Ab initio calculations of Stark induced electric dipole transition amplitudes of singly ionized calcium

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Abstract. We have determined the amplitudes for Stark-induced (SI) transitions, of current interest in atomic physics and astrophysics, between mixed states dominated by same parity configurations of some low-lying states of singly ionized calcium. Well established Relativistic Coupled cluster (RCC) method has been used for the spectroscopic study of these transitions. This method has proved to be a very useful tool for rigorous electron correlation studies. We compare our results with experimental data for allowed electric dipole transition amplitudes and energies and also with other theoretical studies.

1. Introduction

Single photon ‘electric dipole’ (E1) transitions between states having same parity are forbidden by the ‘selection rules’. Transitions between such states that are allowed are the ‘electric quadrupole’ (E2) and the ‘magnetic dipole’ (M1) transitions, which however are very weak. Nevertheless, when an atomic/ionic system is placed in an external electric field, the eigenstates of the perturbed system are admixtures of the eigenstates of the unperturbed system and have components having opposite parities, but having a dominant contribution from states having a particular parity or its opposite. Transitions between these ‘mixed’ states are thus no more forbidden, and are known as ‘Stark-Induced Transitions’.

The mixing of opposite parity states is enhanced with decreasing energy separation between these states [1]. Such Stark induced (SI) transitions can be of importance toward the study of parity nonconservation (PNC) processes. Also, the size of the SI amplitudes relative to the PNC-induced amplitudes determines the extent of the external fields which is controlled [2]. The interference between Stark-induced and magnetic dipole transition can be used to measure highly forbidden magnetic dipole amplitude [3]. Interference between Stark-induced and electric quadrupole amplitude can also be used to measure the decay rate in an alkaline-earth atom [4].

Ions of calcium have gained much attention in atomic physics. The sensitive behaviour of Ca$^+$ in presence of external field makes it an ideal candidate for an optical frequency standard [5]. In particular, the $4s^2 S_{1/2} \rightarrow 3d^2 D_{3/2}$ and $4s^2 S_{1/2} \rightarrow 3d^2 D_{5/2}$ electric quadrupole transitions at 729 nm and 732 nm respectively are important candidates for the development of frequency standards [6]. Large number of calculations have been carried out by various groups to calculate the lifetime, electric dipole moment transition amplitude and ionization energy of
singly ionized calcium [7, 8]. Some magnetic dipole (M1) and electric quadrupole (E2) transition amplitudes have been estimated in literature [8, 9].

The relativistic coupled cluster (RCC) method with single, double and partial triple excitations have been used in the present work to compute different allowed and forbidden transition amplitudes among low-lying states of $^{40}\text{Ca}^+$. 

2. Theory

Any correlated state of Ca$^+$ with one valence electron in the $v^{th}$ orbital is described using open shell coupled cluster approach as

$$|\Psi_v\rangle = e^T\{e^{S_v}\}|\Phi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle,$$  

with the reference state $|\Phi_v\rangle$ for the open shell Ca$^+$ obtained from the closed shell state which is the Dirac-Fock (DF) state $|\Phi_{DF}\rangle$ for Argon-like Ca$^+$:

$$|\Phi_v\rangle = a_\alpha^\dagger |\Phi_{DF}\rangle.$$

$T$ and $S$ are cluster operators associated with closed and open shell hole-particle excitations respectively[10]. We consider single and double excitations. Partial triple excitations are also taken into account as discussed in our earlier work [11, 12]. For computational simplicity, the $T$ amplitudes are solved first for the closed-shell Ca$^{2+}$, and then the valence electron is appended to obtain the open-shell wavefunctions [13].

The matrix element of any operator can be expressed as

$$O_{fi} = \frac{\langle \Psi_f | O | \Psi_i \rangle}{\sqrt{\langle \Psi_f | \Psi_f \rangle \langle \Psi_i | \Psi_i \rangle}} = \frac{\langle \Phi_f | [1 + S_f^\dagger]e^{T^\dagger}Oe^T[1 + S_i] | \Phi_i \rangle}{\sqrt{\langle \Phi_f | [1 + S_f^\dagger]e^{T^\dagger}e^T[1 + S_j] | \Phi_f \rangle \langle \Phi_i | [1 + S_i^\dagger]e^T e^T[1 + S_i] | \Phi_i \rangle}}.$$

The one-electron reduced matrix elements of the E1, M1 and E2 operators are given by [9, 14]

$$\langle k_f | q_1^{(E1)} | k_i \rangle = \langle k_f | C_m^{(1)} | k_i \rangle,$$

$$\times \int \text{d}r \left[ r(P_f(r)P_i(r) + Q_f(r)Q_i(r)) + \frac{\alpha}{10}(k_f - k_i)(\epsilon_i - \epsilon_f)r^2(P_f(r)Q_i(r) + Q_f(r)P_i(r)) + \frac{\alpha}{5}(\epsilon_i - \epsilon_f)r^2(P_f(r)Q_i(r) - Q_f(r)P_i(r)) \right].$$

and

$$\langle k_f | e_2 | k_i \rangle = \langle k_f | C_m^{(2)} | k_i \rangle \frac{15}{k^2} \frac{\kappa_i + \kappa_f}{2} \int \text{d}r j_2(kr) [(P_f(r)Q_i(r) + Q_f(r)P_i(r))]$$

and

$$\times \int \text{d}r \left[ j_2(kr)(P_f(r)P_i(r) + Q_f(r)Q_i(r)) + j_3(kr)\frac{k_f - k_i}{3}(P_f(r)Q_i(r) + Q_f(r)P_i(r)) + (P_f(r)Q_i(r) - Q_f(r)P_i(r)) \right].$$

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respectively. Here \( j_i \) and \( \kappa_i \left( = \pm \left( j_i + \frac{1}{2} \right) \right) \) are the total angular momentum and relativistic angular momentum quantum numbers respectively, of the \( i \)th electron orbital. The quantity \( C_m^{(l)} \) is the Racah tensor and \( j_l(kr) \) is the spherical Bessel function of order \( l \). \( P_l(r) \) and \( Q_l(r) \) are respectively the large and small radial components of the \( i \)th single particle DF wavefunctions.

The SI-E1 transition between same parity states \(|i⟩\) and \(|f⟩\) in the presence of constant electric field \( \vec{E} \) and intrinsic polarization field \( \epsilon \) has amplitude [2]

\[
W_{fi} = \sum_{q,q'} (-1)^{q+q'} A_{q,q'} E \epsilon,
\]

where the field independent part

\[
A_{q,q'} = e^2 \sum_b \left( \frac{⟨f|r_q|b⟩}{E_f - E_b} ⟨b|r_{q'}|i⟩ + \frac{⟨b|r_{q'}|i⟩}{E_i - E_b} ⟨f|r_q|b⟩ \right). \tag{8}
\]

The subscripts \( q, q' \) refer to the spherical vector components and \(|b⟩\) has a parity opposite to that of \(|i⟩\) and \(|f⟩\). Here \( E_f, E_b \) and \( E_i \) are the respective unperturbed energies of the states \(|f⟩\), \(|b⟩\) and \(|i⟩\).

### 3. Results and Discussion

The single reference open shell correlated states of \( Ca^+ \) are obtained from the DF state of the closed shell system \( Ca^{2+} \), as mentioned in Eq. (2.1) and (2.2). The DF orbitals of the closed shell system are generated from the expansion of universal Gaussian Type Orbitals (GTO). Details are available from the work of Chaudhuri et al. [15]. We have used \( \alpha_0 = 0.00925 \) and \( \beta = 2.98 \) for the exponents of the bases. The choice of the parameters are based on the agreement of DF energies and wavefunctions for the bound GTO orbitals with the numerical DF orbitals obtained using the GRASP program [16]. There are 32s, 32p, 25d, 20f, 20g symmetry base functions used for the GTO calculations. Once the exponent parameters are fixed, the number of single particle orbital basis chosen in different symmetries are based on convergence criteria of the DF energies of the system and individual bound orbitals.

For the RCC calculations, the numbers of DF orbital bases of different symmetries considered from the above GTO calculations are 11, 10, 8, 7, 6 for \( l = 0, 1, 2, 3 \) and 4, respectively. All the core orbitals are considered as active in our calculations. This makes core correlations exhaustive enough for the consideration of the single and double excitations. In this work, singles and doubles excitations with some triple excitations, obtained in combinations of single and double excitations operators, have been considered. This technique is thus referred to as (CCSD(T))[13].

In Table I as presented the comparision of our excitation energies of various low-lying states of singly ionized calcium using the RCC calculation with the corresponding NIST results [17] and some previous calculations using many-body perturbation theory (MBPT) [7]. Our results are in better agreement with those of NIST compared to MBPT results. The average disagreement of our calculated results is 0.45% compare to NIST results, excluding the 3d, 6s and 6p states. One of the important features of this table is the ordering of ionization potential of 3d-states compared to 4p-states. 3d-states are more bound than 4p and 5s-states, which is unlikely for the neutral isoelectronic potassium. That shows the strong correlation of 3d orbitals with core orbitals. In MBPT calculations, all the excitation energies are over estimated and their orderings of the states disagree with both NIST and our calculations.
Table 1. Excitation energies (in a.u.) of Ca\(^+\) and their comparisons with the NIST and MBPT values

| States | Multiplets | RCC     | NIST\[17\] | MBPT\[7\] |
|--------|------------|---------|------------|-----------|
| 4s     | \(2S_{1/2}\) | 0.00000 | 0.00000    | 0.00000   |
| 3d     | \(2D_{3/2}\) | 0.06430 | 0.06219    | -         |
|        | \(2D_{5/2}\) | 0.06457 | 0.06247    | -         |
| 4p     | \(2P_{1/2}\) | 0.11518 | 0.11478    | -         |
|        | \(2P_{3/2}\) | 0.11622 | 0.11579    | -         |
| 5s     | \(2S_{1/2}\) | 0.23908 | 0.23769    | -         |
| 4d     | \(2D_{3/2}\) | 0.25975 | 0.25897    | -         |
|        | \(2D_{5/2}\) | 0.25984 | 0.25907    | -         |

In Table II, we report the electric dipole transition amplitudes calculated from the RCC approach and compare them with results obtained from the method using Brueckner approximation (BA) \[8\], MBPT \[7\] and also with NIST result\[17\]. Like excitation energy case, the MBPT calculation underestimates the transition amplitudes compared to the BA, NIST and the RCC results. In the latter two approaches, we find good agreement.

Table 2. Comparison of electric dipole transition amplitudes of Ca\(^+\) from the RCC calculation with BA, MBPT and NIST. All values are in a.u.

| Terms                | Wavelength(Å)[17] | RCC     | BA\[8\] | MBPT\[7\] | NIST\[17\] |
|----------------------|-------------------|---------|---------|-----------|------------|
| 4p\(_{1/2}\) → 4s\(_{1/2}\) | 3968.46           | 3.072   | 3.072   | 3.072     | 3.072      |
| 4p\(_{1/2}\) → 3d\(_{3/2}\) | 8662.14           | 2.561   | 2.561   | 2.561     | 2.561      |
| 4p\(_{3/2}\) → 4s\(_{1/2}\) | 3933.66           | 4.341   | 4.341   | 4.341     | 4.341      |
| 4p\(_{3/2}\) → 3d\(_{3/2}\) | 8498.02           | 1.148   | 1.148   | 1.148     | 1.148      |
| 4p\(_{3/2}\) → 3d\(_{5/2}\) | 8542.09           | 3.450   | 3.450   | 3.450     | 3.450      |

We have performed calculations on many such electric dipole transition amplitudes among different bound states of this system. These values have been used to calculate SI-E1 transition amplitudes amongst some low-lying states of same parity using the Eq. (2.7). Since our electric dipole transition amplitudes are in better agreement with NIST values, the Stark induced transition amplitudes are also expected to be more accurate. In Table III we report these SI-E1 transition amplitudes with other electromagnetically forbidden transitions, like E2 and M1 transitions. The 4s\(_{1/2}\) → 5s\(_{1/2}\) amplitude must be zero from E2 selection rules, whereas, the M1 transition amplitude is zero for 4s\(_{1/2}\) → 3d\(_{3/2}\) and 4s\(_{1/2}\) → 3d\(_{5/2}\). Therefore in these transitions, SI-E1 transition plays a strong role.
Table 3. results of Stark-induced E1, M1 and E2 transitions in atomic units

| Terms               | SI-E1 (in units of $a_0^3$) | E2 (in units of $a_0^2 e$) | M1 (in units of $\mu_B$) |
|---------------------|-----------------------------|----------------------------|--------------------------|
| $4s_{1/2} \rightarrow 5s_{1/2}$ | 2.646                       | 0.000                      | 0.094                    |
| $4s_{1/2} \rightarrow 3d_{3/2}$ | 361.761                     | 8.026                      | 0.000                    |
| $4s_{1/2} \rightarrow 3d_{5/2}$ | 425.919                     | 9.818                      | 0.000                    |

4. conclusion
In the present work we have calculated important SI-E1 transition amplitudes among few low-lying states of singly ionized calcium employing the highly correlated RCC theory at the level of single, double and partial triple excitations. Furthermore, we have estimated excitation energies and E1 transition amplitudes for low-lying states, which are in good agreement with available experimental measurements as well as results from precise calculations using different many-body approaches. These results can serve as benchmarks for testing relativistic many-body theories, and also serve as inputs for some experiments in atomic physics.

Acknowledgments
We are grateful to Professor B.P. Das, Dr. Rajat K. Chaudhuri of Indian Institute of Astrophysics, Bangalore and to Dr. Bijaya K. Sahoo of Max-Plank Institute of Complex system, Dresden, for helpful discussions. This work is partially supported by DST (Government of India).

References
[1] Kwela J 1987 Z. Phys. D 6 25
[2] DeMille David 1 Mar 1998 arXiv:physics/9801034 v2
[3] Bouchiat M A, Guena J and pottier L 1984 J. Phys. (Paris) 45 L61
[4] Hunter I R, Walker W A and Weiss D S 1986 Phys. Rev. Lett. 56 823-826
[5] Kajita M, Li Y, Matsubara K, Hayasaka K and hosokawa M 2005 Phys. Rev. A 72 043404
[6] Nortershauser W, Blaum K, Icker K, Muller P, Schmitt A, Wendt K and Wiche B 1998 Eur. Phys. J. D 2 33-39
[7] Guet C and Johnson W R 1991 Phys. Rev. A 44 1531
[8] Liaw Sy-Sang 1994 Phys. Rev. A 51 1723
[9] Sahoo B K, Islam Md. R, Das B P, Chaudhuri R K and Mukherjee D 2006 Phys. Rev. A 74 062504
[10] Lindgren I and Morrison J 1985 Atomic Many-body Theory, ed G E Lambropoulos and H Walther (Berlin: Springer)
[11] Sahoo B K, Majumder S, Chaudhuri R K, Das B P and Mukherjee D 2004 J. Phys. B 37 3409
[12] Sahoo B K, Majumder S, Merlitz H, Chaudhuri R K, Das B P and Mukherjee D 2006 J. Phys. B 39 355
[13] Gopakumar G, Merlitz H, Majumder S, Chaudhuri R K, Das B P, Mahapatra U S and Mukherjee D 2001 Phys. Rev. A 64 032502
[14] Berestetski I Atomic Spectra and Radiative Transition 2 ed J Peter Toennies (Berlin: Springer)
[15] Chaudhuri R K, Panda P K, Das B P, Mahapatra U S and Mukherjee D 2000 J. Phys. B 33 5129
[16] Grant I P, McKenzie B J, Norrington P H, Myers D F and Pyper N C 1980 Comput. Phys. Commun. 21 07; Dyall K G, Grant I P, Johnson C T, Farjia F A and Plummer E P 1989 Comput. Phys. Commun. 55 425
[17] http://physics.nist.gov/PhysRefData/ASD/levels_form.html