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Singly excited bound states in continuum: a time-dependent perturbation approach

A. K. Das and P. K. Mukherjee

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur,
Calcutta 700 032, India

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Summary. Time-dependent coupled Hartree–Fock (TDCHF) scheme has been applied to study the behaviour of bound excited states embedded in the continuum for the negative ions Li^-, F^-, Na^- and Cl^-. The excited states have been obtained from the position of the poles of the dynamic polarizability values which are evaluated for all the ions within and beyond the normal dispersion region. Transition energies and dipole allowed oscillator strengths have been obtained for several transitions which lie in the continuum. Although the excited state functions are extremely diffuse, they show proper asymptotic behaviour and furnish correct number of nodes. Oscillator strengths are found to follow a different trend than observed in normal bound state calculations.

Key words: Dynamic polarizabilities – Transition energies – Oscillator strengths – Closed shell negative ions

1. Introduction

The existence of bound states embedded in continuum was predicted first by Von Neuman and Wigner [1] long time back using a method based on amplitude modulation of a plane wave. Subsequently there has been a lot of interest for the physical realisation of such states and their properties using different techniques [2–5]. Well known examples are the doubly excited autoionising states of two electron systems which lie much above their first ionisation threshold. These are thoroughly discussed in the literature [6]. With the advent of strong tunable lasers such studies have become quite effective [7]. In the language of collision theory the coupling between various reaction and excitation channels can lead to the existence of bound states in the continuum and other interesting properties like population trapping [8–10] occur which may provide insight into the mechanism for selective laser chemistry.

In the present communication we are interested in finding singly excited bound states which lie above the first ionisation threshold. Negative ions of alkali atoms and halogen family provide very interesting examples where such behaviour is encountered. These systems are highly correlated and as such configuration interaction calculations should be performed for their proper understanding. However, preliminary investigation for qualitative and approximate quantitative estimation for the position and properties of such states can be performed using time-dependent coupled Hartree–Fock (TDCHF) theory which was quite successful in the past in predicting the transition properties of singly excited Rydberg states [11–14] for the neutral and positively charged closed and open shell atomic systems. The success is due to the inclusion of certain class of particle-hole correlation diagrams to all orders which appear in RPA-type calculations [15, 16]. The excited states are obtained from the position of poles of the frequency dependent polarizabilities which in turn are very useful in interpreting photodetachment threshold shift in presence of laser field, in calculating a.c. Stark shift [17] and in evaluating various other physical properties [18].

Theoretical calculations in this line are limited. Using a model potential based on one particle approximation Delone et al. [19] estimated the frequency dependent dipole polarizability of alkali negative ions like Li^-, Na^-, K^- and Cl^-. The position of the first resonance is apparent and subsequently the polarizability value shows a smooth asymptotic behaviour. Similar feature for the dynamic polarizability of Cl^- was observed from the many body perturbation calculation of Kutzner et al. [17]. A very clear picture of bound states in the continuum can be obtained from the coupled cluster based polarization propagator and full CI calculation of Canuto et al. [20] for Li^-. The nonexistence of bound excited states of ^1P symmetry below continuum was explicitly demonstrated in this calculation. The polarizability contribution is due to ionic continuum which is the main reason for the discrepancy of polarizability of such systems in an RPA type calculation as compared to a full CI calculation. Multiconfiguration linear response theory has been applied by Agren et al. [21] for estimating the dynamic polarizability of Li^- within the normal dispersion region. Full CI calculation has also been performed with a view to check the accuracy of the result. Most of these calculations are aimed at the accurate estimate of dynamic polarizability values up to first resonance. The nature of the excited states which are embedded in the continuum are not properly analysed.

In the present communication we study the behaviour of dynamic polarizability values within and beyond normal dispersion region with a veiw to analyse the first few bound excited states for all the four negative ions Li^-, F^-, Na^- and Cl^-. The theory has been discussed earlier [11–14] in detail, and in Sect. 2 we give a brief outline. The results have been discussed in Sect. 3.

2 Method

The closed shell negative ion is described by the usual nonrelativistic Hamiltonian H_0 [we use a.u. throughout]. A time-dependent harmonic field is applied on the system. In the semi-classical picture the interaction Hamiltonian may be represented as:

$$H(\bar{r}, t) = G(\bar{r}) \exp(-i\omega t) + c.c. \tag{1}$$

where $\bar{r}$ denotes collectively all the particle co-ordinates. For dipolar interaction $G(\bar{r})$ may be written as:

$$G(\bar{r}) = \lambda \sum_{k=1}^{N} r_k P_1(\cos \vartheta_k) \tag{2}$$

where λ is the field strength parameter. The perturbation admixes corrections to the ground state orbitals ψ_k. We assume the perturbation strength parameter λ to be small so that only first order corrections $\delta\psi_k^\pm$ are retained. These admixtures are determined by optimising a suitable functional, the procedure being described in detail earlier [11–14]. Frequency dependent polarizability values have been estimated using the standard formula [13]:

$$\alpha_d(\omega) = \sum_k [\langle \delta\psi_k^- | r \cos\theta | \psi_k \rangle + \langle \delta\psi_k^+ | r \cos\theta | \psi_k \rangle]. \tag{3}$$

The radial part of the first-order admixtures are expanded in terms of suitable STO bases:

$$\delta\psi_k^\pm(r) = \sum_q C_{kq}^\pm r^{n_{kq}} \exp(-\varrho_{kq} r) \tag{4}$$

the angular character is determined by the nature of the perturbation operator and the orbital ψ_k on which it acts. The linear variation parameters are determined through optimisation procedure and the exponents are preassigned. The procedural details for the choice of exponents are given earlier [13]. The dynamic polarizability values show monotonic rise with frequency having poles at certain frequencies. The pole positions furnish the excitation energy to different singly excited states and provide analytic representations of excited state wavefunctions and other properties like oscillator strengths connected with the transitions.

3 Results

Presently we have chosen the ions Li^-, F^-, Na^- and Cl^- having ^1S ground state for a detailed study of their dipole allowed excited states. Li^- and Na^- have valence s shell and the single excitations will be of p symmetry whereas for F^- and Cl^- the valence orbital is of p character and single excitations will be of s and d symmetry. The ground state orbitals are obtained from the compilation of Clementi and Roetti [22] and the excited orbitals are taken as 15 parameter linear combination of STO's (Eq. (4)). The number of parameters are adequate as to give convergence in the polarizability values [23] which are evaluated using Eq. (3). In Table 1 we display the $\alpha_d(\omega)$ values at different frequencies in the normal dispersion region for all the ions. The first pole position is clearly seen for all the ions where $\alpha_d(\omega)$ jumps from a high positive value to high negative value. Figure 1 shows such a plot for Li^- only. The multiconfiguration result of Agren et al. [21] which is also displayed in Fig. 1 shows a similar trend but is shifted. This shift is clearly due to multiconfigurational approach to the problem which gives lower energy than single configuration *HF* and furnishes a more accurate description of the ground state. In Fig. 2 we plot the behaviour of dynamic polarizability values corresponding to the first four $p \rightarrow s$ excitations of Cl^-. The pole positions are clearly demonstrated. It is very surprising that the many body calculation of Kutzner et al. [17] reflects only the first resonance and subsequent decay of the polarizability graph with driving frequency without showing any resonance structure. Similar polarizability graph for Li^- and Na^- was also obtained by the model potential calculation of Delone et al. [19]. But the existence of four ^1P excited states of Li^- was clearly demonstrated from the coupled cluster based polarization propagator and CI calculation of Canuto et al. [20].

Table 1. Dynamic polarizabilities of Li$^-$, F$^-$, Na$^-$ and Cl$^-$ in the normal dispersion region

ω (a.u)	$\alpha_d(\omega)$ (a.u)			
	Li$^-$	F$^-$	Na$^-$	Cl$^-$
0.0	1182.93	10.73	1179.98	30.95
0.005			1219.64	
0.01		10.74	1377.47	
0.011	1436.40		1440.39	
0.012	1510.37		1531.33	
0.013	1609.50		1868.38	
0.01305			4657.40	
0.01306			−108.66	
0.014	1759.93			
0.015	6614.73			
0.01501	−3056.7			
0.02		10.77		31.10
0.04		10.88		31.57
0.06		11.07		32.40
0.08		11.38		33.73
0.10		11.81		35.79
0.12		12.45		39.22
0.14		13.42		46.58
0.15		14.14		58.42
0.156				183.20
0.157				−202.71
0.18		21.26		
0.1816		47.03		
0.1817		−10.21		

All these states have been obtained from the first four pole positions of the dynamic polarizability in our calculation. The transition energies and oscillator strength values obtained by the present calculation are displayed in Table 2. The ionisation energies for the valence orbitals for Li$^-$, F$^-$, Na$^-$, and Cl$^-$ calculated by Clementi and Roetti [22] are respectively [in a.u.] 0.0145, 0.1809, 0.0125 and 0.1499 compared to the respective experimental [24, 25] electron affinity values 0.023, 0.125, 0.020 and 0.134. From Table 2 it is clear that all the excited states of a given negative ion under study lie above the ionisation potential of the corresponding ion as listed by Clementi and Roetti [22]. For Li$^-$ ion results obtained by Canuto et al. [20] are also listed in Table 2 for comparison. The results for the transition energies by RPA method as obtained by Canuto et al. [20] are in good agreement with those of our calculation whereas fully correlated results show higher values of transition energies. The discrepancy is mainly due to the neglect of ground state correlations which produces lowering of the ground state energy thereby resulting in higher excitation energies. The value of oscillator strength is also affected.

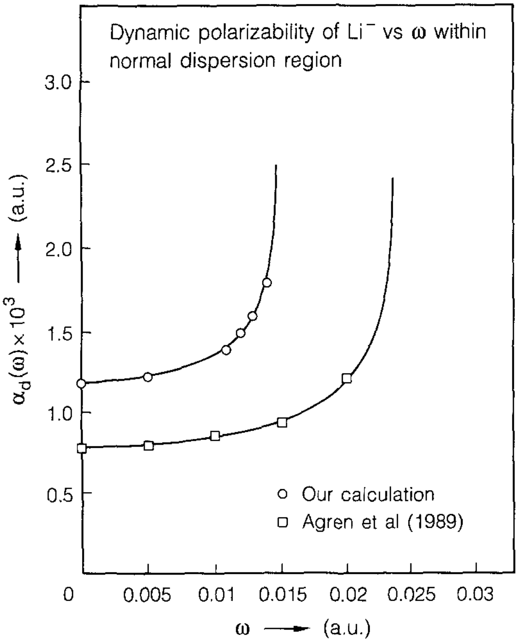

Fig. 1. Plot of the dynamic polarizability of Li$^-$ versus ω within normal dispersion region

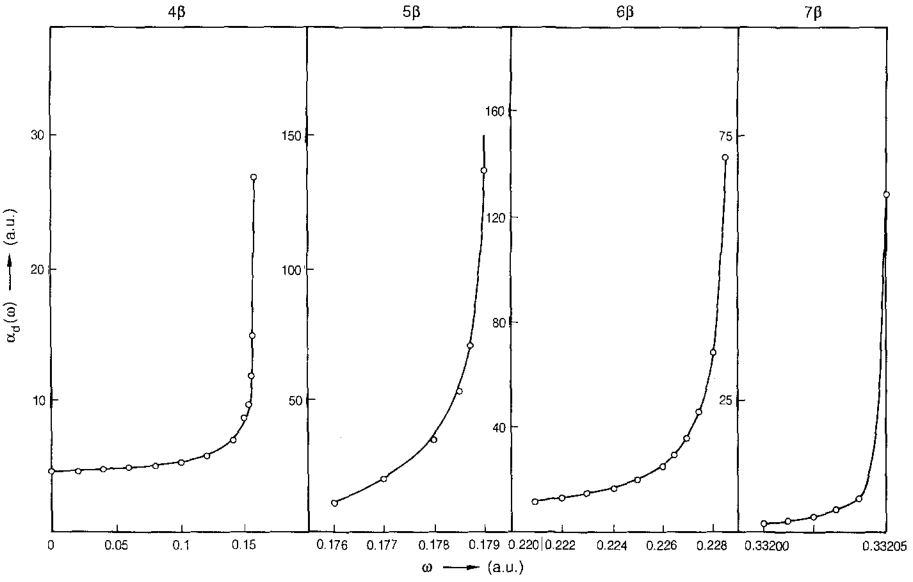

Fig. 2. Plot of the dynamic polarizability of Cl$^-$ versus ω within and beyond normal dispersion region for $p \rightarrow s$ transitions

It is interesting to note that for all the ions under study the oscillator strength value increases continuously for higher lying bound excited state which lie above the continuum. The trend is just the opposite in case of bound states lying below the continuum [26]. In our calculation the position of the first excited state is about 0.015 a.u. for Li$^-$ whereas the accurate result is 0.023 a.u. [20]. For Cl$^-$ we get

Table 2. Transition energies and oscillator strengths as obtained from dynamic polarizability calculation for Li^-, F^-, Na^- and Cl^-

Ion	Transition scheme*	Excitation energies (a.u.)		Oscillator strength	
		Present calculation	Other values	Present calculation	Other values
Li^-	$2s{:}^1S \rightarrow 2p{:}^1P$	0.0150	.0151[a], .0283[b], .0232[c],	0.0063,	.0026[a], .0004[b]
	$\rightarrow 3p{:}^1P$	0.0186	.0176[a], .0309[b], .0254[c]	0.059	.0516[a], .0133[b]
	$\rightarrow 4p{:}^1P$	0.0242	.025[a], .0379[b], .0320[c]	0.198	.332[a], .0922[b]
	$\rightarrow 5p{:}^1P$	0.0351	.0460[a], .0560[b], .0526[c]	0.450	.916[a], .3063[b]
F^-	$2p^6{:}^1S \rightarrow 2p^5 3s{:}^1P$	0.1816		0.00031	
	$\rightarrow 2p^5 4s{:}^1P$	0.1841		0.0026	
	$\rightarrow 2p^5 3d{:}^1P$	0.18898		0.000021	
	$\rightarrow 2p^5 5s{:}^1P$	0.1901		0.0087	
	$\rightarrow 2p^5 4d{:}^1P$	0.19691		0.00025	
	$\rightarrow 2p^5 6s{:}^1P$	0.2034		0.0251	
	$\rightarrow 2p^5 5d{:}^1P$	0.2108		0.0010	
	$\rightarrow 2p^5 6d{:}^1P$	0.2348		0.0049	
Na^-	$3s^2{:}^1S \rightarrow 3s3p{:}^1P$	0.01305		0.000028	
	$\rightarrow 3s4p{:}^1P$	0.0138		0.000406	
	$\rightarrow 3s5p{:}^1P$	0.0153		0.01137	
	$\rightarrow 3s6p{:}^1P$	0.0193		0.0753	
	$\rightarrow 3s7p{:}^1P$	0.0291		0.3923	
Cl^-	$3p^6{:}^1S \rightarrow 3p^5 4s{:}^1P$	0.15665		0.027	
	$\rightarrow 3p^5 3d{:}^1P$	0.17561		0.0056	
	$\rightarrow 3p^5 5s{:}^1P$	0.17929		0.094	
	$\rightarrow 3p^5 4d{:}^1P$	0.20097		0.025	
	$\rightarrow 3p^5 6s{:}^1P$	0.22892		0.178	
	$\rightarrow 3p^5 5d{:}^1P$	0.24559		0.136	
	$\rightarrow 3p^5 6d{:}^1P$	0.32559		0.380	
	$\rightarrow 3p^5 7s{:}^1P$	0.33205		0.369	

* Only the valence orbitals are shown

[a] RPA values listed by Canuto et al. (1988)

[b] Coupled cluster based calculation of Canuto et al. (1988)

[c] Full CI results of Canuto et al. (1988)

0.156 a.u. which is compared with ~0.2 obtained by Kutzner et al. [17]. The lowering of the ground state energy in an extended calculation takes care of more than 90% of this discrepancy. As far as the authors' knowledge no other calculations on $\alpha_d(\omega)$ and transition energies exist for F^- and the results presented here may be used for future reference.

Analytic representations of the excited states have been obtained from our calculation. These wavefunctions are extremely diffuse. From a numerical analysis of these wavefunctions we notice that they may extend well above 100 a.u. but the asymptotic behaviour of the bound state wavefunctions are still retained. Also they produce the correct number of nodes. We do not give a plot here because of difficulty in representing the total structure of the wavefunctions within scale. For open shell negative ions bound states may exist below the continuum. These are under study and results will be reported in due time.

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