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Calculation of rydberg states of lithium isoelectronic sequence

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The transition energies and singly excited P, D and F states of Li, Be^+ and B^{2+} for the Rydberg levels $1s^22s$: $^2S \rightarrow 1s^2nl$: ^2L $(n = 5, 6, \ldots 9)$ have been calculated using time dependent coupled Hartree-Fock (TDCHF) theory. Within single particle model the theory includes RPA type correlations and furnishes reasonable description of the excited states. The transition energies and oscillator strengths for allowed transitions are in good agreement with the experimental and theoretical values, wherever available. Effective quantum numbers have been estimated for all transitions.

Key words: Rydberg states — Atomic wavefunctions — Lithium atom

1. Introduction

Atomic Rydberg states are mostly, expanded orbital states which are attracted by a relatively small ionic core. The shape of Rydberg orbital is mainly determined by the charge of the ionic core and also by the orthogonality constraints to all the lower lying occupied and virtual states. Rydberg states are of considerable importance today for studying superradiance, and recent developments of continuous lasers have made such studies very effective. Hence the study of Rydberg states of atomic systems is interesting from both experimental and theoretical points of view [1-11]. The collisional mixing of such states is also a topic of current interest [12, 13] and theoretical calculations on collisions of Rydberg atoms in an electric field were recently performed by Hickman [14].

There are very few *ab initio* calculations on Rydberg states in the literature. This is mainly due to the complexity of describing the highly diffuse Rydberg functions with large numbers of nodes. Traditional variational calculations are not very effective since they require accurate description of the lower lying states along with the necessary orthogonality constraints. Theoretical calculations employing approximate single-configuration wavefunctions for Rydberg states were carried out by Lefebvre-Brion and Moser [15] and by Hunt and Goddard [16] by using their method of improved virtual orbitals and by the frozen core method of Demoulin and Jungen [17] and by Jungen [18-20]. Iterative and non-iterative numerical methods which use model potentials are rather limited [21-25]. Recently a semi empirical model potential calculation was performed by Theodosiou [26] for the lifetimes of the Rydberg states of alkali metal atoms. In this connection quantum defect theory [27-30] has provided extremely valuable information. Perturbative calculations on such states have been performed with hydrogenic unperturbed wavefunctions and a polarization potential as perturbation for some atomic systems [31]. Using an optical potential analysis the Rydberg states of the helium atom have been studied by Drachman [32]. Very recently Rydberg energy levels of lithium have been *ab initio* determined from the poles of the Schwinger T-matrix [33]. Several good reviews on the Rydberg states of atomic systems are now available, in the literature [30, 34, 35].

In a recent paper [36] we demonstrated that the time-dependent coupled Hartree-Fock (TDCHF) method can be applied to calculate the excitation energy and singly excited wavefunctions of n^2S $(n=3, \ldots, 8)$ states of the lithium isoelectronic sequence with reasonable accuracy. Similar calculations for the helium isoelectronic sequence were carried out earlier [37]. Details of TDCHF theory and reviews of earlier work were given by Oddershede [38] and also by McCurdy et al. [39]. Although the theory is based on a single-particle model, its success is mainly due to its inclusion of random phase approximation (RPA) type correlations [38]. In this paper, we have studied the transition energies and singly excited wavefunctions of the first three ions of the lithium isoelectronic sequence for the transitions $2^2S \rightarrow n^2P$, n^2D and $n^2F (n=5, \ldots 9)$. For the lower lying states similar calculations have been done earlier [40] but with a different form of the external perturbation. Results for the transitions which are common tally almost exactly. The present method is non-relativistic and ignores the rearrangement of the core orbitals due to the excitation of the valence orbital; relativistic and core rearrangement effects, however, should be quite small for the present system. The theory was discussed in detail in earlier papers [36, 37], and we give, in the next section, a very brief outline.

2. Method

We consider the ground ^2S state of lithium like ions to be described by the usual non-relativistic hamiltonian. A time dependent perturbation of the form

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

is applied to the system. The single particle perturbation is of the form

$$h(r) = \lambda f(r) Y_{l0}(\theta, \varphi) \tag{2}$$

where λ is the perturbation strength, $f(r)$ is a suitable function of r and here we choose

$$f(r) \sim r^l \tag{3}$$

for a given multipolarity $l(\geq 1)$ of the transition. Y_{l0} induces the proper multipolar excitation. The first order correction $\delta\psi_i$ to the ground orbital ψ_i is determined by

$$h\psi_i \sim \delta\psi_i. \tag{4}$$

The first-order correction $\delta\psi_i$ is determined variationally by expanding it in terms of a suitable Slater basis, the expansion coefficients being treated as variation parameters. The excitation energies are obtained from the position of the poles of the first order perturbed function with respect to the external frequency. Excited state wavefunctions are obtained from the renormalised perturbed functions at the poles. The procedural details are given elsewhere [36, 37].

3. Results

The first three members of the lithium isoelectronic sequence, Li, Be^+ and B^{2+}, are chosen for our investigation, and the transitions $1s^22s{:}\ {}^2S \rightarrow 1s^2nl{:}\ {}^2L(n = 5, \ldots 9)$ for $l = 1, 2, 3$ have been studied. The ground state wavefunctions are those of Clementi [41]. The radial parts of the perturbed functions are expanded in a suitable Slater basis, of twelve to fifteen terms depending upon the specific transition.

We tried to obtain as many poles as possible with a 12-parameter basis. In most cases the required number of excitations are obtained wth reasonable accuracy. But for large principal quantum numbers the functions are highly diffuse and the 12-parameter basis is insufficient to describe such functions; as a consequence the transition energies are further off from the experimental values. In such cases a 15-parameter representation is used.

The transition energies, as obtained from the positions of the poles of the TDCHF functional are displayed in Table 1. The basis chosen along with the coefficients are displayed in Table 2.

The present transition energies in Table 1 are compared with the values listed by Bashkin and Stoner (Jr) [42]. The maximum deviation is 1%, and the deviation is as low as 0.3% for the higher order transitions for the higher members of the isoelectronic series. The accurate theoretical estimates of some of the levels by Knight and Sanders [43] are also listed here for comparison. The oscillator strengths for all the allowed transitions have also been calculated and displayed in Table 1. For comparison, the values quoted by Wiese et al. [44] are also listed here. The oscillator strengths, in general, are in good agreement with the values listed by Wiese et al. [44]. However, we get a discrepancy in the case of the $2^2S \rightarrow 8^2P$ transition in lithium. Here the oscillator strength calculated by us is 0.0015 compared to 0.000916 by Wiese et al. This is probably due to the inadequacy of the present basis set for large n. To check this we calculated the oscillator strength with a different but more suitable basis for $8p$ function and obtained a

Table 1. Transition energies (in a.u.), oscillator strength values and effective quantum numbers as obtained from frequency dependent calculations

Ion	Transition scheme	Excitation energies[a]			% dev. w.r.t. (a)	Oscillator strength		Effective Quantum No.	
		Present	Observed[b]	Calculated[c]		Present	Other values[d]	Present	Exptl.[e]
Li	$2^2S \rightarrow 5^2P$	0.1761	0.1778	0.1779	0.96	0.00258	0.00316	4.975	4.954
	$\rightarrow 6^2P$	0.1822	0.1840	0.1840	0.98	0.00139	0.00192	5.955	5.953
	$\rightarrow 7^2P$	0.1864	0.1878	0.1878	0.75	0.00134	0.00128	7.107	6.953
	$\rightarrow 8^2P$	0.1888	0.1902		0.74	0.00150	0.000916	8.165	7.951
	$\rightarrow 9^2P$	0.1904	0.1919		0.78	0.000622	0.000679	9.206	8.953
	$2^2S \rightarrow 5^2D$	0.1763	0.1781	0.1780	1.01			5.000	4.998
	$\rightarrow 6^2D$	0.1832	0.1843	0.1842	0.60			6.178	5.998
	$\rightarrow 7^2D$	0.1872	0.1879	0.1878	0.37			7.412	6.998
	$\rightarrow 8^2D$	0.1895	0.1903		0.42			8.575	7.997
	$\rightarrow 9^2D$	0.1909	0.1920		0.57			9.623	8.996
	$2^2S \rightarrow 5^2F$	0.1763	0.1782		1.07			5.000	5.004
	$\rightarrow 6^2F$	0.1824	0.1843		1.03			5.998	
	$\rightarrow 7^2F$	0.1861	0.1880		1.01			7.001	
	$\rightarrow 8^2F$	0.1885	0.1903		0.95			8.006	
	$\rightarrow 9^2F$	0.1902	0.1920		0.94			9.054	
Be^+	$2^2S \rightarrow 5^2P$	0.5851	0.5877	0.5878	0.44	0.0125		4.966	4.950
	$\rightarrow 6^2P$	0.6099	0.6128	0.6128	0.47	0.00661		5.960	5.951
	$\rightarrow 7^2P$	0.6257	0.6279	0.6278	0.33	0.00351		7.027	6.951
	$\rightarrow 8^2P$	0.6368				0.00202		8.248	
	$\rightarrow 9^2P$	0.6420				0.00468		9.100	
	$2^2S \rightarrow 5^2D$	0.5863	0.5892	0.5891	0.49			5.003	4.998
	$\rightarrow 6^2D$	0.6106	0.6137	0.6136	0.51			5.998	5.998
	$\rightarrow 7^2D$	0.6253	0.6284	0.6283	0.49			6.993	6.998
	$\rightarrow 8^2D$	0.6358	0.6380		0.35			8.111	7.998
	$\rightarrow 9^2D$	0.6442						9.535	

	$2^2S \to 5^2F$	0.5861	0.5893		0.54		4.997	5.000
	$\to 6^2F$	0.6105	0.6137		0.52		5.992	6.000
	$\to 7^2F$	0.6253	0.6285		0.51		6.993	7.000
	$\to 8^2F$	0.6355					8.071	
	$\to 9^2F$	0.6425					9.186	
B^{2+}	$2^2S \to 5^2P$	1.2075	1.2108	1.2108	0.27	0.0224	4.967	4.956
	$\to 6^2P$	1.2633	1.2672	1.2671	0.31	0.0125	5.962	
	$\to 7^2P$	1.2971	1.3010	1.3009	0.30	0.00831	6.964	
	$\to 8^2P$	1.3188				0.00469	7.960	
	$\to 9^2P$	1.3376				0.00294	9.279	
	$2^2S \to 5^2D$	1.2099	1.2138	1.2138	0.32		5.000	
	$\to 6^2D$	1.2649	1.2689	1.2689	0.32		6.000	
	$\to 7^2D$	1.2980	1.3021	1.3020	0.32		6.998	
	$\to 8^2D$	1.3196					8.001	
	$\to 9^2D$	1.3347					9.029	
	$2^2S \to 5^2F$	1.2098	1.2140		0.35		4.999	
	$\to 6^2F$	1.2648	1.2690		0.33		5.998	
	$\to 7^2F$	1.2980	1.3022		0.32		6.998	
	$\to 8^2F$	1.3198					8.012	
	$\to 9^2F$	1.3352					9.070	

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[a] For Li: 1 a.u. = 219 457.446 cm^{-1}, Be^{+}: 1 a.u. = 219 461.246 cm^{-1}, B^{2+}: 1 a.u. = 219 463.67 cm^{-1}

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Table 2. Excited state wavefunctions as obtained from frequency dependent calculations

Ion	n	ρ	C	C	n	ρ	C	C	C
			$5p$	$6p$			$7p$	$8p$	$9p$
Li	1	4.0	6.86182 (−2)[a]	5.88262 (−2)	1	4.0	−1.02082	−1.18890	−6.62382 (−1)
	2	4.0	6.25119 (−1)	5.12143 (−1)	1	2.5	1.06778	1.23258	7.00425 (−1)
	3	2.0	2.18136 (−1)	1.83477 (−1)	2	2.5	−2.28456	−2.66579	−1.48866
	4	2.0	1.23783 (−2)	8.22031 (−3)	2	1.6	1.18197	1.36967	7.79586 (−1)
	5	1.2	4.46194 (−3)	3.71347 (−3)	3	1.6	−6.41164 (−1)	−7.51368 (−1)	−4.21150 (−1)
	6	1.2	−7.58840 (−4)	−6.31651 (−4)	3	1.0	1.45644 (−1)	1.69186 (−1)	9.75519 (−2)
	6	0.5	−6.12787 (−6)	−4.33742 (−6)	4	1.0	−3.20751 (−2)	−3.77046 (−2)	−2.15319 (−2)
	7	0.5	4.84550 (−7)	3.67292 (−7)	4	0.6	2.44209 (−3)	2.91659 (−3)	1.67540 (−3)
	7	0.2	−1.59208 (−10)	−3.80866 (−10)	5	0.6	−3.21877 (−4)	−3.79731 (−4)	−2.21740 (−4)
	8	0.2	1.65859 (−12)	9.28412 (−12)	5	0.3	7.83055 (−6)	9.69436 (−6)	6.20677 (−6)
	8	0.1	1.00583 (−16)	−8.46293 (−17)	6	0.3	−3.66403 (−7)	−4.77504 (−7)	−3.16800 (−7)
	9	0.1	−9.68849 (−19)	8.21337 (−19)	6	0.15	1.29993 (−9)	3.05839 (−9)	2.62310 (−9)
					7	0.15	−1.74229 (−11)	−5.80692 (−11)	−5.50437 (−11)
					7	0.08	−9.35343 (−14)	9.39793 (−14)	2.79663 (−13)
					8	0.08	6.26743 (−16)	−3.91052 (−16)	2.36643 (−15)

Ion	n	ρ	C	C	C	C	C
			$5d$	$6d$	$7d$	$8d$	$9d$
Li	2	3.0	4.53599 (−2)	2.16391 (−2)	2.00738 (−2)	2.57238 (−2)	9.38952 (−3)
	3	3.0	−1.04339 (−1)	−6.16657 (−2)	−6.52555 (−2)	−8.72941 (−2)	−2.92695 (−2)
	4	1.0	−3.57040 (−3)	−3.52994 (−3)	−4.53410 (−3)	−6.37432 (−3)	−1.94614 (−3)
	5	1.0	1.79672 (−5)	2.97323 (−4)	4.84134 (−4)	7.13344 (−4)	2.06162 (−4)
	5	0.5	−4.70593 (−5)	−5.10544 (−5)	−6.65540 (−5)	−9.62502 (−5)	−2.72464 (−5)
	6	0.5	4.25494 (−6)	5.16714 (−6)	7.12234 (−6)	1.04161 (−5)	3.13311 (−6)
	6	0.25	2.71126 (−8)	−2.07742 (−8)	−5.91832 (−8)	−1.01257 (−7)	−3.73529 (−8)
	7	0.25	−1.36648 (−9)	3.11623 (−10)	1.66690 (−9)	3.08532 (−9)	1.19929 (−9)
	7	0.1	−1.10378 (−15)	8.92690 (−13)	3.30183 (−13)	−9.27132 (−13)	−7.33226 (−13)
	8	0.1	5.80708 (−19)	−8.57871 (−15)	−6.48707 (−15)	1.04496 (−14)	9.95365 (−15)
	8	0.05	1.67401 (−20)	3.21523 (−18)	4.09413 (−18)	1.81375 (−18)	−1.79915 (−17)
	9	0.05	−7.42360 (−23)	−1.34487 (−20)	−1.71269 (−20)	−8.00650 (−21)	6.95521 (−20)

Ion	n	ρ	C	C	C	C	C
			5f	6f	7f	8f	9f
Li	3	2.1	9.85553 (−3)	6.62242 (−3)	4.42042 (−3)	3.30279 (−3)	3.68495 (−3)
	4	2.1	−9.07548 (−3)	−6.28541 (−3)	−4.39732 (−3)	−3.32853 (−3)	−3.57019 (−3)
	4	0.75	1.46621 (−4)	6.15538 (−5)	−1.71554 (−6)	−1.03460 (−5)	1.20412 (−6)
	5	0.75	−9.99652 (−5)	−7.43018 (−5)	−5.65911 (−5)	−4.43034 (−5)	−3.64769 (−5)
	5	0.3	−3.43924 (−6)	−3.21662 (−6)	−3.12145 (−6)	−2.66331 (−6)	−1.31043 (−6)
	6	0.3	1.64240 (−7)	1.86972 (−7)	2.04040 (−7)	1.84388 (−7)	1.00170 (−7)
	6	0.15	5.45612 (−10)	−4.20443 (−10)	−2.02245 (−9)	−2.72476 (−9)	−2.03269 (−9)
	7	0.15	−8.13318 (−12)	−1.43741 (−12)	3.53261 (−11)	5.78618 (−11)	4.79083 (−11)
	7	0.08	1.44219 (−14)	1.87465 (−14)	4.64675 (−14)	−2.06416 (−13)	−3.94409 (−13)
	8	0.08	−1.22580 (−16)	−1.62952 (−16)	−3.91873 (−16)	1.40758 (−15)	3.75406 (−15)
	8	0.05	5.67332 (−19)	7.98901 (−19)	1.76483 (−18)	−3.25449 (−18)	−1.36118 (−17)
	9	0.05	−2.09069 (−21)	−2.95555 (−21)	−6.48103 (−21)	1.13178 (−20)	4.81652 (−20)

Ion	n	ρ	C	C	C	C	n	ρ	C
			5p	6p	7p	8p			9p
Be$^+$	1	5.5	−1.46845 (−2)	−5.83222 (−3)	2.22039 (−2)	3.80988 (−2)	1	4.5	3.88791 (−1)
	2	5.5	5.02262	3.86610	2.67044	2.11864	2	4.0	6.05955 (−1)
	3	2.0	9.83156 (−1)	7.66525 (−1)	5.84109	5.05949 (−1)	3	3.0	1.07116
	4	2.0	−3.22478 (−1)	−2.58018 (−1)	−2.16560	−2.01824 (−1)	4	2.6	−1.79549 (−2)
	5	1.2	−7.47802 (−4)	−5.95597 (−4)	1.44084 (−3)	2.82388 (−3)	5	1.6	2.16770 (−2)
	6	1.2	−1.15679 (−3)	−9.37523 (−4)	−1.27299 (−3)	−1.52871 (−3)	6	1.6	−1.30629 (−2)
	6	0.7	7.29633 (−5)	7.66899 (−5)	1.00389 (−4)	1.20477 (−4)	6	1.0	7.85886 (−4)
	7	0.7	−3.18927 (−6)	−4.27505 (−6)	−8.13367 (−6)	−1.13154 (−5)	7	1.0	−1.30911 (−4)
	7	0.4	−7.03910 (−8)	−1.35422 (−7)	−5.67789 (−8)	3.05329 (−8)	7	0.6	8.93778 (−6)
	8	0.4	1.74663 (−9)	6.63705 (−9)	3.80864 (−9)	−2.43846 (−10)	8	0.6	−1.25793 (−6)
	8	0.2	−1.95344 (−13)	1.54435 (−14)	−7.68144 (−12)	−8.49270 (−12)	7	0.4	1.01856 (−6)
	9	0.2	3.14333 (−15)	−3.40309 (−17)	1.11208 (−13)	1.91569 (−13)	8	0.4	−3.58449 (−8)
							8	0.2	1.67795 (−11)
							9	0.2	−3.04973 (−13)
							9	0.1	−4.28596 (−19)

Table 2.—*cont.*

Ion	n	ρ	C	C	C	C	C
			$5d$	$6d$	$7d$	$8d$	$9d$
Be$^+$	2	3.5	2.25865 (−1)	1.69336 (−1)	1.27919 (−1)	4.61100 (−2)	6.19980 (−3)
	3	3.5	−8.24741 (−1)	−6.36580 (−1)	−4.97176 (−1)	−2.58450 (−1)	−1.35596 (−1)
	4	1.3	−5.66259 (−2)	−4.60212 (−2)	−3.81152 (−2)	−3.07906 (−2)	−2.58654 (−2)
	5	1.3	7.89549 (−3)	7.14641 (−3)	6.60347 (−3)	8.70644 (−3)	9.27181 (−3)
	5	0.8	−3.63868 (−4)	−3.50591 (−4)	−4.12697 (−4)	−1.28306 (−3)	−1.67934 (−3)
	6	0.8	3.62514 (−5)	4.91781 (−5)	7.34520 (−5)	2.98477 (−4)	4.03682 (−4)
	6	0.6	3.79692 (−5)	3.22862 (−5)	2.24066 (−5)	−3.51561 (−5)	6.45559 (−5)
	7	0.6	−3.11054 (−6)	−3.25502 (−6)	−2.80075 (−6)	1.04857 (−6)	3.15055 (−6)
	7	0.3	−3.02063 (−9)	6.21312 (−9)	1.68831 (−8)	1.05660 (−8)	3.53516 (−9)
	8	0.3	7.85233 (−11)	−9.79191 (−11)	−5.67331 (−10)	−4.14250 (−10)	−1.70514 (−10)
	8	0.15	−2.11392 (−14)	−3.01596 (−16)	2.07281 (−14)	5.70240 (−13)	6.43099 (−13)
	9	0.15	2.62092 (−16)	9.30254 (−18)	−2.44177 (−16)	−6.33378 (−15)	−1.05178 (−14)

Ion	n	ρ	C	C	C	C	C
			$5f$	$6f$	$7f$	$8f$	$9f$
Be$^+$	3	2.8	5.71149 (−3)	1.35485 (−2)	1.75588 (−2)	5.89503 (−2)	9.81057 (−2)
	4	2.8	−2.07969 (−2)	−2.92812 (−2)	−3.25495 (−2)	−8.47776 (−2)	−1.37811 (−1)
	4	1.0	−5.01440 (−3)	−3.63382 (−3)	−2.44469 (−3)	1.80182 (−3)	4.69625 (−3)
	5	1.0	3.16819 (−4)	−3.11471 (−4)	−7.53183 (−4)	−3.81224 (−3)	−6.75329 (−3)
	5	0.7	−4.04453 (−4)	−9.20828 (−5)	1.32302 (−4)	1.39943 (−3)	2.63379 (−3)
	6	0.7	2.52895 (−5)	−1.65889 (−5)	−4.75996 (−5)	−2.46022 (−4)	−4.54450 (−4)
	6	0.5	3.05589 (−7)	7.94237 (−6)	1.28698 (−5)	3.99902 (−5)	7.28985 (−5)
	7	0.5	1.86939 (−7)	−2.56073 (−7)	−5.86351 (−7)	−2.26239 (−6)	−4.34030 (−6)
	7	0.3	1.94293 (−10)	−6.39735 (−9)	−1.11302 (−8)	8.23621 (−9)	3.58738 (−8)
	8	0.3	−4.05974 (−12)	1.20649 (−10)	4.23102 (−10)	−1.18488 (−10)	−9.93328 (−10)
	8	0.15	3.78627 (−16)	−1.18673 (−14)	−2.39149 (−14)	−4.20099 (−13)	7.38720 (−14)
	9	0.15	−4.44399 (−18)	1.42115 (−16)	2.85384 (−16)	4.69160 (−15)	9.93842 (−16)

Ion	n	ρ	C	C	C	n	ρ	C	C
			5p	6p	7p			8p	9p
B^{2+}	1	7.0	1.29879	1.01142	8.54295 (−1)	1	6.0	6.75307 (−1)	6.64390 (−1)
	2	7.0	7.22610	5.67584	4.70582	2	4.5	2.30984	1.21041
	3	4.0	1.12401 (+1)	8.74814	7.39917	3	3.2	1.42884	2.21300
	4	4.0	−5.17023	−4.03433	−3.52116	4	3.2	−1.50127 (−1)	−1.31780
	5	2.9	1.39640	1.06121	9.13593 (−1)	5	2.0	−7.10854 (−2)	1.13798 (−1)
	6	2.9	−8.33370 (−1)	−6.53621 (−1)	−5.71300 (−1)	6	2.0	4.08290 (−3)	−1.17986 (−1)
	6	1.7	−8.66221 (−3)	−7.20229 (−3)	−5.27986 (−3)	6	1.4	−2.34644 (−3)	2.40206 (−2)
	7	1.7	−8.76653 (−5)	2.21754 (−4)	6.80634 (−5)	7	1.4	8.98813 (−4)	−5.11989 (−3)
	7	1.0	2.64941 (−4)	2.57548 (−4)	2.49439 (−4)	7	0.9	2.20588 (−5)	3.11904 (−4)
	8	1.0	−2.98390 (−5)	−3.32514 (−5)	−3.45998 (−5)	8	0.9	−3.67381 (−6)	−5.64138 (−5)
	8	0.5	−1.56341 (−8)	2.10527 (−8)	7.59738 (−8)	7	0.6	−4.74647 (−6)	2.79283 (−5)
	9	0.5	5.79293 (−10)	−3.61211 (−10)	−3.78523 (−9)	8	0.6	5.74465 (−7)	−1.51203 (−6)
						8	0.4	−2.01842 (−8)	4.20461 (−9)
						9	0.4	6.75019 (−10)	−4.41997 (−11)
						9	0.2	8.86848 (−17)	−4.26713 (−14)

Ion	n	ρ	C	C	C	C	C
			5d	6d	7d	8d	9d
B^{2+}	2	4.5	4.83905 (−1)	3.52555 (−1)	2.64981 (−1)	1.82740 (−1)	9.96039 (−2)
	3	4.5	−3.22793	−2.47614	−1.95195	−1.50373	−1.05289
	4	1.8	−4.41054 (−1)	−3.55553 (−1)	−2.93110 (−1)	−2.48047 (−1)	−2.04097 (−1)
	5	1.8	1.29686 (−1)	1.12827 (−1)	9.89749 (−2)	9.29846 (−2)	8.82025 (−2)
	5	1.2	−1.50836 (−2)	−1.37728 (−2)	−1.28042 (−2)	−1.39111 (−2)	−1.55473 (−2)
	6	1.2	3.97746 (−3)	3.88637 (−3)	3.71686 (−3)	4.00304 (−3)	4.41259 (−3)
	6	0.8	4.90718 (−5)	−1.91870 (−5)	−6.80105 (−5)	−1.46035 (−4)	−2.43369 (−4)
	7	0.8	−1.60148 (−5)	−1.51843 (−5)	−1.21836 (−5)	−3.60427 (−6)	9.34473 (−6)
	7	0.45	−7.98041 (−8)	2.41024 (−7)	6.02631 (−7)	7.69633 (−7)	6.96827 (−7)
	8	0.45	3.56151 (−9)	−6.67040 (−9)	−3.05477 (−8)	−4.80579 (−8)	−5.08368 (−8)
	8	0.3	−2.64711 (−11)	1.05373 (−11)	4.85289 (−11)	6.10143 (−10)	1.42623 (−9)
	9	0.3	5.43367 (−13)	−1.82284 (−13)	−9.28035 (−13)	−1.01732 (−11)	−3.54325 (−11)

Table 2.—*cont.*

Ion	n	ρ	C	C	C	C	C
			$5f$	$6f$	$7f$	$8f$	$9f$
B^{2+}	3	3.5	3.16810 (−2)	3.84683 (−2)	4.22145 (−2)	1.35596 (−1)	2.33038 (−1)
	4	3.5	−1.54064 (−1)	−1.50938 (−1)	−1.43689 (−1)	−2.90574 (−1)	−4.52325 (−1)
	4	1.2	−3.53945 (−2)	−2.87500 (−2)	−2.28410 (−2)	−7.19943 (−3)	6.93214 (−3)
	5	1.2	7.12802 (−3)	3.37681 (−3)	2.42473 (−4)	−2.16337 (−2)	−4.60628 (−2)
	5	0.9	−3.95322 (−3)	−1.53987 (−3)	4.02119 (−4)	1.36064 (−2)	2.86479 (−2)
	6	0.9	5.29483 (−4)	5.58078 (−5)	−3.47759 (−4)	−3.30739 (−3)	−6.83460 (−3)
	6	0.7	−1.64573 (−5)	1.17995 (−4)	2.19006 (−4)	8.98415 (−4)	1.76172 (−3)
	7	0.7	3.56207 (−6)	−6.94140 (−6)	−1.54082 (−5)	−6.61290 (−5)	−1.32076 (−4)
	7	0.45	−1.02088 (−8)	−1.76340 (−7)	−2.86913 (−7)	4.90160 (−7)	1.73262 (−6)
	8	0.45	3.80376 (−10)	4.86409 (−9)	1.78258 (−8)	−1.19996 (−8)	−6.83587 (−8)
	8	0.25	−2.33265 (−13)	−1.30578 (−12)	−2.50397 (−12)	−5.14896 (−11)	2.86217 (−12)
	9	0.25	4.44974 (−15)	2.41789 (−14)	4.62545 (−14)	8.78399 (−13)	4.63693 (−13)

[a] $(\pm)n = 10^{\pm n}$

value 0.00132. (These more extensive calculations are, however, not included in the tables.) For Be^+, for the transition $2^2S \rightarrow 9^2P$, we get a value for the oscillator strength which is slightly higher than that for the transition $2^2S \rightarrow 8^2P$. This also, we believe, is an artifact of the choice of basis set. Since all these functions are highly diffuse and contain a large number of nodes, a proper representation of these functions should incorporate more parameters. Assuming complete screening we have also evaluated the effective quantum number $n^* = 1/\sqrt{2\varepsilon}$ where ε is the ionization potential of the particular orbital concerned. These results are aso displayed in Table 1. For comparison, the experimental values of n^* are also listed. For transitions having low values of the principal quantum number we observe very good agreement. However, for higher order transitions, the values deviate and the quantum defect ($\Delta = n - n^*$) tends to become negative. This general trend is observed for all the series.

The large discrepancy of quantum defect values for higher n is probably caused by the poor description of such diffuse functions by a limited basis set. For example, for the $7p$ quantum defect for Li, the experimental value is 0.047, the static-exchange value is 0.034 [33], and the present result is −0.107. Thus although TDCHF theory is in principle an improvement over Hartree–Fock, the possible improvement is more than offset by basis set errors. To describe the response of the Rydberg electron to the long-range Coulomb potential properly, a very diffuse set of functions is necessary. An additional problem is that to calculate ε theoretically we have taken the Clementi orbital eneriges which are not correlated. Since transition energies as found by TDCHF methods do not have a specific bound, this may contribute to the error.

Within the framework of a single-particle model TDCHF calculations presented here furnish a very good representation of single excited states and provide excellent results for transition properties when n is not too large. A similar study for systems with higher nuclear charge is under present investigation, and the results will be reported in due course.

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