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Study of Oscillator Strengths (F_l and F_v) And Transition Probabilities (A_l and A_v) For The Inner-Shell Excitation $1s^22s^22p^63s\ {}^2s^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ {}^2p^0_{1/2}$ Transition In The Sodium Isoelectronic Sequence

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ABSTRACT

OOS (Optical Oscillator Strengths) provides confidence about the reliability of the wavefunctions that are employed in the matrix elements. Ridder and Schneider[1], 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. In this paper, we have carried out a study of oscillator strengths (f_l and f_v) and transition probabilities (a_l and a_v) for the inner-shell excitation $1s^22s^22p^63s\ {}^2s^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ {}^2p^0_{1/2}$ transition in the sodium isoelectronic sequence.

Keywords : CI Configuration, Hartee-Fock, Optical Strength

I. INTRODUCTION

After the beginning of computational quantum chemistry[1-10], the description of electronic structure based on the Hartree Fock (HF) approximation still forms the basis of most theoretical approaches. The number of problems that one may solve performing Hartree-Fock calculations is rather limited. Excited states, transition states, and many atomic, molecular, and ionic properties are not adequately described by a single-determinant Hartree-Fock function. Even ground states of atoms and molecules may require Hartree-Fock treatment not only for a quantitative but sometimes even for a qualitatively correct description. For such hard cases, the concept of correlation energy, defined as the difference between the exact energy from the non-relativistic Shroedinger equation and the Hartree-Fock energy, is not useful because the single determinant HF model is no longer adequate as the zeroth-order solution. Despite great efforts to develop the many-body theory, configuration-interaction (CI) is the most frequently used for Hartree-Fock calculations. We have also performed theoretical calculations of the threshold energy and dimensionless absorption optical oscillator strengths (OOS), of both the length and velocity forms (f_L and f_v respectively), for the electric dipole-allowed resonance excitation in the same ions as mentioned above using the configuration interaction wave functions for the ${}^2S^e$ and ${}^2P^0$ states involved in the transition matrix elements.

II. OSCILLATOR STRENGHTS

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

$$H\Psi = i h\frac{\partial\Psi}{\partial t} \qquad (1)$$

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[11-16].

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

$$\Psi = \sum_n c_n(t) exp\left(-\frac{i}{h}E_n t\right)\Psi_n \qquad (2)$$

where the sum includes as integration over the continuum. If the atom is in state |i > at time t = 0, then (c_i (0) = 0 for n≠i. If the velocity potential is expanded in a Fourier series of plane waves of the form A_0cos(wt-k.r.), then first-order perturbation theory gives, for absorption in one-electron atoms.

$$\frac{1}{t}\left|c_j(t)\right|^2 = \frac{2\pi}{3}\frac{c^2}{h^2\upsilon_{ji}^2}|< j|\frac{e}{mc}Pexp\,(ik.r)|i >|^2\rho(\upsilon_{ji}) \qquad (3)$$

$$= B_{ij}\rho(\upsilon_{ji}) \qquad (4)$$

where $h\upsilon_{ji} = E_j - E_i$ (5)

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

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

$$f_{ij} = \frac{m}{\pi e^2}h\upsilon_{ji}B_{ij} \qquad (6)$$

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

The magnitude of wave vector k is k = 2π/λ. Hence for wavelengths large compared with the size of the atom, k.r << 1, and the expansion

$$\exp(ik.r) = 1 + ik.r + \frac{1}{2!}(ik.r)^2 + \cdots \qquad (7)$$

will converge rapidly. The use of the first leading term of equation (7) constitutes the dipole approximation of the multipole expansion. Also,

$$\frac{i\hbar}{m}p \equiv i\hbar\dot{r} \equiv [r, H_0] \qquad (8)$$

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

$$< j\left|\frac{e}{mc}p\right|i >= \frac{ie}{\hbar c}j|H_0 r - rH_0|i >= \frac{i}{\hbar c}\left(E_j - E_i\right) < j|er| > \qquad (9)$$

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

$$f_{ij}^{1} = \frac{2m}{3\hbar^2}\left(E_j - E_i\right)|< j|r|i >|^2 \qquad (10)$$

$$f_{ij}^{v} = \frac{2}{3}\frac{1}{m}\frac{1}{\left(E_j - E_i\right)}|< j|p|i >|^2 \qquad (11)$$

These are the length and velocity forms respectively. The identities (11) may be applied to r instead of r, and in this way an acceleration form may be derived:

$$\mathrm{f}_{\mathrm{ij}}^{\mathrm{a}} = \frac{2}{3}\frac{\hbar^2}{\mathrm{m}}\frac{1}{\left(\mathrm{E_j}-\mathrm{E_i}\right)^3}|< j|\nabla\mathrm{V}\bigg|\mathrm{i} >|^2 = \frac{2}{3}\frac{\mathrm{z^2e^4}\hbar^2}{\mathrm{m}\left(\mathrm{E_j}-\mathrm{E_i}\right)^3}\left|< j\left|\frac{1}{\mathrm{r}^3}\vec{\mathrm{r}}\right|\mathrm{i} >|^2\right. \qquad (12)$$

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 $(2J_j+1)$ parameters m_j, then there are several 'Channels' open for the transition. The total absorption oscillator strength (length form) is then

$$f_{ij}^{1} = \frac{2}{3}\frac{m}{\hbar^2}\left(E_j - E_i\right)\sum_{m_j}\left|< jm_j\right|r|i > |^2 \qquad (13)$$

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

$$S_{ij}^{1} = S_{ji}^{1} = \sum_{m_i m_j}\left|< jm_j\right|er|im_i > |^2 \qquad (14)$$

$$= \sum_{m_i m_j \mu}\left|< jm_j\right|er\left[\frac{4\pi}{3}\right]^{1/2} Y_1\mu|im_i >|^2 \qquad (15)$$

where $\{Y_1m\}$ are normalized spherical harmonics. Now, according to the Wigner-Eckart theorem [17-22], the m dependence of the matrix element in (15) is contained in the Clebsch-Gordan coefficient C $(J_i l J_j;\ m_i \mu m_j)$, for which

$$\sum_{m_j\mu}|C\left(J_i l J_i; m_i \mu m_j\right)|^2 = \qquad (16)$$

Thus the sum over m_i in (15) contains $g_i = (2j_i+1)$ equal contributions, where g_i is the statistical weight of level i. Then (16) may be written

$$f_{ij}^{1} = \frac{2}{3}\frac{m}{e^2\hbar^2}\left(E_j - E_i\right)\frac{S_{ij}^{l}}{g_i} \qquad (17)$$

with similar expression for velocity and acceleration forms.

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

$$r \rightarrow \sum_{k=1}^{N} r_k, P \rightarrow \sum_{k=1}^{N} P_k, \frac{1}{r^3} r \rightarrow \sum_{k=1}^{N} \frac{1}{r_k^3} i'_k \qquad (18)$$

in (15) - (16) although the third of these replacements follows from (18) only since

$$\sum_{k=1}^{N} \nabla_{\mathrm{k}}\left(\sum_{i<j}\frac{1}{r_{ij}}\right) = \sum_{i<j}\left(\nabla_{\mathrm{i}} + \nabla_{\mathrm{j}}\right)\frac{1}{r_{ij}} = 0 \qquad (19)$$

In jj or intermediate coupling, (19) holds with $g_i = (2J_i+1)$. For LS coupling (with which we shall be mainly concerned), the form of (19) 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

$$S_{ij}^{1} = \sum_{\substack{ML_j MS_i \\ ML_i MS_j}}\left|< L_j S_j M_{L_j} M_{S_j}\right|\left|\sum_{k=1}^{N} er_k\right| L_i S_i M_{L_i} M_{S_i} > |^2 \qquad (20)$$

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 $\rho\ (\upsilon_{ij})$].

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

$$A_{ji} = \frac{8\pi\upsilon_{ji}^2}{c^3}\left(E_j - E_i\right)B_{ji} \qquad (21)$$

and,

$$g_i B_{ij} = g_j B_{ji} \qquad (22)$$

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

$$f_{ij} = \frac{mc}{8\pi^2 e^2}\lambda_{ji}^2\frac{g_j}{g_i}A_{ji} \qquad (23)$$

where $\lambda_{ji} = c/\upsilon_{ji}$ 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

$$g_i f_{ij} = -\ g_j f_{ji} \qquad (24)$$

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

To compare the contributions to the oscillator strengths from individual configurations, it is convenient to define the length form

$$F_{ij} = \left(\frac{2\Delta E}{3g_i}\right)^{1/2} a_i b_j \langle \psi_i | \vec{r} | \chi_j \rangle \qquad (25)$$

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:

$$\Psi_i = \sum_i a_i \psi_i \qquad (26)$$

$$\chi_j = \sum_j b_j \chi_j \qquad (27)$$

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

$$f = \left(\sum_i \sum_j F_{ij}\right)^2 \qquad (28)$$

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

$$A_{ij} = \frac{2(\lambda+1)}{\lambda(2\lambda+1)[(2\lambda-1)!!]^2} \frac{1}{g_i} \left(\frac{E_i - E_j}{\hbar c}\right)^{2\lambda+} \qquad (29)$$

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

and the lifetime $\tau^{-1} = \sum_j A_{ij}$ (30)

where $(2\lambda-1)!! = 1\times3\times5\ldots\times(2\lambda-1)$

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

$$Q_{\lambda\mu}^{(el)} = e \sum_{k=1}^{N} r_k^{\lambda} \left(\frac{4\pi}{2\lambda+1}\right)^2 Y_{\lambda}^{\mu}(k) \qquad (31)$$

$$Q_{\lambda\mu}^{(mag)} = \frac{e}{mc} \sum_{k=1}^{N} \nabla \left[r_k^{\lambda} \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} Y_{\lambda}^{\mu}(k) \right] \qquad (32)$$

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

with $g_s = 2.00232$, the gyromagnetic spin ratio. These operators can be expressed as tensors with rank λ. For the electric dipole (E_1) 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 1-2 for Ca^{9+}, SC^{10+} in sodium isoelectronic sequence.

III.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 atuo-ionization $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{1/2}$ and $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{3/2}$ 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 Tiwary[19-20].

Displays the J-dependent HF and CI optical oscillator strengths (OOS), of both the length and velocity forms, of the inner-shell excitation $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{1/2}$ in the of the sodium isoelectronic sequence.

Table represents exactly the same quantities as in table but for the transition $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{3/2}$. 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 $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{1/2}$ and $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{3/2}$ 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.

IV. 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: Oscillator Strengths (f_L and f_V) and transition probabilities (A_L and A_V) for the inner-shell excitation $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{1/2}$ transition in the sodium isoelectronic sequence

	HF				CI			
System	f_L	f_V	A_L	A_V	f_L	f_V	A_L	A_V
Ca^{9+}	0.240288E-01	0.215148E-01	0.126783E+12	0.113496E+12	0.317136E-01	0.307436E-01	0.167278E+12	0.162459E+12
SC^{10+}	0.235478E-01	0.211989E-01	0.165887E+12	0.149428E+12	0.344648E-01	0.302888E-01	0.221878E+12	0.213514E+12

Table-2: Oscillator Strengths (f_L and f_V) and transition probabilities (A_L and A_V) for the inner-shell excitation $1s^22s^22p^63s\ ^2S^e_{1/2} \rightarrow 1s^22s^22p^53s^2\ ^2P^0_{3/2}$ transition in the sodium isoelectronic sequence

	HF				CI			
System	f_L	f_V	A_L	A_V	f_L	f_V	A_L	A_V
Ca^{9+}	0.475864E-01	0.434604E-01	0.123016E+12	0.112863E+12	0.625478E-01	0.616988E-01	0.161635E+12	0.159816E+12
SC^{10+}	0.465826E-01	0.438616E-01	0.160687E+12	0.147865E+12	0.619457E-01	0.667659E-01	0.218554E+12	0.269589E+12

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