

Excitation in Sodium Isoelectronic Sequence

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ABSTRACT

The optical oscillator strengths (f), of atoms and positive atomic ions is needed in astrophysics, atmospheric physics, laser physics, plasma physics, radiation physics, gas discharge, mass spectroscopy, space research and fusion research. The most serious problem in fusion research with magnetically confined high temperature plasmas (eg. Tokamaks) is caused by plasma impurities, eg., highly ionized metal atoms. It is, therefore vital to determine and reduce the impurity concentration. For this purpose, the values of f are required. The abundances of the chemical elements in the sun are of considerable interest because they contain information about the creation of the solar system term.

Keywords : CI Configuration, Hartee Fock, Optical Strength.

I. INTRODUCTION

In the solar spectra large number of spectral lines are observed from the measured equivalent width, the abundances are derived if the f values are known. OOS (Optical Oscillator Strengths) provide the confidence about the reliability of the wavefunctions which are employed in the matrix elements. Ridder and Schneider¹, Peterson et al.^{2,3} and Dahl et al. have studied several transitions in P^{4+} ions of the sodium isoelectric sequence in ion-atom collision experiments. The inner shell excitation $1s^2 2s^2 2p^6 3s^1 2s^e \rightarrow 1s^2 2s^2 2p^5 3s^2 \ 2p^0$ transition, which leads to autoionization, plays very important role to explain the structure observed in the electron impact ionization cross-section curves. Recently Tiwar and

his co-workers⁶⁻¹⁶, have extensively calculated the excitation energies and optical oscillator strengths for the outer as well as inner-shell excitation transitions in several atoms and ions using the HF and CI wavefunctions for both initial and final states within the LS coupling scheme.

Our investigation shows that the inclusion of correlation is indispensable in order to obtain reliable results. From the survey of literature, it is clear that neither experimental observations nor theoretical predictions for OSS are available for the inner-shell excitation transition, which leads to auto-ionization in P^{4+} ions.

Recently, we⁹ have calculated the transition energies (ΔE in atomic unit) and OSS of both length and velocity forms for several transitions like Li atom using the HF as well as CI wave functions for both initial and final states. In our earlier work we have reported the excitation energies and oscillator strengths, of both length and velocity forms (f_l and f_v respectively), for the resonance transition and non-resonance transitions in several ions of the sodium isoelectronic sequence. We have also calculated the ΔE , f_l and f_v values for several outer-shell transitions as-well-as the inner-shell excitation transition in P^4 ion which leads to auto-ionization using non-relativistic HF and large CI wavefunctions for both initial and final states involved in the transition. However, there is a considerable discrepancy between the length and velocity forms of the oscillator strengths.

It is well known that the relativistic effects play an extremely important role in obtaining accurate results. Consequently, it is indispensable to incorporate the relativistic effects into the study of atomic structure in order to generate reliable results. In our earlier work we have calculated the oscillator strengths using the non-relativistic CI wavefunction. In this work we have taken into account of the relativistic effects which may then be used to calculate transitions which are forbidden in purely L - S coupling.

We have calculated the transition probabilities and oscillator strengths, of both the length and velocity forms, for the inner-shell excitation $1s^2 2s^2 2p^6 3s^2 s_{1/2}^e \rightarrow 1s^2 2s^2 2p^5 3s^2 p_{1/2}^0$ and $1s^2 2s^2 2p^6 3s^2 s_{3/2}^e \rightarrow 1s^2 2s^2 2p^5 3s^2 p_{3/2}^0$ transition in Ca^{9+} ions T_i^{11+} of the Sodium isoelectronic sequence employing the Tiwary¹⁷⁻³⁰ approach in the intermediate coupling scheme.

II. THEORY

With reference to the increasing accuracy of experimental data obtained from high resolution techniques, it becomes really necessary to introduce relativistic effects into the reliable study of atomic structure. For this there are so many methods but a general method of evaluating relativistic effects in atomic structure problems is described, which may be used to calculate transitions which are forbidden in purely L-S coupling.

The relativistic corrections to the non-relativistic energy may be determined to order $(\alpha Z)^2$ in terms of the Breit operator (H_B) by first order perturbation theory, Bethe and Salpeter²¹. That is these corrections are given as the expectation value of the Breit operator with respect to the zero order wave function Φ_0 which satisfies

$$H_0 \Phi_0 = \sum_i h_i + \sum_{i < j} \frac{1}{r_{ij}} \Phi_0 = E_0 \Phi_0 \quad (1)$$

where, h_i is a one electron Dirac operator and α is the fine structure constant. Bethe and Salpeter point out that the further development of the perturbation treatment, in which the full Hamiltonian is taken as $(H_0 + H_B)$ leads to higher order corrections which are of the wrong order of magnitude. As a consequence, the use of the resulting Breit equation to determine the corresponding correction to the wave function is therefore unjustified. This point is emphasised by Detrich²² who develops an alternative perturbation formalism in which the relativistic energy corrections are not given in terms of an effective Hamiltonian H_B .

In the calculation of transition probabilities, it is not sufficient that the energy corrections are treated properly. The corrections to the wavefunction must also be included as well as possible. For fairly low value of Z the Pauli approximation is satisfactory. In this approximation the chief contribution to the fine structure splitting are the nuclear spin-orbit term and the spin-other-orbit and spin-spin-terms. If indeed

the correct wavefunction is given as an eigenfunction of H_0 and not of $(H_0 + H_B)$, then in the Pauli approximation, one must determine the wavefunction as an eigenfunction of the non-relativistic Hamiltonian plus the nuclear spin-orbit operator. The spin other term should not be included. For low Z , all relativistic effects are small, but the nuclear spin-orbit and the spin other orbit terms are of comparable order of magnitude. It seems at best anomalous to determine the wavefunction by including one but not the other in the full Hamiltonian.

Since relativistic effects are small, they should have little influence on the form of the radial functions. The time-consuming optimisation of these functions

may thus be determined in a non-relativistic approximation.

The corresponding relativistic corrections to transition probabilities have been derived from quantum electrodynamics by Drake²³⁻²⁴. He finds that in the Pauli approximation, the multipole matrix element should be evaluated between eigenfunctions of $(H_0 + H_B)$ provided that only terms up to relative order $(\alpha Z)^2$ are retained. Higher-order powers of αZ will necessarily be included in a variational treatment of $(H_0 + H_B)$, but the errors should be small when αZ is small.

The many electrons Dirac-Hamiltonian (H_D) for an N -electron system is in atomic unit.

$$H_D = \sum_{i=1}^N \{c^2 \beta_i + \alpha_i [c P_i + A(r_i)] - \Phi(r_i)\} + \sum_{i < j} \frac{1}{r_{ij}} \tag{2}$$

where P_i is the momentum operator;

$\Phi(r_i)$ and $A(r_i)$ denotes the scalar and vector potentials of the external electromagnetic field, respectively; c is the speed of light; $r_{ij} = |r_i - r_j|$ is the distance between the i th and j th electrons; r_i = position vector of the i th electron and β are the Dirac matrices, written, respectively, in terms of the Pauli 2×2 matrices and the 2×2 unit matrix

$$I = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i \text{ and } \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{3}$$

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4}$$

In the theory of atomic structure we are concerned with electrons interacting with each other as well as with an electromagnetic field. The Dirac theory is not sufficient. The most commonly used approximation for describing the relativistic interaction between electrons in an approximate way is the Breit Hamiltonian, Breit.^{25,26}

$$H = H_D + H_B \tag{5}$$

where,

$$H_B = -\frac{1}{2} \sum_{i < j} \frac{1}{r_{ij}} (\alpha_i \cdot \alpha_j) + \frac{(\alpha_i r_{ij})(\alpha_j r_{ij})}{r_{ij}^2} \tag{6}$$

The interaction, equation (5), is of the order $(\alpha Z)^2$ relative to the Coulomb interaction and terms of higher order in (αZ) are omitted.

Provided that the velocities of the electrons in the system are sufficiently low that terms of orders higher than $(\alpha^2 Z^2)$ may be neglected the Breit Hamiltonian for the case where there is no external field becomes

$$H_{BP} = H_{NR} + H_R \tag{7}$$

Where

$$H_{NR} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - Z \sum_{i=1}^N \frac{1}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \tag{8}$$

is the non-relativistic Hamiltonian and

$$H_R = H_{SO} + H_{mass} + H_{D_1} + H_{SOO} + H_{SS} + H_{OO} + H_{D_2} + H_{SSC} \tag{9}$$

is the relativistic correction. HBP is the Breit-Pauli Hamiltonian for low Z $[Z < 137]$

For derivation of the Breit-Pauli Hamiltonian we refer the reader to Bethe and Salpeter²¹, Slater²⁸, Iroh²⁹, Akhiezer and Berestetky³⁰, and Amstrong and Feneuille.³¹

$$H_{SO} = \frac{\alpha^2 Z}{2} \sum_{i=1}^N \frac{1}{r_i^3} (L_i \cdot S_i) \tag{10}$$

represents the one-body spin interaction of each electron's magnetic moment with the magnetic field arising from the electron's own motion in the Coulomb field of the nucleus;

$$H_{mass} = -\frac{\alpha^2}{8} \sum_{i=1}^N \nabla_i^4 \tag{11}$$

is the relativistic mass correction;

$$H_{D_1} = -\frac{\alpha^2 Z}{8} \sum_{i=1}^N \nabla_i^2 \left(\frac{1}{r_i} \right) \tag{12}$$

is the one body Darwin term; the relativistic correction to the potential energy;

$$H_{SOO} = -\frac{\alpha^2}{2} \sum_{i \neq j} \left(\frac{r_{ij}}{r_{ij}^3} \times P_i \right) \cdot (S_i + 2S_j) \tag{13}$$

represents the spin other orbit interaction and is made up of two parts.

The first one, containing the factor S_i , is the spin-orbit coupling of electrons i in the Coulomb field of electron j .

The second, with the factors $2S_j$ comes from the interaction of the spin magnetic moment of electron j with the orbital current of electron i ;

$$H_{SS} = \alpha^2 \sum_{i < j} \frac{1}{r_{ij}^3} (S_i \cdot S_j) - 3 \frac{(S_i \cdot S_{ij})(S_j \cdot S_{ij})}{r_{ij}^2} \tag{14}$$

is the ordinary dipole interaction of the spin magnetic moments of two electrons;

$$H_{00} = -\frac{\alpha^2}{2} \sum_{i<j} \left\{ \frac{P_i P_j}{r_{ij}} + \frac{r_{ij}(r_{ij} P_i) \cdot P_j}{r_{ij}^3} \right\} \quad (15)$$

is the orbit-orbit interaction

$$H_{D_2} = \frac{\alpha^2}{4} \sum_{i<j} \nabla_i^2 \left(\frac{1}{r_{ij}} \right) \quad (16).$$

is the two body Darwin term; the relativistic correction to the potential energy.

$$H_{SSC} = -\frac{8\pi\alpha^2}{3} \sum_{i<j} (S_i \cdot S_j) \delta(r_i, r_j) \quad (17)$$

is the electron-spin-contact term.

we can re-write equation (7) as

$$H_{BP} = \text{non fine structure} + \text{fine structure} \quad (18)$$

where,

$$\text{non fine structure} = H_{NR} + H_{\text{mass}} + H_{D_1} + H_{OO} + H_{D_2} + H_{SSC} \quad (19)$$

and,

$$\text{Fine structure} = H_{SO} + H_{SOO} + H_{SS} \quad (20)$$

The non-fine structure interactions commute with S^2 , S_z , L^2 and L_z can therefore be considered in the $|\alpha L S M_L M_S\rangle$ representation.

The fine-structure interactions only commute with L^2 ; S^2 , J^2 and J_z where J and J_z are the total angular momentum and its azimuthal component, respectively. For these we use the $|\alpha L S J M_J\rangle$ representation.

J-dependent CI expansion takes the form

$$\Psi(J, M_J) = \sum_j a_j \Phi_j(\alpha_j L_j S_j J M_j) \quad (21)$$

where $\{\phi_i\}$ denotes a set of single configuration wavefunctions, α_j defines the coupling of the angular momenta of the electrons

$$J = L + S \quad (22)$$

for each j , and $\{a_j\}$ are determined as the components of the appropriate eigenvector of the Hamiltonian matrix with basis $\{\phi_j\}$. The Hamiltonian consists of the usual non-relativistic terms plus the relativistic corrections.

The Hamiltonian matrix with typical element is

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle \quad (23)$$

Once we have the J-independent and J-dependent CI wave functions, we can calculate the oscillator strengths.

III.OSCILLATOR STRENGTHS

In order to obtain formulae for transition probabilities, we must begin with the time-dependent Schrodinger equation

$$H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{24}$$

where the Hamiltonian H contains not only the electrostatic interaction, but because of the radiation field involved, it also contains electromagnetic corrections which, for one-electron systems, have the form $(e/mc) A.P$. Here, A is the vector potential associated with the electromagnetic field, and P is the momentum of the electron.

The wave function is then expanded in terms of the stationary-state wave functions $\{\Psi_n\}$, with energies $\{E_n\}$.

$$\Psi = \sum_n c_n(t) \exp\left(-\frac{i}{\hbar} E_n t\right) \Psi_n \tag{25}$$

where the sum includes as integration over the continuum. If the atom is in state $|i\rangle$ at time $t = 0$, then $c_i(0) = 1$ for $n=i$. If the velocity potential is expanded in a Fourier series of plane waves of the form $A_0 \cos(\omega t - k.r)$, then first-order perturbation theory gives, for absorption in one-electron atoms.

$$\frac{1}{t} |c_j(t)|^2 = \frac{2\pi}{3} \frac{e^2}{\hbar^2 \nu_{ji}^2} |\langle j | \frac{e}{mc} P \exp(ik.r) | i \rangle|^2 \rho(\nu_{ji}) \tag{26}$$

$$= B_{ij} \rho(\nu_{ji}) \tag{27}$$

$$\text{where } \hbar \nu_{ji} = E_j - E_i \tag{28}$$

B_{ij} is the Einstein coefficient for absorption, and $\rho(\nu_{ij})$ is the energy density per unit frequency range.

The absorption Oscillator strength f_{ij} is related to the Einstein coefficient by

$$f_{ij} = \frac{m}{\pi e^2} \hbar \nu_{ji} B_{ij} \tag{29}$$

thus, retaining the usual convention that absorption oscillator strengths are positive.

The magnitude of wave vector k is $k = 2\pi/\lambda$. Hence for wavelengths large compared with the size of the atom, $k.r \ll 1$, and the expansion

$$\exp(ik.r) = 1 + ik.r + \frac{1}{2!} (ik.r)^2 + \dots \tag{30}$$

will converge rapidly. The use of the first leading term of equation (30) constitutes the dipole approximation of the multipole expansion. Also

$$\frac{i\hbar}{m} p \equiv i\hbar \dot{r} \equiv [r, H_0] \tag{31}$$

whenever the matrix elements of these operators are being taken with respect to exact eigenfunctions of H_0 , the electrostatic part of the Hamiltonian. Hence the matrix element within the dipole approximation can be expressed as

$$\langle j | \frac{e}{mc} p | i \rangle = \frac{ie}{\hbar c} j | H_0 r - r H_0 | i \rangle = \frac{i}{\hbar c} (E_j - E_i) \langle j | er | i \rangle \quad (32)$$

Hence, we have two equivalent forms for the absorption oscillator strength:

$$f_{ij}^1 = \frac{2m}{3\hbar^2} (E_j - E_i) |\langle j | r | i \rangle|^2 \quad (33)$$

$$f_{ij}^v = \frac{2}{3} \frac{1}{m} \frac{1}{(E_j - E_i)} |\langle j | p | i \rangle|^2 \quad (34)$$

These are the length and velocity forms respectively. The identities (30) may be applied to r instead of r , and in this way an acceleration form may be derived:

$$f_{ij}^a = \frac{2}{3} \frac{\hbar^2}{m} \frac{1}{(E_j - E_i)^3} |\langle j | \nabla V | i \rangle|^2 = \frac{2}{3} \frac{z^2 e^4 \hbar^2}{m(E_j - E_i)^3} \left| \langle j | \frac{1}{r^3} \vec{r} | i \rangle \right|^2 \quad (35)$$

where V is the electrostatic potential energy.

So far, we have assumed that the levels i and j are non-degenerate. If level j is degenerate, with different states being distinguished by the $(2j+1)$ parameters m_j , then there are several 'Channels' open for the transition. The total absorption oscillator strength (length form) is then

$$f_{ij}^1 = \frac{2}{3} \frac{m}{\hbar^2} (E_j - E_i) \sum_{m_j} |\langle j m_j | r | i \rangle|^2 \quad (36)$$

The level i may also be degenerate, with different states distinguished by m_i . It is then convenient to introduce the line strength S_{ij} , whose length form is defined by

$$S_{ij}^1 = S_{ji}^1 = \sum_{m_i m_j} |\langle j m_j | er | i m_i \rangle|^2 \quad (37)$$

$$= \sum_{m_i m_j \mu} |\langle j m_j | er \left[\frac{4\pi}{3} \right]^{1/2} Y_{1\mu} | i m_i \rangle|^2 \quad (38)$$

where $\{Y_{1\mu}\}$ are normalised spherical harmonics. Now, according to the Wigner-Eckart theorem (Rose³² 1957), the m dependence of the matrix element in (38) is contained in the Clebsch-Gordan coefficient $C(J_i J_j; m_i \mu m_j)$, for which

$$\sum_{m_j \mu} |C(J_i J_j; m_i \mu m_j)|^2 = \quad (39)$$

Thus, the sum over m_i in (38) contains $g_i = (2j_i+1)$ equal contributions, where g_i is the statistical weight of level i . Then (35) may be written

$$f_{ij}^1 = \frac{2}{3} \frac{m}{e^2 \hbar^2} (E_j - E_i) \frac{S_{ij}^1}{g_i} \quad (40)$$

with similar expression for velocity and acceleration forms.

The above formulation assumes a single-electron atom. In the calculations we shall be discussing, we shall be concerned with N-electron atoms, and for them we make the replacements

$$r \rightarrow \sum_{k=1}^N r_k, P \rightarrow \sum_{k=1}^N P_k, \frac{1}{r^3} \rightarrow \sum_{k=1}^N \frac{1}{r_k^3} \quad (41)$$

in (32) - (37) although the third of these replacements follows from (3.38) only since

$$\sum_{k=1}^N \nabla_k \left(\sum_{i<j} \frac{1}{r_{ij}} \right) = \sum_{i<j} (\nabla_i + \nabla_j) \frac{1}{r_{ij}} = 0 \quad (42)$$

In jj or intermediate coupling, (40) holds with $g_i = (2J_i+1)$. For LS coupling (with which we shall be mainly concerned), the form of (40) continues to hold with $g_i = (2L_i + 1) (2S_i + 1)$, the degeneracy of the multiplet, while S_{ij} , the multiplet strength is given by

$$S_{ij}^1 = \sum_{ML_i MS_i} \left| \langle L_j S_j M_{L_j} M_{S_j} \middle| \sum_{k=1}^N e r_k \middle| L_i S_i M_{L_i} M_{S_i} \rangle \right|^2 \quad (43)$$

Thus, the emission of radiation resulting in an atom de-exciting can be spontaneous (for which the transition rate depends only on the population of the upper level) or induced [for which the transition rate also depends upon the density $\rho(\nu_{ij})$].

The Einstein coefficients for these emission processes, respectively A_{ji} , B_{ji} , satisfy

$$A_{ji} = \frac{8\pi\nu_{ji}^2}{c^3} (E_j - E_i) B_{ji} \quad (44)$$

and,

$$g_i B_{ij} = g_j B_{ji} \quad (45)$$

Then the absorption oscillator strength is related to the (emission) transition probability by

$$f_{ij} = \frac{mc}{8\pi^2 e^2} \lambda_{ji}^2 \frac{g_j}{g_i} A_{ji} \quad (46)$$

where $\lambda_{ji} = c/\nu_{ji}$ is the wavelength of the transition. (Note that A_{ji} , although termed simply 'transition probability' has units $[T]^{-1}$. The absorption and emission oscillator strengths are related by

$$g_i f_{ij} = -g_j f_{ji} \quad (47)$$

$$g_i f_{ij} + g_j f_{ji} = 0$$

In order to compare the contributions to the oscillator strengths from individual configuration, it is convenient to define for the length form

$$F_{ij} = \left(\frac{2\Delta E}{3g_i} \right)^{1/2} a_i b_j \langle \psi_i | \vec{r} | \chi_j \rangle \quad (48)$$

The value of F_{ij} are given in table (with an equivalent expression for the velocity form) in terms of the CI wavefunctions of the two states involved in the transition:

$$\Psi_i = \sum_i a_i \psi_i \tag{49}$$

$$\chi_j = \sum_j b_j \chi_j \tag{50}$$

Then, in either form, the electric dipole oscillator strength is

$$f = (\sum_i \sum_j F_{ij})^2 \tag{51}$$

General expression for the transition probability of the 2-pole radiation emission from state |i > to state |j > is

$$A_{ij} = \frac{2(\lambda+1)}{\lambda(2\lambda+1)[(2\lambda-1)!!]^2} \frac{1}{g_i} \left(\frac{E_i-E_j}{\hbar c}\right)^{2\lambda+1} \tag{52}$$

$$\frac{1}{\hbar} \sum_{m_i, \mu, m_j} |\langle j m_j | Q_{\lambda, \mu} | i m_i \rangle|^2$$

and the lifetime $\tau^{-1} = \sum_j A_{ij}$ (53)

where $(2\lambda-1)!! = 1 \times 3 \times 5 \dots \times (2\lambda-1)$

g_i is the multiplicity of the upper state, and the electric and magnetic multipole operators for an N-electron atom are

$$Q_{\lambda\mu}^{(el)} = e \sum_{k=1}^N r_k^\lambda \left(\frac{4\pi}{2\lambda+1}\right)^2 Y_\lambda^\mu(k) \tag{54}$$

$$Q_{\lambda\mu}^{(mag)} = \frac{e}{mc} \sum_{k=1}^N \nabla \left[r_k^\lambda \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} Y_\lambda^\mu(k) \right] \tag{55}$$

$$\left[(\lambda + 1)^{-1} l_k + \frac{1}{2} g_s g_k \right]$$

with $g_s = 2.00232$, the gyromagnetic spin ratio. These operators can be expressed as tensor with rank λ . For the electric dipole (E1) transition, A_{ij} are determined using the CIV3 code.

The parameters for the basis orbitals used in the present calculations chosen on the criterion is a sum of Slater-type orbitals which are shown in tables 1-5 for Ca^{9+} , SC^{10+} in sodium isoelectronic sequence. Tables give Hamiltonian matrix and 6W-15W give the configuration weights.

IV. RESULTS AND DISCUSSION

We have calculated the OOS, of both the length and velocity forms, of the oscillator strengths for the inner-shell excitation, which leads to auto-ionization $1s^2 2s^2 2p^6 3s^2 S^{e_{1/2}} \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_{0/1/2}$ and $1s^2 2s^2 2p^6 3s^2 S^{e_{1/2}} \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_{3/2}$ transition in Ca^{9+} , SC^{10+} systems of the sodium isoelectronic sequence employing J-dependent HF and CI wavefunctions generated by using a new approach proposed by Tiwary¹⁹⁻²⁰.

Displays the J-dependent HF and CI optical oscillator strengths (OOS), of both the length and velocity forms, of the inner-shell excitation $1s^2 2s^2 2p^6 3s^2 S^{e_{1/2}} \rightarrow 1s^2 2s^2 2p^5 3s^2 {}^2P_{0/1/2}$ in the of the sodium isoelectronic sequence.

Table represents exactly the same quantities as in table but for the transition $1s^2 2s^2 2p^6 3s^2 S_{e1/2} \rightarrow 1s^2 2s^2 2p^5 3s^2 P_{03/2}$. Several features of importance emerge from table. First, the optical oscillator strengths, of both length and velocity forms, increase with increase of atomic number (Z) for both transitions $1s^2 2s^2 2p^6 3s^2 S_{e1/2} \rightarrow 1s^2 2s^2 2p^5 3s^2 P_{01/2}$ and $1s^2 2s^2 2p^6 3s^2 S_{e1/2} \rightarrow 1s^2 2s^2 2p^5 3s^2 P_{03/2}$ in all ions of our present consideration. Second, the values of CI f_L and f_V are larger than HF f_L and f_V for both transitions given in table in all ions which reflect that the correlation enhances the oscillator strengths. Third, the disagreement between CI f_L and f_V decreases with increase of Z which shows that the effect of correlations increases in all ions of our present consideration. Fourth, the disagreement between HF f_L and f_V is substantially large whereas the CI f_L and f_V are in good agreement which demonstrate the importance of correlation. Fifth, the relativistic f_L and f_V values for $\Delta J=0$ are significantly smaller compared to the f_L and f_V values for the $\Delta J = 1$ transition. Finally, our present investigation indicates that it indispensable to incorporate the relativistic and correlation effects simultaneously in order to obtain accurate results.

V. CONCLUSION

Our present theoretical investigation of J-dependent transition probabilities (A_L and A_V) and oscillator strengths (f_L and f_V), of both the length and velocity formulations, demonstrates that the Tiwary approach is very compact, convenient, economic from computational point of view and capable of yielding encouraging results for the complex inner-shell excitation transition in the medium ionized atoms of the sodium isoelectronic sequence. This approach may provide significant advantages also in the case of the CI calculations in molecules, clusters and solids. The present CI wave functions may be of use for calculations of scattering cross sections for the inner-shell excitation process in Ca^{9+} , Sc^{10+} ions. However, there is disagreement between the length and velocity forms of atomic transition probabilities and oscillator strengths which may be probably due to the lack of inseparable way of including correlation and relativity, quantum electrodynamic (QED) or Lamb shift and nuclear size effects. Our theoretical results suggest that the reliable theoretical predictions of atomic transition probabilities and oscillator strengths require methods that account for correlation, relativistic, QED and nuclear- size effects in a systematic and coheherent manner. At present we do not have a comprehensive and practical method that accounts for all effects mentioned above on equal footing. We hope that this work will stimulate reliable experimental as well as other accurate theoretical investigations.

Table-1

Parameters for the bound orbitals used in the present calculation for Ca^{9+} . Each orbital is a sum of Clementi-type and Slater-type orbitals

Orbitals	Clementi-type Coefficient	Slater-Type Coefficient	Power of r	Exponent
1s	0.9181687	167.6041870	1	20.2716064
	0.0207600	7.1944447	1	31.0809024
	0.0035400	0.6669434	2	7.6744404
	0.0740599	122.7318120	2	18.3130955
	0.0002600	0.0140933	3	4.0049801
	0.0013700	-0.4169066	3	6.5566196
2s	-0.2649509	-48.3646088	1	20.2716064

	-0.0081700	-2.8313532	1	31.0809021
	1.0751629	202.5633540	2	7.6744404
	-0.1472206	-243.9732510	2	18.3130951
	0.0009500	0.0514950	3	4.0049801
	0.0456902	13.9040546	3	6.5566196
3s	-0.1105004	-20.1709442	1	20.2716064
	-0.0032000	-1.1089754	1	31.0809021
	0.4956020	93.3726044	2	7.6744404
	-00.0666903	-110.5189210	2	18.3130955
	-1.3161945	-71.3444824	3	4.0049804
	0.3022813	91.9877777	3	6.556196
2p	0.7259261	101.8049320	2	6.81496602
	0.2817987	116.1832120	2	10.49776998
	0.0216599	32.5886688	2	17.6188049
3p	5.9909449	840.1789550	2	6.8196603
	-6.0151453	-9506.3515600	3	10.4976997
3d	0.9999996	349.2272950	3	6.8196603

Table-2

Parameters for the bound orbitals used in the present calculation for Sc¹⁰⁺. Each orbital is a sum of Clementi-type and Slater-type orbitals

Orbitals	Clementi-type Coefficient	Slater-Type Coefficient	Power of r	Exponent
1s	0.9280059	180.3726500	1	21.1378024
	0.0213799	7.8733130	1	32.3654022
	0.0029400	0.6512018	2	8.1876698
	0.0621097	111.9006350	2	18.9356995
	0.0001900	0.0136523	3	4.3408604
	0.0010500	-0.3940876	3	6.9615298
2s	-0.2724483	-52.9546356	1	21.1378024
	-0.0074500	-2.7435007	1	32.3654022
	1.0777836	238.7270810	2	8.1876698
	-0.1517589	-273.4179690	2	18.9356995
	-0.0012900	-0.0926917	3	4.3408604
	0.0539297	20.2410431	3	6.9615297
3s	-0.1165200	-22.6475067	1	21.1378021
	-0.0026900	-0.9906133	1	32.3654022
	0.5066005	112.2110290	2	8.1876698
	-0.0699200	-125.9721370	2	18.935695
	-1.3505297	-97.0417175	3	4.3408604
	0.3400303	127.6211700	3	6.9615297
2p	0.7303165	121.7976680	2	7.3090897

	0.2764527	130.8816680	2	11.0946999
	0.0207102	36.4648590	2	18.7624054
3p	6.4064493	1068.4279800	2	7.3090897
	-6.4381752	-12348.2500000	3	11.0946999
3d	0.9999996	445.1025390	3	7.3090898

Table-3H

Hamiltonian Matrix (H_{ij}) for the excited ²P_{0½} state used in the present calculation for Ca⁹⁺

-638.08520500	0.06975889	0.08046442	0.00004613	0.00000000
0.06968093	-632.94751000	0.60615331	-0.00003163	0.06245163
0.08048201	0.58272207	-632.29199200	-0.00002364	-0.10818565
0.00000000	0.00000000	0.00000000	-577.28149400	0.19378930
0.00000000	0.06245881	-0.10818154	0.27342641	-577.38671900

Table-3W

Configurations used for the excited ²P_{0½} state used in the present calculation for Ca⁹⁺.

The numbers below the configuration give their weights.

² P _{0½}	2P ⁵ 3p ² (³ P)	2P ⁵ 3s(⁵ P)3d	2P ⁵ 3p ² (¹ D)	2P ⁵ 3s(¹ P)3d	2P ⁵ 3s ²
2P ⁵ 3s ²	0.00000029	-0.01702558	0.00000152	-0.00390998	0.99984744
2P ⁵ 3s(¹ P)3d	-0.00066664	-0.51223552	-0.00087828	-0.85875914	-0.01208065
2P ⁵ 3s ² (³ P)3d	0.00118498	-0.85867578	0.00155904	0.51236022	-0.01261803
2P ⁵ 3p ² (³ P)	-0.79415333	0.00000333	0.60771781	-0.00000702	-0.00000074
2P ⁵ 3p ² (¹ D)	-0.60771573	-0.00111679	-0.79415190	0.00195020	-0.00001008

Table-4H

Hamiltonian Matrix (H_{ij}) for the excited ²P_{0½} state used in the present calculation for Sc¹⁰⁺

-711.35571300	0.07847345	0.08802545	0.00006770	0.00000000
0.07837862	-705.68774400	0.65833253	-0.00003256	0.05910773
0.08803529	0.62866116	-704.98339800	-0.00002323	-0.10239196
0.00000000	0.00000000	0.00000000	-633.46191400	0.14946818
0.00000000	0.05911407	-0.10238832	0.27528161	-633.52954100

Table- 4W

Configurations used for the excited ²P_{0½} state used in the present calculation for SC¹⁰⁺.

The numbers below the configuration give their weights.

² P _{0½}	2P ⁵ 3p ² (³ P)	2P ⁵ 3s(⁵ P)3d	2P ⁵ 3p ² (¹ D)	2P ⁵ 3s(¹ P)3d	2P ⁵ 3s ²
2P ⁵ 3s ²	-0.00000018	-0.01711213	0.00000117	-0.00417774	0.99984455
2P ⁵ 3s(¹ P)3d	-0.00050175	-0.51414633	-0.00063090	-0.85761279	-0.01238294
2P ⁵ 3s ² (³ P)3d	0.00088816	-0.85753107	0.00111504	0.51427728	-0.01252760
2P ⁵ 3p ² (³ P)	-0.78104025	0.00000120	0.62448066	-0.00000315	-0.00000086
2P ⁵ 3p ² (¹ D)	-0.62448013	-0.00080800	-0.78103870	0.00142443	-0.00000708

Table-5H

Hamiltonian Matrix (Hij) for the excited $2P_{3/2}^0$ state used in the present calculation for Ca^{9+} .

-638.21240200	0.06964189	0.08049077	0.00002306	0.00000000
0.06968093	-632.92968700	0.57100642	0.00001581	0.06246239
0.08048201	0.58272207	-632.25732400	0.00001182	-0.10817945
0.00000000	0.00000000	0.00000000	-577.15356400	0.31324500
0.00000000	0.06245881	-0.10818154	0.27342641	-577.32324200

Table-5W

Configurations used for the excited $2P_{3/2}^0$ state used in the present Ca^{9+} .

The numbers below the configuration give their weights.

$2P_{3/2}^0$	$2P^53p^2(^3P)$	$2P^53s(^5P)3d$	$2P^53p^2(^1D)$	$2P^53s(^1P)3d$	$2P^53s^2$
$2P^53s^2$	0.00000109	-0.01662077	0.00000083	-0.00412944	0.99985313
$2P^53s(^1P)3d$	-0.00066595	-0.496544645	-0.00087946	-0.86792880	-0.01183877
$2P^53s^2(^3P)3d$	0.00118109	-0.86785078	0.00156144	0.49666768	-0.01237518
$2P^53p^2(^3P)$	-0.79404575	0.00000692	0.60785764	-0.00001064	0.00000043
$2P^53p^2(^1D)$	-0.60785562	-0.00115134	-0.79404432	0.00192982	-0.00000984

Table-6H

Hamiltonian Matrix (Hij) for the excited $2P_{3/2}^0$ state used in the present calculation for Sc^{10+} .

-711.51660200	0.07833117	0.08804017	-0.00003385	0.00000000
0.07837862	-705.66406200	0.61382544	0.00001628	0.05911724
0.08803529	0.62866116	-704.93994100	0.00001161	-0.10238647
0.00000000	0.00000000	0.00000000	-6.33.26684600	0.33818829
0.00000000	0.05911407	-0.10238832	0.27528161	-633.44921900

Table-6W

Configurations used for the excited $2P_{3/2}^0$ state used in the present Sc^{10+} .

The numbers below the configuration give their weights.

$2P_{3/2}^0$	$2P^53p^2(^3P)$	$2P^53s(^5P)3d$	$2P^53p^2(^1D)$	$2P^53s(^1P)3d$	$2P^53s^2$
$2P^53s^2$	0.00000082	-0.01663761	0.00000037	-0.00441737	0.99985218
$2P^53s(^1P)3d$	-0.00048778	-0.49618924	-0.00064226	-0.86813003	-0.01209203
$2P^53s^2(^3P)3d$	0.00086146	-0.86805487	0.00113545	0.49631554	-0.01225175
$2P^53p^2(^3P)$	-0.79375005	0.00000421	0.60824430	-0.00000642	0.00000047
$2P^53p^2(^1D)$	-0.60824376	-0.00083703	-0.79374856	0.00140750	-0.00000691

Table-7

Table for F_{ij} [contribution to the Oscillator Strengths from Individual configuration] Obtained from equation 3.48.

Ca^{9+}		Sc^{10+}	
F_{ij}^I	F_{ij}^V	F_{ij}^I	F_{ij}^V
-0.15498E+00	-0.14666E+00	-0.15343E+00	-0.14556E+00
-0.72494E-02	-0.10384E-00	-0.74978E-02	-0.10594E-01
-0.13115E-01	-0.18786E-01	-0.13138E-01	-0.18563E-01

0.14157E-02	-0.24730E-03	0.16842E-02	-0.35274E-03
-0.19828E-04	0.760867E-05	-0.22615E-04	0.86744E-05
-0.18385E-07	-0.32114E-08	-0.15387E-07	-0.3225E-08
-0.40959E-02	0.71545E-03	-0.49360E-02	0.10338E-02
-0.34592E-04	0.13274E-04	-0.38712E-04	0.14849E-04
0.53190E-07	0.92910E-08	0.45094E-07	0.94442E-08
-0.21809E+00	-0.20844E+00	-0.21580E+00	-0.20698E+00
-0.99971E-02	-0.14464E-01	-0.10298E-01	-0.14710E-01
-0.18100E-01	-0.26187E-01	-0.18072E-01	-0.25816E-01
0.19923E-02	-0.35148E-03	0.23689E-02	-0.50160E-03
-0.27343E-04	0.10597E-04	-31060E-04	0.12045E-04
-0.25322E-07	-0.44673E-08	-0.21145E-07	-0.44774E-08
-0.57637E-02	0.10168E-02	-0.69423E-02	0.14700E-02
-0.47741E-04	0.18503E-04	-0.53249E-04	0.20650E-04
0.73259E-07	0.12924E-07	0.61970E-07	0.13122E-07

Table-8

Oscillator Strengths (f_l and f_v) and transition probabilities (A_L and A_V) for the inner-shell excitation 1s²2s²2p⁶3s²S_{1/2} → 1s²2s²2p⁵3s² ²P_{0/2} transition in the sodium isoelectronic sequence

System	HF				CI			
	f _l	f _v	A _L	A _V	f _l	f _v	A _L	A _V
Ca ⁹⁺	0.240288 E-01	0.215148 E-01	0.126783E+ 12	0.113496E+ 12	0.317136 E-01	0.307436 E-01	0.167278E+ 12	0.162459E+ 12
SC ¹⁰⁺	0.235478 E-01	0.211989 E-01	0.165887E+ 12	0.149428E+ 12	0.344648 E-01	0.302888 E-01	0.221878E+ 12	0.213514E+ 12

Table-9

Oscillator Strengths (f_l and f_v) and transition probabilities (A_L and A_V) for the inner-shell excitation 1s²2s²2p⁶3s²S_{1/2} → 1s²2s²2p⁵3s² ²P_{3/2} transition in the sodium isoelectronic sequence

System	HF				CI			
	f _l	f _v	A _L	A _V	f _l	f _v	A _L	A _V
Ca ⁹⁺	0.475864 E-01	0.434604 E-01	0.123016E+ 12	0.112863E+ 12	0.625478 E-01	0.616988 E-01	0.161635E+ 12	0.159816E+ 12
SC ¹⁰⁺	0.465826 E-01	0.438616 E-01	0.160687E+ 12	0.147865E+ 12	0.619457 E-01	0.667659 E-01	0.218554E+ 12	0.269589E+ 12

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