2D$	0.3163	0.3257^{a} 0.3158^{b}	2.89	2.9816	2.9696	1.76[2]	1.75[2]	1.48[−5]	1.47[−5]^{b} 2.94[−5]^{c}
	$\to4\,^2D$	0.4147	0.4252^{a} 0.4141^{b}	2.47	3.9750	3.9637	5.64	6.34	1.07[−6]	1.20[−6]^{b} 2.24[−6]^{b}
	$\to5\,^2D$	0.4604	0.4712^{a} 0.4597^{b}	2.29	4.9727	4.9599	6.44[−1]	9.48[−1]	1.66[−7]	2.45[−7]^{b} 5.12[−7]^{c}
	$\to6\,^2D$	0.4851	0.4962^{a} 0.4845^{b}	2.24	5.9666	5.9602	6.71[−2]	2.59[−1]	2.04[−8]	7.85[−8]^{b} 1.67[−7]^{c}
	$\to7\,^2D$	0.5001	0.5112^{a} 0.4994^{b}	2.17	6.9690	6.9599	9.13[−3]	9.88[−2]	3.04[−9]	3.28[−8]^{b} 7.10[−8]^{c}
Al^{2+}	$3\,^2S\to4\,^2S$	0.5555	0.5749^{a} 0.5635^{b}	3.38	3.0767	3.0923				
	$\to5\,^2S$	0.7633	0.7775^{a} 0.7636^{b}	1.83	4.1009	4.0981				
	$\to6\,^2S$	0.8584	0.8725^{a} 0.8577^{b}	1.62	5.1078	5.1007				
	$\to7\,^2S$	0.9105	0.9246^{a} 0.9094^{b}	1.53	6.1141	6.1021				
	$\to8\,^2S$	0.9423	0.9562^{a} 0.9409^{b}	1.45	7.1275	7.1029				
	$\to3\,^2D$	0.5183	0.5283^{a} 0.5177^{b}	1.89	2.9630	2.9500	6.49[1]	6.50[1]	2.41[−5]	
	$\to4\,^2D$	0.7428	0.7554^{a}	1.67	3.9523	3.9392	1.73[−2]	3.55[−2]	1.89[−8]	

TABLE II. (*Continued*).

		Excitation energies		% Deviation with respect to Ref. 44	Effective quantum number		Quadrupole multiplet strength		Quadrupole oscillator strength (wf)	
Ion	Transition scheme	Calc.	Other values		Calc.	Expt.^{a}	Calc.	Other value^b	Calc.	Other values
			0.7418^b							
	$\rightarrow 5\,^2D$	0.8471	0.8606^a	1.57	4.9489	4.9346	5.57[−2]	6.35[−2]	9.02[−8]	
			0.8460^b							
	$\rightarrow 6\,^2D$	0.9035	0.9175^a	1.53	5.9437	5.9316	5.06[−2]	7.34[−2]	9.94[−8]	
			0.9024^b							
	$\rightarrow 7\,^2D$	0.9378	0.9517^a	1.46	6.9531	6.9301	4.82[−2]	5.74[−2]	1.06[−7]	
			0.9364^b							
Si^{3+}	$3\,^2S \rightarrow 4\,^2S$	0.8641	0.8838^a	2.23	3.2085	3.2127				
	$\rightarrow 5\,^2S$	1.1932	1.2093^a	1.33	4.2256	4.2183				
	$\rightarrow 6\,^2S$	1.3489	1.3654^a	1.21	5.2312	5.2208				
	$\rightarrow 7\,^2S$	1.4362	1.4523^a	1.11	6.2463	6.2222				
	$\rightarrow 8\,^2S$	1.4978	1.5056^a	0.52	7.4681	7.2231				
	$\rightarrow 3\,^2D$	0.7206	0.7307^b	1.38	2.9479	2.9358	2.91[1]		2.90[−5]	
	$\rightarrow 4\,^2D$	1.1245	1.1391^a	1.28	3.9347	3.9231	3.59[−1]		1.36[−6]	
	$\rightarrow 5\,^2D$	1.3120	1.3282^a	1.22	4.9293	4.9185	3.32[−1]		2.00[−6]	
	$\rightarrow 6\,^2D$	1.4134	1.4303^a	1.18	5.9256	5.9175	1.90[−1]		1.43[−6]	
	$\rightarrow 7\,^2D$	1.4744	1.4916^a	1.15	6.9246	6.9151	1.19[−1]		1.02[−6]	
P^{4+}	$3\,^2S \rightarrow 4\,^2S$	1.2226	1.2437^a	1.70	3.3028	3.3028				
	$\rightarrow 5\,^2S$	1.6969	1.7161^a	1.12	4.3142	4.3080				
	$\rightarrow 6\,^2S$	1.9267	1.9463^a	1.01	5.3191	5.3099				
	$\rightarrow 7\,^2S$	2.0561	2.0757^a	0.94	6.3256	6.3107				
	$\rightarrow 8\,^2S$	2.1754			8.0457					
	$3\,^2S \rightarrow 3\,^2D$	0.9197	0.9304^a	1.15	2.9373	2.9268	1.51[1]		3.13[−5]	
	$\rightarrow 4\,^2D$	1.5566	1.5739^a	1.09	3.9238	3.9144	8.71[−1]		8.75[−6]	
	$\rightarrow 5\,^2D$	1.8518	1.8710^a	1.03	4.9185	4.9095	4.01[−1]		6.78[−6]	
	$\rightarrow 6\,^2D$	2.0113	2.0313^a	0.99	5.9156	5.9065	1.94[−1]		4.20[−6]	
	$\rightarrow 7\,^2D$	2.1071	2.1273^a	0.95	6.9152	6.9033	1.07[−1]		2.67[−6]	
S^{5+}	$3\,^2S \rightarrow 4\,^2S$	1.6216	1.6539^a	1.95	3.3653	3.3732				
	$\rightarrow 5\,^2S$	2.2748	2.2969^a	0.97	4.3850	4.3784				
	$\rightarrow 6\,^2S$	2.5927	2.6145^a	0.83	5.3959	5.3825				
	$\rightarrow 7\,^2S$	2.7843			6.4955					
	$\rightarrow 8\,^2S$	2.9236			7.9149					
	$\rightarrow 3\,^2D$	1.1152	1.1275^a	1.09	2.9307	2.9219	8.51		3.14[−5]	
	$\rightarrow 4\,^2D$	2.0384	2.0586^a	0.98	3.9181	3.9103	1.02		2.30[−5]	
	$\rightarrow 5\,^2D$	2.4653	2.4879^a	0.91	4.9133	4.9059	3.47[−1]		1.38[−5]	
	$\rightarrow 6\,^2D$	2.6958	2.7196^a	0.88	5.9112	5.9051	1.52[−1]		7.93[−6]	
	$\rightarrow 7\,^2D$	2.8340	2.8579^a	0.84	6.9104	6.9016	7.99[−2]		4.84[−6]	
Cl^{6+}	$3\,^2S \rightarrow 4\,^2S$	2.0818	2.1142^a	1.53	3.4277	3.4300				
	$\rightarrow 5\,^2S$	2.9241	2.9510^a	0.91	4.4398	4.4350				
	$\rightarrow 6\,^2S$	3.3467	3.3703^a	0.70	5.4650					
	$\rightarrow 7\,^2S$	3.6663			6.9950					
	$\rightarrow 8\,^2S$	3.8825			9.2795					
	$\rightarrow 3\,^2D$	1.3073	1.3224^a	1.14	2.9270	2.9196	5.15		3.06[−5]	
	$\rightarrow 4\,^2D$	2.5690	2.5934^a	0.94	3.9458	3.9092	9.72[−1]		4.39[−5]	
	$\rightarrow 5\,^2D$	3.1514	3.1786^a	0.86	4.9116	4.9058	2.71[−1]		2.26[−5]	
	$\rightarrow 6\,^2D$	3.4655	3.4939^a	0.81	5.9098	5.9047	1.10[−1]		1.22[−5]	
	$\rightarrow 7\,^2D$	3.6539			6.9100		5.51[−2]		7.16[−6]	
Ar^{7+}	$3\,^2S \rightarrow 4\,^2S$	2.5877	2.6240^a	1.38	3.4759	3.4763				

TABLE II. (*Continued*).

Ion	Transition scheme	Excitation energies		% Deviation with respect to Ref. 44	Effective quantum number		Quadrupole multiplet strength		Quadrupole oscillator strength (wf)	
		Calc.	Other values		Calc.	Expt.[a]	Calc.	Other value[b]	Calc.	Other values
	$\rightarrow 5\,^2S$	3.6459	3.7017[a]	1.48	4.4869	4.5141				
	$\rightarrow 6\,^2S$	4.1806	4.2110[a]	0.72	5.5054	5.4916				
	$\rightarrow 7\,^2S$	4.6458			7.3611					
	$\rightarrow 8\,^2S$	4.9108			9.9136					
	$3\,^2S\rightarrow 3\,^2D$	1.4968	1.5153[a]	1.22	2.9252	2.9186	3.29		2.94[−5]	
	$\rightarrow 4\,^2D$	3.1487	3.1779[a]	0.92	3.9151	3.9091	8.45[−1]		7.02[−5]	
	$\rightarrow 5\,^2D$	3.9099	3.9416[a]	0.80	4.9116	4.9044	2.06[−1]		3.28[−5]	
	$\rightarrow 6\,^2D$	4.3202	4.3539[a]	0.77	5.9099	5.9038	7.94[−2]		1.71[−5]	
	$\rightarrow 7\,^2D$	4.5664			6.9109		3.87[−2]		6.54[−6]	

[a] Reference 44.

[b] Reference 17.

[c] B. Warner, Mon. Not. R. Astron. Soc. **139**, 115 (1968).

tations studied here. The dynamic quadrupolar polarizability values $\alpha_q(\omega)$ are estimated from Eq. (5) and the static limit $\alpha_q(\omega)_{\omega\rightarrow 0}$ has been evaluated. The static limits for the entire series are compared in Table I with other available static results. The value given by Kastner and Wolf[36] are consistently lower than ours. For sodium, from the host of data available we find that our results compare well with the frozen-core results of Maeder and Kutzelnigg[37] and also with the available coupled and uncoupled HF results.[38–40] However, it is considerably higher than those obtained from the pseudopotential calculation of Maeder and Kutzelnigg,[37] the Coulomb approximation (CA) results of Lamm and Szabo[41] and the quantum defect orbital (QDO) result of Manakov, Ovsyannikov and Rapport.[42] For Mg^+ to Ar^{7+} our results agree fairly well with those of Kastner and Wolf[36] and the uncoupled calculation of Langhoff and Hurst.[43] In Fig. 1 we have plotted the quadrupolar polarizability values, $\alpha_q(\omega)$ versus ω for the five transitions listed here. The plot clearly shows the discontinuities.

The transition energies ($3\,^2S\rightarrow n\,^2S$;$3\,^2S\rightarrow n\,^2D$) obtained from the position of the poles of the frequency-dependent functional are displayed in Table II. These are compared with the spectroscopic values of Bashkin and Stoner[44] and with the compilation of Tull *et al.*[17] The $3s\rightarrow 4s$ transition energy of sodium is off by 8% but the discrepancy diminishes as we proceed along the isoelectronic series, falling to as low as 0.7% for the higher-order transitions in the higher members of the isoelectronic series. The $3s\rightarrow 3d$ transition energy of sodium is off by 5% and compares well with that of Tull *et al.*[17] We have also calculated the quadrupolar multiplet strength and quadrupolar oscillator strength using the formulas[17] (in a.u.)

$$S_{nm}=\tfrac{4}{3}\,|\langle m\,|r^2|\,n\rangle|^2 \tag{7}$$

and

$$w_m f_{mn}=\frac{E^3_{nm}}{20c^2}S_{nm}\ , \tag{8}$$

where w_m is the statistical weight of the initial level and other quantities have their usual significance. These values have also been listed in Table II and compared with the frozen-core HF calculations of Tull *et al.*[17] The results compare favorably with data wherever available. For Si^{3+} to Ar^{7+} no other data are available and as such, our quoted values may be used for future reference. The ($3s\rightarrow nd$) oscillator strength values are plotted against the principal quantum number n for sodium in Fig. 2. A regular pattern is observed. Assuming complete screening the effective quantum numbers for the Rydberg orbitals have been calculated 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 along with the values obtained from spectroscopic observations.[44] The results compare well for the lower principal quantum numbers and this trend is observed for the entire isoelectronic series studied here. However, for higher principal quantum numbers the results are not very consistent. This may be attributed to the limited basis sets used in our calculation for evaluating such states. More extensive and diffuse

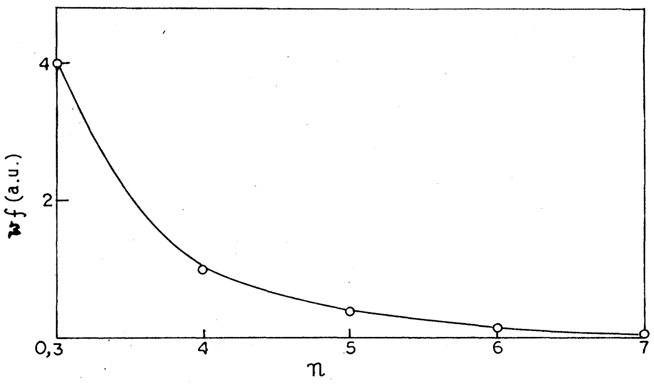

FIG. 2. Plot of quadrupolar oscillator strength wf vs principal quantum number n for Na atom.

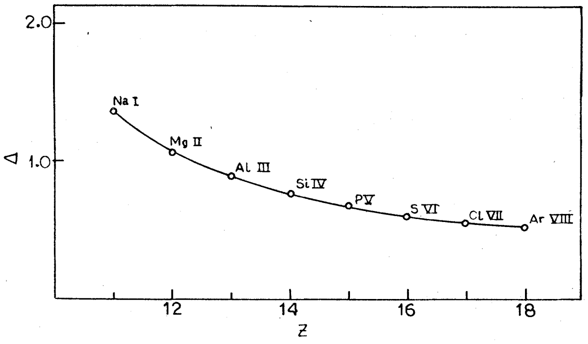

FIG. 3. Plot of Δ vs Z for the $3s \rightarrow 4s$ transition for the sodium isoelectronic series.

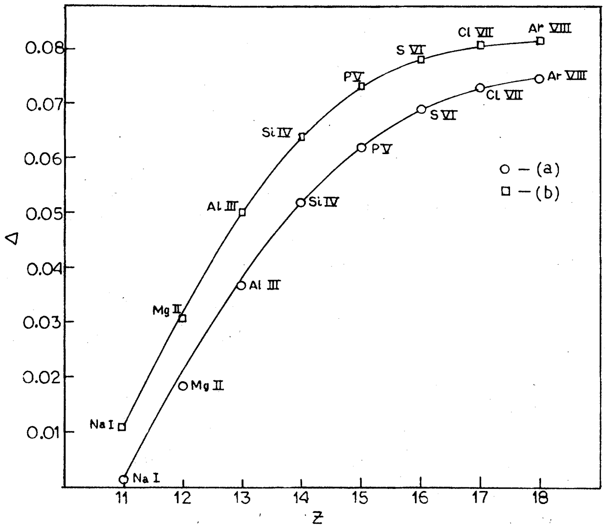

FIG. 4. Plot of Δ vs Z for the $3s \rightarrow 3d$ transition for the sodium isoelectronic series. (a) Present calculation, (b) Ref. 44.

basis sets should be used for proper description of such states. We, however, do not adopt such a procedure because of the excessive computer time involved. The quantum-defect values $\Delta = n - n^*$ are plotted against the atomic number Z for the $3s \rightarrow 4s$ and $3s \rightarrow 3d$ transitions, respectively, in Figs. 3 and 4. Figure 3 is similar to that observed by Mizushima.[45] It may be mentioned that the Δ values for the $3s \rightarrow 3p$ transition as obtained in our previous calculation (paper I) show a similar trend. However, it is fairly interesting to observe that the nature of the curve for the $3s \rightarrow 3d$ quantum defect values against Z (Fig. 4) is the exact opposite to that of Fig. 3. To make a comparison we have also plotted in the same figure the $3s \rightarrow 3d$ Δ values of Bashkin and Stoner.[44] The agreement as seen from Fig. 4 is fairly good. For sodium our calculated Δ values averaged over the entire set of principal quantum numbers for s and d transitions can be compared with existing theoretical calculations. Our values are 1.367 and 0.0119, respectively, compared to 1.348 and 0.0148 of Johanson[46] and Risberg,[47] 1.357 and 0.0069 of Jaffé and Reinhardt[11] using the Hamilton-Jacobi method, and 1.352 and 0.0150 by the quantum-mechanical method. This comparison may indicate the consistency of our results for other members of the isoelectronic sequence. We do not list the parameters of the wave functions here but the consistency of the wave functions could be checked directly with the listed oscillator and multiplet strength values in Table II. (The list of excited-state wave functions can be obtained on request from the authors.) For Na there happens to be a side check. The $\langle 3s | r^2 | 3d \rangle$ matrix element calculated by us is 10.60 compared to 10.67 as obtained by Tull *et al.*,[17] 10.38 by numerical HF method of Boyle and Murray,[48] and 10.25 by using hypervirial form of the operator.[48] The value 9.82 as given by Boggard and Orr[49] is slightly lower.

From the host of calculated data we may conclude that TDCHF theory is quite adequate to study the single Rydberg excitations in atoms and transition properties connected with them. Results with improved accuracy may be obtained by using more extensive and diffuse basis sets, and also by incorporating correlations and core-relaxation effects and other finer interactions which are completely ignored here.

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