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Dynamic polarizabilities and Rydberg states of open shell atomic systems

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Time dependent coupled Hartree-Fock (TDCHF) theory is applied to calculate frequency dependent polarizabilities, transition energies, oscillator strengths and effective quantum numbers of several excited states of the open shell ions Al, Si^+, P^{2+}, S^{3+}, Cl^{4+}, Ar^{5+}, Cl and Ar^+ in the ^2P state within and beyond the normal dispersion region. The Roothaan formalism has been adopted to deal with the open shell problem. The excitation energies are extracted from the positions of the poles of an appropriate functional. Analytic representations of the singly excited Rydberg states have been found. The results obtained compare well with spectroscopic and other elaborate theoretical data wherever available. Inner shell excitations have been found for the first time within TDCHF theory.

Key words: Dynamic polarizabilities — Rydberg states — Open shell ions

1. Introduction

Knowledge of highly excited states of many electron systems is limited [1]. However recent experiments using beam foil [2-8], tunable lasers [9-11] and other methods [12, 13] provide very useful information about the excited states of such systems. Such studies are of interest for a number of reasons e.g. in the interpretation of the spectra of solar flares [14-18], and in the calculation of

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radiative and forbidden decay rates and collision strengths for electron impact excitation of highly charged ions (such as occur in astrophysical observation or laser produced plasmas [19–21] and high temperature tokamak plasma [22–24]). They are particularly useful for the estimation of energy loss in controlled thermonuclear plasmas, determination of electron temperature and density of solar corona, fusion plasma diagnostics, and for the estimation of relative abundance of elements [25–28]; [29] is a good review on the subject.

Lines of neutral and ionised atoms of the $3p$ open shell are quite dominant in the emission and absorption spectra of the solar photosphere and chromosphere [14, 15, 30, 31]. Many of these lines have been recorded by space shuttle experiments [32]. Very recent experiments, using Copernicus and International Ultraviolet Explorer [IUE] satellites, on intersteller matter [33, 34], and observation on the extreme ultraviolet spectrum of the Jupiter planetary system during Voyager 1 and 2 encounters [35, 36] reveal the presence of many such ions. Laboratory experiments on such systems are also in progress [37–39]. These observations are useful for detecting low density clouds in interstellar medium, stellar winds and the absorbing material in front of some quasars and Syefert galaxies and also for determining the abundance of elements in it.

Because of their importance, theoretical studies on such systems are quite interesting. Most of the few such studies which have been performed have been confined to the determination of accurate oscillator strengths by configuration interaction (CI) methods [30, 31, 40–48], multiconfiguration Hartree-Fock (MCHF) calculations [49–51], relativistic parametic potential methods with CI [52], close coupling method [53] etc. All these calculations show explicitly the importance of configuration mixing for the assignment of spectral terms and calculation of oscillator strengths.

TDCHF theory has been found very successful in the past for estimating frequency dependent response properties particularly for closed shell ions and ions having an s electron in the open shell [54–58]. Application to p and other open shell systems is rather limited [59]. In addition to the dynamic polarizability which is very important for estimating several interesting properties of the system [60], the method can yield the correct static limit of the polarizability values, transition energies and transition properties, such as allowed and forbidden transition probabilities, and furnish reasonably accurate quantum defects and analytic representations of the singly excited Rydberg states. (By Rydberg orbital we mean any orbital outside the valence shell [61].) The excited states may be utilised for calculating expectation values of different operators and are useful in perturbation theory and for estimating collision cross sections. The theory is successful mainly because of its implicit inclusion of certain classes of correlation diagrams [62] which are present in the random phase approximation (RPA) method [63]. We shall apply TDCHF theory here to estimate the Rydberg states and transition properties of few ions of $3p$ open shell system. The closed shell theory is well known. The salient features of the open shell theory is described in Sect. 2 and the results are discussed in Sect. 3.

2. Method

The open shell system is described by the usual non relativistic Hamiltonian Ho. An external perturbation of the form

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

is imposed on the system. We are interested in dipolar excitations from the ground state and we take

$$G(\mathbf{r}) = \lambda \sum_{i=1}^{N} r_i P_1(\cos\theta_i) \tag{2}$$

where λ is an appropriate perturbation strength parameter. We adopt the Roothaan scheme [64] to describe the ground state of open shell system. This scheme reduces "s" or "p" type open shell energies to that of an effective closed shell energy with certain parameters in the energy expression which take care of the open shell structure. The external perturbation of Eq. (1) admixes first order corrections $\delta\psi_i^{\pm}$ to the ground orbital ψ_i. These oscillate with the two components given by Eq. (1). Frequency dependent response properties are obtained by taking the Fourier transform of the time dependent problem as follows:

$$J = \frac{1}{T}\int_0^{\tau} dt \frac{\langle\Phi|H - i\,\partial/dt|\Phi\rangle}{\langle\Phi|\Phi\rangle} \tag{3}$$

where Φ is the total wavefunction and H is the total Hamiltonian. Atomic units are used here. The details of the theory was discussed earlier [59]. Variation of the functional J of Eq. (3) with respect to parameters introduced in $\delta\psi_i^{\pm}$ yields the perturbed admixtures of [59]. In terms of orbitals the dynamic polarizability is given by

$$\alpha_d(\omega) = \sum_k [\langle\delta\psi_k^-|r\cos\theta|\psi_k\rangle + \langle\delta\psi_k^+|r\cos\theta|\psi_k\rangle]. \tag{4}$$

$\alpha_d(\omega)$ passes through poles at certain frequencies which correspond to natural excitations of the system. From the pole positions one can extract transition energies, singly excited wavefunction and other properties connected with transitions.

3. Results

In the present communication we confine our analysis to ions having ^{2}P ground states e.g. Al, Si$^+$, P^{2+}, S^{3+}, Cl^{4+}, Ar^{5+}, Cl and Ar$^+$. Although all these ions are all described by the ^{2}P ground configuration, their excitation properties are different. For the isoelectric series of aluminium the excitation of the valence $3p$ orbital leaves a closed shell core $3s^2$:^{1}S, but that of Cl sequence leaves an open shell core $3p^4$ which has different valence excited LS coupled states resulting in a very complex final spectrum. For the Al sequence we studied excitations $3p \rightarrow ns$ ($n = 4, 5, \ldots, 7$) and $3p \rightarrow nd$ ($n = 3, 4, \ldots, 7$) while for Cl and Ar$^+$, we obtained a smaller number of transitions as will be apparent from subsequent tables. The ground state wavefunctions are taken from Clementi and Roetti [65]. The radial parts of the first order admixtures to the ground state are represented as linear combinations of Slater bases viz.

$$\delta\psi_k^{\pm}(r)=\sum_i C_{ik}^{\pm} r^{n_{ik}} \exp(-\zeta_{ik} r). \tag{5}$$

Where the C_{ik} are linear variation parameters. The exponents n_{ik} and ζ_{ik} are preassigned. The choice of n_{ik} depends upon the angular symmetry of the orbital $\delta\psi_k$. Once a starting n_{ik} is fixed one can include higher powers depending on the number of nodes. The choice of maximum and minimum ζ_{ik} depends roughly on the short and long range behaviour of the wavefunction. There are in general no strict guidelines for an appropriate choice but the optimised ground exponents of Clementi and Roetti [65] together with experience give a guideline. Once the maximum and minimum value of the exponents are chosen intermediate ones can be appropriately chosen. Further it is observed from a large number of calculations [54–59] that given a sufficiently flexible exponent set the choice of the maximum value of the exponent is not very critical. The innermost core 1s is assumed frozen. To test the method we calculated the static limit of the dynamic polarizability $\alpha_d(\omega)_{\omega\to 0}$ for all the ions and compared them in Table 1 with existing CHF static results of Roy et al. [66]. Roy et al. used 8 parameters for the representation of perturbed valence admixtures, we used a similar basis set to compare with their values. As observed form Table 1, the static limit is in excellent agreement with the static values for all ions whose data exists. To test the basis set convergence we performed two sets of calculations for Al and Cl. For the excitations $p\genfrac{}{}{0pt}{}{\nearrow s}{\searrow d}$ types we used 12 or 15 parameter representations while for the excitations $s\to p$ type we used only 8 or 10 parameter representations. The variations of the core admixtures usually does not affect the polarizability values. From the results in Table 1, we notice that fairly good convergence of polarizability values is achieved for Al with 15 parameters while for the ions

Table 1. Static limit of dynamic polarizability $\alpha_d(\omega)_{\omega\to 0}$

Ion	Present static limit (Å^3)	Other static results (Å^3)
Al	8.68^a, 9.09^b, 9.11^c	8.71^d
Si$^+$	2.90^a, 2.92^c	2.93^d
P^{2+}	1.42^a, 1.42^c	1.43^d
S^{3+}	0.82^a, 0.82^c	
Cl^{4+}	0.53^a, 0.53^c	
Ar^{5+}	0.36^a, 0.36^c	
Cl	1.98^a, 2.08^b, 2.08^c	1.97^d
Ar$^+$	0.99^a, 1.00^c	

[a] 8 parameter calculation
[b] 12 parameter calculation
[c] 15 parameter calculation
[d] [66]

variation of parameters from 8 to 15 does not affect the results much. Hence in our subsequent calculations we have used 12 and 15 parameter representations for Al and Cl and for all other ions we used the 15 parameter representation for the valence perturbed admixture. In Table 2 we have listed the dynamic polarizability values for all the ions with respect to incident frequency in the normal dispersion region. The positions of the first poles are clearly indicated by a change in sign of the polarizability values. It is further observed that only very near to poles does the functional representation by 12 or 15 parameters affect the polarizability values, although the pole position is practically unaffected. In Table 3 we list for the Al isoelectronic series up to Ar^{5+} the transition energies obtained from the position of the poles in dynamic polarizability calculation, the oscillator strengths in length form and effective quantum numbers n^* for the Rydberg orbitals. The transition energies are compared with available [67, 68] spectroscopic data. Agreement is obtained for all the cases to within 5%. The deviation usually decreases as we proceed along the higher Z isoelectronic members. We missed a few resonances, e.g., for Al $7d$, for Si^+ $7s$ and for P^{2+} $6d$ and $7d$. This is probably due to existence of other transitions in that region which effectively mask these transitions. The oscillator strengths are evaluated using the dynamic polarizability values [69]

$$\alpha_d(\omega)=\sum_n{}' \frac{f_{n0}}{\omega_{n0}^2-\omega^2}. \tag{6}$$

The method of extracting oscillator strengths from Eq. (6) is detailed in earlier calculations [59]. The oscillator strengths compare reasonably with the existing data using elaborate CI calculations, experiments and other sophisticated results except for $3p\to 3d$ transitions. Here we get somewhat larger values. The reason is well known in CI studies. It was shown by Weiss [40] and subsequently by other workers [30, 31, 41–53] that a very strong perturbation is caused by $3s3p^2$ terms. One must include such configurations explicitly to obtain better results for oscillator strengths. The effect is most prominent for Al $3s\to nd$ series. The TDCHF theory, which is equivalent to the RPA method [63], does not take care of such correlations explicitly resulting in errors in the oscillator strengths. The oscillator strengths are consistently better for the $3p\to ns$ transitions. The effect of $3s\to 3p$ mixing is very apparent in our numerical results. We notice in most cases a strong mixing of dipolar matrix elements from the $3s$ shell contributing to total polarizability values near the poles corresponding to different excitations.

The effective quantum number n^* for the Rydberg orbitals are calculated using the formula $n^*=Z_{\text{eff}}/\sqrt{2\varepsilon}$, where ε is the ionisation potential of the orbital and Z_{eff} is the effective charge. $Z_{\text{eff}}=1$ in the complete screening model for a neutral atom. These are compared with similar quantities obtained from spectroscopic data [67, 68]. Consistent results are obtained.

In Table 4 we list similar results for Cl and Ar^+ in the ^2P state. The situation is more complex here because of different multiplets associated with the dipolar transitions $3p^5\to 3p^4 \begin{smallmatrix}\nearrow ns\\ \searrow nd\end{smallmatrix}$. Here the spin of the excited electron is unrestricted

Table 2. Dynamic polarizability values in the normal dispersion region for open shell ions in ^2P state

Frequency ω (a.u.)	Al		$\alpha_d(\omega)$ (a.u.)					Cl		Ar$^+$
	a	b	Si$^+$ b	P^{2+} b	S^{3+} b	Cl^{4+} b	Ar^{5+} b	a	b	b
0.0001	6.138 (+1)^c	6.147 (+1)	1.97 (+1)	9.58	5.57	3.58	2.45	1.403 (+1)	1.404 (+1)	6.80
0.01	6.158 (+1)	6.168 (+1)								
0.02	6.221 (+1)	6.230 (+1)	1.98 (+1)	9.60				1.405 (+1)	1.406 (+1)	6.80
0.03	6.330 (+1)	6.340 (+1)								
0.04	6.492 (+1)	6.503 (+1)	1.99 (+1)	9.64	5.59	3.59	2.46	1.411 (+1)	1.412 (+1)	6.81
0.06	7.042 (+1)	7.053 (+1)	2.03 (+1)	9.72				1.421 (+1)	1.422 (+1)	6.83
0.08	8.169 (+1)	8.181 (+1)	2.07 (+1)	9.84	5.66	3.62	2.48	1.435 (+1)	1.436 (+1)	6.86
0.10	1.189 (+2)	1.189 (+2)	2.14 (+1)	9.99				1.454 (+1)	1.455 (+1)	6.90
0.111	8.336 (+2)	7.502 (+2)								
0.112	−1.696 (+3)	−2.501 (+3)								
0.12			2.22 (+1)	1.02 (+1)	5.79	3.68	2.50	1.478 (+1)	1.479 (+1)	6.94
0.14			2.33 (+1)	1.04 (+1)				1.507 (+1)	1.508 (+1)	6.99
0.16			2.47 (+1)	1.07 (+1)	5.97	3.76	2.55	1.543 (+1)	1.544 (+1)	7.05
0.18			2.66 (+1)	1.11 (+1)				1.587 (+1)	1.588 (+1)	7.13
0.20			2.90 (+1)	1.15 (+1)	6.23	3.87	2.60	1.641 (+1)	1.642 (+1)	7.21
0.22			3.23 (+1)	1.20 (+1)						7.30
0.24			3.71 (+1)	1.26 (+1)	6.58	4.01	2.67	1.789 (+1)	1.790 (+1)	7.41
0.26			4.49 (+1)	1.33 (+1)						7.52
0.28			6.21 (+1)	1.43 (+1)	7.06	4.21	2.76	2.033 (+1)	2.034 (+1)	7.66
0.29			9.87 (+1)							
0.295			1.14 (+3)							
0.296			−2.44 (+3)							
0.30				1.55 (+1)						7.81
0.32					7.72	4.45	2.88	2.537 (+1)	2.539 (+1)	7.97

0.34	1.92 (+1)						8.16
0.36		8.69	4.78	3.02	5.692 (+1)	5.726 (+1)	8.37
0.370					8.190 (+2)	1.040 (+3)	
0.371					−7.059 (+2)	−5.849 (+2)	
0.38	2.78 (+1)						8.60
0.40		1.02 (+1)	5.22	3.20			8.87
0.41	2.82 (+2)						
0.411	1.05 (+3)						
0.412	−5.06 (+2)						
0.44		1.30 (+1)	5.85	3.44			9.51
0.48		2.11 (+1)	6.79	3.75			1.04 (+1)
0.50		4.13 (+1)					
0.512		3.43 (+2)					
0.514		−5.90 (+2)					
0.52			8.44	4.18			1.15 (+1)
0.56			1.23 (+1)	4.82			1.33 (+1)
0.60			3.93 (+1)	5.87			1.65 (+1)
0.608			1.11 (+2)				
0.612			−2.54 (+3)				
0.64				8.00			2.66 (+1)
0.66							8.78 (+1)
0.664							8.77 (+4)
0.668							−1.11 (+3)
0.68				1.56 (+1)			
0.70				4.49 (+1)			
0.708				5.59 (+2)			
0.712				−1.04 (+2)			

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[a] 12 parameter calculation
[b] 15 parameter calculation
[c] $(\pm n) \equiv 10^{\pm n}$

Table 3. Transition energies, oscillator strengths and effective quantum numbers for aluminium isoelectronic sequence as obtained from frequency dependent calculation

Ion	Transition	Transition energy (a.u.)		Oscillator strength (a.u.)		Effective quantum number n^*	
		Present calculation	Expt*	Present calculation	Other results	Present** calculation	Expt
Al	$3p \rightarrow 4s$	0.1117^a 0.1117^b	0.1155	0.118^a 0.119^b	0.115^c, 0.11^d, 0.118^e 0.116 ± 0.001^f 0.113 ± 0.07^g 0.115 ± 0.005^h	2.255	2.187
	$\rightarrow 5s$	0.1634^a 0.1635^b	0.1717	0.016^a 0.016^b	0.014^c, 0.015^i 0.018^j	3.279	3.217
	$\rightarrow 6s$	0.1827^a 0.1860^b	0.1920	0.0051^a 0.0058^b	0.00403^c	4.564	4.226
	$\rightarrow 7s$	0.2018^a 0.1965^b	0.2017	0.013^a 0.014^b	0.00288^c	6.086	5.227
	$\rightarrow 3d$	0.1479^a 0.1479^b	0.1478	0.271^a 0.271^b	0.175^c, 0.18^g 0.179^k, 0.192^l 0.193 ± 0.007^m 0.147^n, 0.18 ± 0.02^g 0.12^e	2.838	2.632
	$\rightarrow 4d$	0.1753^a 0.1753^b	0.1774	0.038^a 0.030^b	0.044^c 0.038^i, 0.045^k	3.796	3.426
	$\rightarrow 5d$	0.1881^a 0.1880^b	0.1924	0.056^a 0.0052^b	0.120^c 0.121^k	4.764	4.256
	$\rightarrow 6d$	0.1950^b	0.2012	0.0032^b	0.098^c, 0.102^k	5.774	5.157
Si^+	$3p \rightarrow 4s$	0.2952^b	0.2984	0.140	0.130^c, 0.132^d, 0.13^e 0.119^o, 0.127^b, 0.23^q 0.08^n, 0.08 ± 01^s, 0.11^t	2.623	2.573
	$\rightarrow 5s$	0.4354^b	0.4464	0.017	0.021^c, 0.0198^k, 0.017^t	3.645	3.601
	$\rightarrow 6s$	0.4945^b	0.5066	0.0076	0.0067^t	4.678	4.613
	$\rightarrow 3d$	0.3559^b	0.3615	2.062	1.2^c, 1.18^e, 1.14^l, 1.34^n 1.12^o, 1.08^b, 0.96^a	2.949	2.892

					0.98 ± 0.13^s, 0.97 ± 0.06^u 1.13 ± 0.13^v		
	$\rightarrow 4d$	0.4469^b	0.4603	0.171	0.20^c, 0.205^o, 0.168^t	3.793	3.776
	$\rightarrow 5d$	0.4985^b	0.5121	0.039	0.022^t	4.784	4.754
	$\rightarrow 6d$	0.5264^b	0.5400	0.016	0.007^t	5.798	5.745
	$\rightarrow 7d$	0.5433^b	0.5566	0.0093	0.007^t	6.852	6.742
P^{2+}	$3p \rightarrow 4s$	0.5333^b	0.5369	0.029	0.073^d, 0.078^e, 0.098^j	2.842	2.806
	$\rightarrow 5s$	0.7887^b	0.8021	0.016		3.861	3.832
	$\rightarrow 6s$	0.9007^b	0.9163	0.0064		4.869	4.839
	$\rightarrow 7s$	0.9601^b		0.0032		5.874	
	$3p \rightarrow 3d$	0.5124^b	0.5325	1.96	1.29^e, 1.27^l 1.25^n, 0.97 ± 0.1^u	2.790	2.795
	$\rightarrow 4d$	0.7703^b	0.7856	0.022		3.749	3.733
	$\rightarrow 5d$	0.8914^b	0.9133	0.0013		4.754	4.801
S^{3+}	$3p \rightarrow 4s$	0.8231^b	0.8310	0.081	0.094^c, 0.083^d 0.088^e, 0.093^j	2.992	2.969
	$\rightarrow 5s$	1.2196^b	1.2348	0.018		4.012	3.986
	$\rightarrow 6s$	1.4001^b		0.0072		5.027	
	$\rightarrow 7s$	1.4975^b		0.0030		6.041	
	$\rightarrow 3d$	0.6671^b	0.6932	1.593	1.19^e, 1.18^l, 1.13^n 0.91 ± 0.15^u, 1.18^w, 1.44^y	2.992	2.969
	$\rightarrow 4d$	1.1495^b	1.1636	0.00024		3.756	3.731
	$\rightarrow 5d$	1.3613^b		0.021		4.744	
	$\rightarrow 6d$	1.4757^b		0.0024		5.761	
	$\rightarrow 7d$	1.5417^b		0.0022		6.761	
Cl^{4+}	$3p \rightarrow 4s$	1.1637^b	1.1679	0.090	0.091^c, 0.087^e, 0.092^j	3.104	3.072
	$\rightarrow 5s$	1.7250^b		0.019		4.121	
	$\rightarrow 6s$	1.9856^b		0.0070		5.128	
	$\rightarrow 7s$	2.1286^b		0.0037		6.132	
	$3p \rightarrow 3d$	0.8160^b	0.8469	1.368	1.06^e, 1.057^l 1.01^n, 1.02^x	2.757	2.756
	$\rightarrow 4d$	1.5786^b	1.5925	0.019		3.764	3.727
	$\rightarrow 5d$	1.9117^b	1.9273	0.010		4.770	4.704
	$\rightarrow 6d$	2.0854^b		0.010		5.769	
	$\rightarrow 7d$	2.1886^b		0.008		6.774	

Table 3—continued

Ion	Transition	Transition energy (a.u.)		Oscillator strength (a.u.)		Effective quantum number n^*	
		Present calculation	Expt*	Present calculation	Other results	Present** calculation	Expt
Ar^{5+}	$3p \rightarrow 4s$	1.5548^b	1.5596	0.088	0.088^c, 0.083^e, 0.088^j	3.192	3.165
	$\rightarrow 5s$	2.3044^b		0.025		4.207	
	$\rightarrow 6s$	2.6593^b		0.0071		5.214	
	$\rightarrow 7s$	2.8565^b		0.0041		6.223	
	$\rightarrow 3d$	0.9603^b	0.9961	1.209	0.95^c, 0.977^l 0.933^n, 0.56 ± 0.06^u 0.915^x, 0.67 ± 0.02^z	2.761	2.741
	$\rightarrow 4d$	2.0572^b	2.0722	0.055		3.774	3.744
	$\rightarrow 5d$	2.5331^b	2.5308	0.025		4.779	4.670
	$\rightarrow 6d$	2.7822^b		0.018		5.778	
	$\rightarrow 7d$	2.9288^b		0.024		6.772	

* [67, 68]

** Values of n^* are estimated using 15 parameter results

[a] 12 Parameter calculation

[b] 15 Parameter calculation

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Table 4. Transition energies, oscillator strengths *and effective quantum numbers for* Cl and Ar$^+$

Ion	Transition	Transition energy (a.u.)		Oscillator strength (a.u.)		Effective quantum number n^*	
		Present calculation	Expt*	Present calculation	Other values	Present** calculation	Other values
Cl	$3p^5(^2P)\rightarrow 3p^4(^1D)4s{:}^2D$	0.3704^a	0.3833	0.282^a	0.088^c	1.918	1.849^e
		0.3703^b		0.281^b			
	$3p^4(^1D)5s{:}^2D$	0.4481^a	0.4698	0.021^a		2.934	2.892^e
		0.4481^b		0.030^b			
	$3p^4(^1D)6s{:}^2D$	0.4742^b		0.087^b		3.953	
	$3p^4(^1D)3d{:}^2D$	0.4489^a	0.4656	0.240^a		2.954	2.795^e
		0.4489^b		0.241^b			
	$3p^4(^1D)4d{:}^2D$	0.4740^a		0.094^a	0.111^d	3.934	4.038^f
		0.4739^b		0.028^b			
	$3p^4(^1D)5d{:}^2D$	0.4857^b		0.050^b		4.951	5.031^f
	$3p^4(^1D)6d{:}^2D$	0.4920^b		0.033^b		5.934	6.026^f
Ar$^+$	$3p^5(^2P)\rightarrow 3p^4(^1D)4s{:}^2D$	0.6666^b	0.6777	0.122^b		2.298	
	$3p^4(^1D)5s{:}^2D$	0.8639^b	0.8924	0.089^b		3.320	
	$3p^4(^1D)6s{:}^2D$	0.9386^b	0.9702	0.031^b		4.327	
	$3p^4(^1D)7s{:}^2D$	0.9845^b		0.163^b		5.731	
	$3p^4(^1D)3d{:}^2D$	0.8036^b	0.7863	1.907^b		2.876	
	$3p^4(^1D)4d{:}^2D$	0.9077^b	0.9105	0.726^b		3.811	
	$3p^4(^1D)5d{:}^2D$	0.9578^b	0.9781	0.318^b		4.778	
	$3p^4(^1D)6d{:}^2D$	0.9845^b		0.163^b		5.731	
	$3p^4(^1D)7d{:}^2D$	1.0033^b		0.146^b		6.892	

* [68]

** Values of n^* are estimated using 15 parameter results

[a] Present result with 12 parameter

[b] Present result with 15 parameter

[c] [70]

[d] Brown ER, Carter SL, Kelly HP (1980) Phys Rev A 21:1237

[e] Results obtained by using the series limit of $3p^4{:}^1D$ given in [77]

[f] [76]

and hence the core ($2p^4$) must be in such a state as to produce the same multiplicity for the initial and final states. This left the singlet as the possible multiplicity of the ($2p^4$) configuration. Energetically ^1D is more favourable as we observe from the table. For Cl ^1S the valence excited states are also pretty high in energy. Experimental transition energies are obtained from the compilation of Bashkin and Stoner [68]. The excited states we are interested in are very high and we get fewer resonances than in the Al sequence, but agreement of transition energies is within 5% in all cases where data exist. Our oscillator strengths are poor here because of the neglect of the very strong CI mixing of $3s^2 3p^5 \rightarrow 3s3p^6$ configuration which was explicitly shown by other workers [48, 71-75] to be extremely important for any such calculation. This is also explicitly apparent in our calculation and we get very strong dipolar $3s \rightarrow np$ mixing resulting in large change of the dipolar matrix elements. It appears that there is significant cancellation among such matrix elements. The effective quantum numbers agree well with the results obtained by Rusic and Berkowitz [76], calculated using the series limit given by Hansen et al. [77]. For Ar^+ there is practically no data available for the transitions with which we are concerned. Most of the experimental work was restricted to the $3p^4 4p$ configuration of Ar^+ [78].

In the present calculation we get resonance in the polarizability values for transitions corresponding to $3s \rightarrow 3p$. This has not been seen in TDCHF calculations reported so far. The transition energies are about 8 to 10% away from experimentally observed energies for Al series, however for Ar^+ there is much more error. The level is autoionising for Al and Cl. As we have neglected configuration interactions the oscillator strengths are inaccurate and we have not quoted them here. We may only point out that the functional representation of the $3s$ excited $3p$ orbital is very similar to that of the occupied $3p$ orbital of Clementi and Roetti [65]. For comparison we give in Fig. 1 such a plot for Al atom. In this case the $3s \rightarrow 3p$ excitation energy lies beyond the $3p$ ionisation limit. A very close similarity is observed. It is further observed that our computed

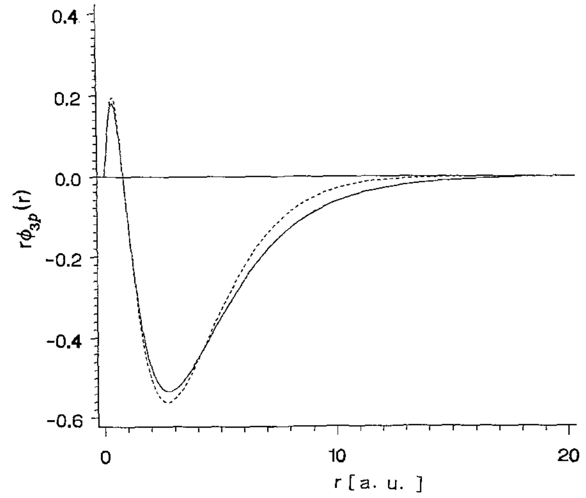

Fig. 1. Plot of the inner shell ($3s$) excited $3p$ function and that of ground state function $3p$ of Clementi and Roetti against r. The *solid line* represents our function while the *dotted one* corresponds to that of Clementi and Roetti

orbital is more diffuse than that of Clementi and Roetti [65], as is physically the case. We hope to present more detailed results on such transition later on.

4. Conclusion

TDCHF theory is shown to yield fairly accurate estimates of transition properties of open shell system including transition energies and the effective quantum of the Rydberg orbitals. The theory gives good transition properties except in those cases where configuration mixing from singly excited configurations is very important. The analytic representations of the Rydberg orbitals in terms of Slater bases may be obtained from the authors on request.

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