

振盪強度總數之數量關係式

Quantitative Relation for Oscillator Strength Sums

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ABSTRACT — With the aid of RHF atomic functions numerical evaluations of the oscillator strength sum  $S(1)$  for polyelectron atoms He-Xe are performed. Numerical evaluations of  $S(K)$  are formidable and those with non-integral  $K$  are unable to be evaluated directly. Therefore we also present a quantitative relation between  $S(K)$  and  $K$  and numerical results of  $S(K)$  at least over a range of  $K$  from  $-2$  to  $2$  both integral or fractional can be easily performed therefrom.

1. Introduction

The sum rules for expressions of the form  $R_n^a = \sum_k \left( \frac{E_k - E_n}{\hbar} \right)^a |r_{kn}|^2$  have been derived by Bethe, sum results are well known for  $a=0,1,2,3,4$  [1]. These are

$$\begin{aligned} R_n^0 &= \langle n | r^2 | n \rangle, \\ R_n^1 &= \frac{3\hbar}{2m}, \\ R_n^2 &= \frac{1}{2} \langle n | p^2 | n \rangle = \frac{2}{m} \langle n | E_n - v | n \rangle, \\ R_n^3 &= \frac{\hbar}{2m^2} \langle n | \nabla^2 v | n \rangle \\ R_n^4 &= \frac{1}{m^2} \langle n | (\nabla v)^2 | n \rangle. \end{aligned} \quad (1)$$

The general sum rules of the form  $S_n^a = \sum_k (E_k - E_n)^a |A_{kn}|^2 = \sum_k (E_k - E_n)^a A_{kn} A_{kn}^*$  with  $|a| = 0, 1, 2, 3, \dots$  have been derived by Jackiw [2], the simplest expressions for  $S_n^a$  and  $S_n^{-a}$  are

$$\begin{aligned} S_n^{2a} &= (-)^a \langle n | (A_a)^2 | n \rangle, \\ S_n^{2a+1} &= \frac{1}{2} (-)^a \langle n | [A_a, A_{a+1}] | n \rangle, \\ S_n^{-2a} &= \langle n | A_{-a}^* A_a | n \rangle - \langle n | A^* | m \rangle \langle m | A_{-2a} | n \rangle, \\ S_n^{-(2a+1)} &= \langle n | A_{-a-1}^* A_{-a} | n \rangle - \langle n | A^* | m \rangle \langle m | A_{-2a-1} | n \rangle, \end{aligned} \quad (2)$$

where the commutant  $A_a$  and inverse commutant are defined recursively by

$$A_0 = A, \quad A_a = [H, A_{a-1}], \quad [H, A_{-a}] = A_{-a+1}. \quad (3)$$

The symmetric version of these results,  $R_n^a$  defined above, agrees with (1). Applications of (2) are extended to higher  $a$  and to any operator  $A$ .

The oscillator strength also satisfies several sum rules and may be defined in terms of the matrix elements of the electron dipole-moment operator  $R$  between two states  $J$  and  $J'$  [3-5],

$$S(K) = \frac{2}{3} \sum_J \langle JM | R^{(1)} | J'M' \rangle \langle J'M' | R^{(1)} | JM \rangle (E_J - E_{J'})^{K+1} \quad (4)$$

Based on (4), further numerical evaluations  $S(K)$  with  $k=-3, -2, -1, 0$ , and 2 have been performed previously [3]. For  $K > 2.5$ ,  $S(K)$  becomes infinite [4]. Numerical evaluation of  $S(1)$  requires extra effort or ability and is presented in this paper. Numerical evaluations of (4) are formidable and those of  $S(K)$  with non-integral  $K$ , e.g.  $S(-1.5)$ , are unable to be evaluated from (4). Therefore, a quantitative relation for oscillator strength sums obtained from numerical results of sums  $S(-2)$  through  $S(1)$  are also presented and the values of  $S(-1.5)$  are obtained therefrom. Atomic units are used throughout this article.

## II. Explicit Expression of $S(1)$

To derive the desired expression of the sum  $S(1)$  defined by (4) we utilize the identity  $[H, X] = -\frac{i\hbar}{m} P_x$  and Hermitian property of the Hamiltonian operator  $H$ . We then have

$$\begin{aligned} \langle J | X | J' \rangle \langle J' | X | J \rangle (E_J - E_{J'})^2 &= -\langle J | [H, X] | J' \rangle \langle J' | [H, X] | J \rangle \\ &= \langle J | P_x | J' \rangle \langle J' | P_x | J \rangle. \end{aligned} \quad (5)$$

Thus definition (4) of the sum  $S(1)$  for atom in its ground state reads

$$S(1) = \frac{2}{3} \sum_J \langle J | \sum_i r_i | J' \rangle \langle J' | \sum_i r_i | J \rangle (E_J - E_{J'})^2 = \frac{2}{3} \langle J | (\sum_i \vec{p}_i)^2 | J' \rangle. \quad (6)$$

For convenience, (6) is separated into two parts: one-electron operator part and two-electron operator part,

$$S(1) = \frac{2}{3} \langle \psi | (\sum_i \vec{p}_i)^2 | \psi \rangle = \frac{2}{3} \langle \psi | \sum_i \vec{p}_i^2 | \psi \rangle + \frac{2}{3} \langle \psi | \sum_{i \neq j} \vec{p}_i \cdot \vec{p}_j | \psi \rangle. \quad (7)$$

Knowledge of the ground state functions of an atom permits us to evaluate  $S(1)$ .

## III. Numerical Evaluation of $S(1)$

The total ground state wavefunctions of  $N$ -electron atom with closed shell is represented by the Slater determinant (SD). The expansion of the SD has  $N!$  terms. In the case of  $\langle \psi | \vec{p}_i^2 | \psi \rangle$ , there are  $(N!)^2$  terms over all from these

matrix elements but most of which are zero due to orthogonality of orbital functions and the fact that  $P_i$  is an one-electron operator. This implies that  $i$ th electron must be in the same orbital and, therefore, the number of terms is reduced to  $N!$  corresponding to the  $i$ th electron being in each of the  $N$  orbitals with all possible arrangements of the remaining  $N-1$  electrons. After integration, these  $N!$  terms are actually the same owing to both orthonormality and antisymmetry of orbital functions [6]. Thus there are only  $N$  different terms in the expansion of  $\langle \psi | \sum_i P_i^2 | \psi \rangle$ , each of these  $N$  different terms appears  $N!$  times. This  $N!$  is then cancelled by the normalization factor in the SD leaving us with just  $N$  terms, i.e.,

$$\begin{aligned} \langle \psi | \sum_i P_i^2 | \psi \rangle &= \sum_{k=1}^N \langle \phi_k(i) | P^2 | \phi_k(i) \rangle \\ &= -\hbar^2 \sum_{kst} \sum_s \sum_t C_s C_t [((n_t-1)(n_t-2) + 2(n_t-1) - \ell(\ell+1)) \times \\ &\quad \langle X_s | \frac{1}{r^2} | X_t \rangle - (2(n_t-1)\xi_t + 2\xi_t) \langle X_s | \frac{1}{r} | X_t \rangle \\ &\quad + (\xi_t)^2 \langle X_s | X_t \rangle], \end{aligned} \tag{8}$$

where the orbital wavefunction  $\phi$  is expanded in terms of Slater type orbital (STO) [7] and  $P^2 = -\frac{\hbar^2 d^2}{dr^2} + \frac{2\hbar^2}{r} \frac{d}{dr} - \frac{1}{r^2} \ell(\ell+1)\hbar^2$  [8]. Thus the integral of interest are in the form of  $\langle X_s | r^q | X_t \rangle$  with  $q = -2, -1, 0, 1$ . For which we have

$$\langle X_s | r^q | X_t \rangle = N_s N_t \frac{(n_s + n_t + q)!}{(\xi_s + \xi_t)^{n_s + n_t + q + 1}} \tag{9}$$

The explicit expression for numerical evaluation of  $\langle \psi | \sum_i P_i^2 | \psi \rangle$  yields finally,

$$\begin{aligned} \langle \psi | \sum_i P_i^2 | \psi \rangle &= -\hbar^2 \sum_{kst} \sum_s \sum_t C_s C_t \left[ \frac{(2\xi_s)^{2n_s+1} (2\xi_t)^{2n_t+1}}{(2n_s)! (2n_t)!} \right]^{1/2} \left[ \frac{(n_s + n_t - 2)!}{(\xi_s + \xi_t)^{n_s + n_t + 1}} \right] \times \\ &\quad [(n_t(n_t-1) - \ell(\ell+1)) (\xi_s + \xi_t)^2 - 2n_t(n_s + n_t - 1)\xi_t(\xi_s + \xi_t) \\ &\quad + (n_s + n_t)(n_s + n_t - 1)(\xi_t)^2]. \end{aligned} \tag{10}$$

Considering  $\langle \psi | \sum_i \vec{P}_i \cdot \vec{P}_j + \sum_j \vec{P}_j \cdot \vec{P}_i | \psi \rangle$  for an atom with closed shell, we realized that most of the  $(N!)^2$  expansion terms are zero in which the remaining  $N-2$  electrons are not each in the same orbital. Thus we are interested in the form as

$$\begin{aligned} \langle \phi_k(i) | P_i^0 | \phi_k(i) \rangle \langle \phi_\ell(j) | P_j^0 | \phi_\ell(j) \rangle - \langle \phi_k(i) | P_i^{-1} | \phi_k(i) \rangle \langle \phi_\ell(j) | P_j^1 | \\ | \phi_\ell(j) \rangle - \langle \phi_k(i) | P_i^1 | \phi_k(i) \rangle \langle \phi_\ell(j) | P_j^{-1} | \phi_\ell(j) \rangle \quad \text{or} \end{aligned} \tag{11a}$$

$$\begin{aligned} &\langle \phi_k(i) | P_i^0 | \phi_\ell(i) \rangle \langle \phi_\ell(j) | P_j^0 | \phi_k(j) \rangle - \langle \phi_k(i) | P_i^{-1} | \phi_\ell(i) \rangle \langle \phi_\ell(j) \\ &| P_j^1 | \phi_k(j) \rangle - \langle \phi_k(i) | P_i^1 | \phi_\ell(i) \rangle \langle \phi_\ell(j) | P_j^{-1} | \phi_k(j) \rangle, \end{aligned} \quad (11b)$$

where the spherical tensor forms are used. For the matrix elements  $\langle \ell' m' m_s' | P_1^M | \ell m m_s \rangle$ , the selection rule  $\ell' = \ell \pm 1$  eliminates (11a) and reduces (11b) to s-p or p-d orbital combinations for atoms through Xe. In the case of s-p, we have

$$\begin{aligned} \langle \psi | \sum_{ij} \sum_{\alpha\beta} (i \neq j) \vec{p}_i \cdot \vec{p}_j | \psi \rangle &= -4 \sum_{nn'} \langle ns_0 | P^0 | n' p_0 \rangle \langle n' p_0 | P^0 | ns_0 \rangle \\ &\quad - \langle ns_0 | P^{-1} | n' p_1 \rangle \langle n' p_1 | P^1 | ns_0 \rangle - \langle ns_0 | P^1 | \\ &\quad n' p_{-1} \rangle \langle n' p_{-1} | P^{-1} | ns_0 \rangle \\ &= -4C \sum_{nn'} \langle ns || P || n' p \rangle \langle n' p || P || ns \rangle, \end{aligned} \quad (12)$$

where the overall negative sign comes from interchange of electrons  $i$  and  $j$  in the SD, a factor 2 from the equivalence of the  $\alpha$  and  $\beta$  series in spin functions, a factor 2 from the equivalence of  $\langle \psi | \vec{p}_i \cdot \vec{p}_j | \psi \rangle$  and  $\langle \psi | \vec{p}_j \cdot \vec{p}_i | \psi \rangle$ ,  $C$  is a sum of products of Clebsch-Gordan (CG) coefficients or 3-j symbols, and  $\langle n \ell || P || n' \ell' \rangle$  is a reduced matrix element [9]. These are in general

$$\begin{aligned} &\langle \phi_{n\ell m}(i) \phi_{n'\ell'm'}(j) | P^M P^{-M} | \phi_{n\ell m}(j) \phi_{n'\ell'm'}(i) \rangle \\ &= \langle n \ell m | P^M | n' \ell' m' \rangle \langle n' \ell' m' | P^{-M} | n \ell m \rangle \\ &= (-)^{\ell-m+\ell'-m'} \begin{pmatrix} \ell & 1 & \ell' \\ -m & M & m' \end{pmatrix} \begin{pmatrix} \ell' & 1 & \ell \\ -m' & -M & m \end{pmatrix} \langle n \ell || P || n' \ell' \rangle \times \\ &\langle n' \ell' || P || n \ell \rangle, \end{aligned} \quad (13)$$

Where we must have  $-m+M+m'=0$  or the CG coefficients vanish.

For open shell atoms, we are interested in the average value shown by

$$\begin{aligned} \langle \psi | \sum_{ij} \sum_{\alpha\beta} (i \neq j) \vec{p}_i \cdot \vec{p}_j | \psi \rangle &= - \frac{N_{n\ell}}{(2\ell+1)} \frac{N_{n'\ell'}}{2\ell'+1} \langle n, \ell || P || n', \ell' \rangle \times \\ &\langle n', \ell' || P || n, \ell \rangle, \end{aligned} \quad (14)$$

since coefficients squared always add to 1. Where  $N_{n\ell}$  is number of electrons in the  $n\ell$  shell and  $N_{n'\ell'}$  is number of electrons in the  $n'\ell'$  shell.

Recalling (12), we have an expression for  $\langle n', \ell' || P || n, \ell \rangle$  in (14) with  $\ell' = \ell + 1$ ,  $m = \ell$

$$\langle n', \ell' || P || n, \ell \rangle = (-)^{\ell+1} \begin{pmatrix} \ell+1 & 1 & \ell \\ -\ell & 0 & \ell \end{pmatrix}^{-1} \langle n', \ell+1, \ell | P^0 | n, \ell, \ell \rangle. \quad (15)$$

In terms of spherical polar coordinates and angular momentum operator  $L, P^0$

can be expressed [9] by

$$p^0 = i\hbar \cos\theta \frac{d}{dr} + \frac{i \sin\theta}{r} [\exp(-i\phi)L^1 + \exp(i\phi)L^{-1}] \quad (16)$$

We then obtain

$$\begin{aligned} \langle n', \ell+1, \ell | p^0 | n, \ell, \ell \rangle &= \langle n', \ell+1 | [-i\hbar \frac{d}{dr} \langle \ell+1, \ell | \cos\theta | \ell, \ell \rangle \\ &+ \frac{1}{r} \langle \ell+1, \ell | \sin\theta e^{-i\phi} L^1 | \ell, \ell \rangle + \frac{1}{r} \langle \ell+1, \\ &\ell | \sin\theta e^{i\phi} L^{-1} | \ell, \ell \rangle] | n, \ell \rangle \\ &= \langle n', \ell+1 | -2(\frac{\pi}{3})^{\frac{1}{2}} i\hbar \frac{d}{dr} \langle Y_{\ell+1}^{\ell} | Y_1^0 | Y_{\ell}^{\ell} \rangle - \\ &\frac{i\hbar}{r} 4(\frac{\pi}{3})^{\frac{1}{2}} \frac{1}{2} \frac{1}{2} \langle Y_{\ell+1}^{\ell} | Y_1^{\ell} | Y_{\ell}^{\ell-1} \rangle | n, \ell \rangle \end{aligned} \quad (17)$$

where the irreducible tensor operator and spherical harmonics are used [5], i.e.,

$$L^{\pm} | Y_{\ell}^m \rangle = \mp \hbar [\frac{1}{2}(\ell \mp m)(\ell \pm m + 1)]^{\frac{1}{2}} Y_{\ell}^{m \pm 1} \quad (18a)$$

$$Y_{\ell}^m = (\frac{2\ell+1}{4\pi})^{\frac{1}{2}} [ \frac{(\ell-|m|)!}{(\ell+|m|)!} ]^{\frac{1}{2}} e^{im\phi} P_{\ell}^{|m|}(\cos\theta). \quad (18b)$$

Notice in order that  $\langle Y_{\ell_3}^{m_3} | Y_{\ell_2}^{m_2} | Y_{\ell_1}^{m_1} \rangle \neq 0$  it is necessary that  $-m_3^* + m_2 + m_1 = 0$ , [10] e.g.,  $\langle Y_{\ell+1}^{\ell} | Y_1^{-1} | Y_{\ell}^{\ell-1} \rangle = 0$ . Composition relation for spherical harmonics [9] is

$$\begin{aligned} \langle Y_{\ell_3}^{m_3} | Y_{\ell_2}^{m_2} | Y_{\ell_1}^{m_1} \rangle &= [ \frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)} ]^{\frac{1}{2}} C(\ell_1 \ell_2 \ell_3; m_1 m_2 m_3) \times \\ &C(\ell_1 \ell_2 \ell_3; 000) \end{aligned} \quad (19)$$

tables of these C coefficients have been provided by Condon & Shortley [11] e.g., the explicit results of C coefficients with  $\ell_2=1$  are

$$C(\ell 1 \ell+1; 000) = (\frac{\ell+1}{2\ell+1})^{\frac{1}{2}}, \quad (20a)$$

$$C(\ell 1 \ell+1; 101) = (\frac{1}{\ell+1})^{\frac{1}{2}}, \quad (20b)$$

$$C(\ell 1 \ell+1; \ell-1 \ell) = \frac{1}{\ell+1}. \quad (20c)$$

CG coefficients satisfy the condition:  $((-)^{\ell+1} \begin{pmatrix} \ell+1 & 1 & \ell \\ -\ell & 0 & \ell \end{pmatrix})^{-1} = ((-)^{\ell+1} \begin{pmatrix} \ell+1 & \ell & 1 \\ \ell & -\ell & 0 \end{pmatrix})^{-1} = ((2\ell+3)(\ell+1))^{\frac{1}{2}}$  [5], therefore, the explicit expression for numerical evaluation of  $\langle n', \ell' | |p| | n, \ell \rangle$  in (14) with  $\ell' = \ell+1$  &  $m = \ell$  yields finally,

$$\begin{aligned} \langle n', \ell+1 | |p| | n, \ell \rangle &= \langle n', \ell+1 | [-i\hbar(\ell+1)^{\frac{1}{2}} (\frac{d}{dr} + \frac{\ell\sqrt{2}}{r})] | n, \ell \rangle \\ &= -i\hbar(\ell+1)^{\frac{1}{2}} \sum_{kst} C_s C_t [ \frac{(2\xi_s)^{2n_s+1} (2\xi_t)^{2n_t+1}}{(2n_s)! (2n_t)!} ]^{\frac{1}{2}} \times \end{aligned}$$

$$\left[ \frac{(n_s+n_t-1)!}{(\xi_s+\xi_t)^{n_s+n_t+1}} \right] [(n_t-1+\ell\sqrt{2})\xi_s - (n_s+1-\ell\sqrt{2})\xi_t]. \quad (21)$$

In analogous manner, the explicit expression for numerical evaluation of  $\langle n, \ell || p || n', \ell' \rangle$  in (14) with  $\ell' = \ell + 1$  &  $m = \ell$  becomes

$$\langle n, \ell || p || n', \ell + 1 \rangle = i^{\ell} (\ell + 1)^{\frac{1}{2}} \sum_{kst} C_s C_t \left[ \frac{(2\xi_s)^{2n_s+1} (2\xi_t)^{2n_t+1}}{(2n_s)! (2n_t)!} \right] \left[ \frac{(n_s+n_t-1)!}{(\xi_s+\xi_t)^{n_s+n_t+1}} \right] [(n_s-1-(\ell+2)\sqrt{2})\xi_t - (n_t+1+(\ell+2)\sqrt{2})\xi_s]. \quad (22)$$

Numerical results of  $\langle \psi | \sum_i^N \sum_j^N (i \neq j) \vec{p}_i \cdot \vec{p}_j | \psi \rangle$  are then found by substituting both (21) and (22) into (14).

#### IV. Quantitative Relation for the Oscillator Strength Sums

With the aid of Clementi's Roothaan-Hartree-Fock (RHF) atomic functions, [7]. Numerical results of  $\langle \psi | \sum_i^N \vec{p}_i^2 | \psi \rangle$ ,  $\langle \psi | \sum_i^N \sum_j^N (i \neq j) \vec{p}_i \cdot \vec{p}_j | \psi \rangle$ , and  $S(1)$  are evaluated. By plotting the natural logarithms of sums  $S(K)$  vs.  $K$  with  $K = -2, -1, 0$ , and 1 for atoms Li-Ar, we obtain some smooth curves. Such plots are shown in Fig. 1 and 2.

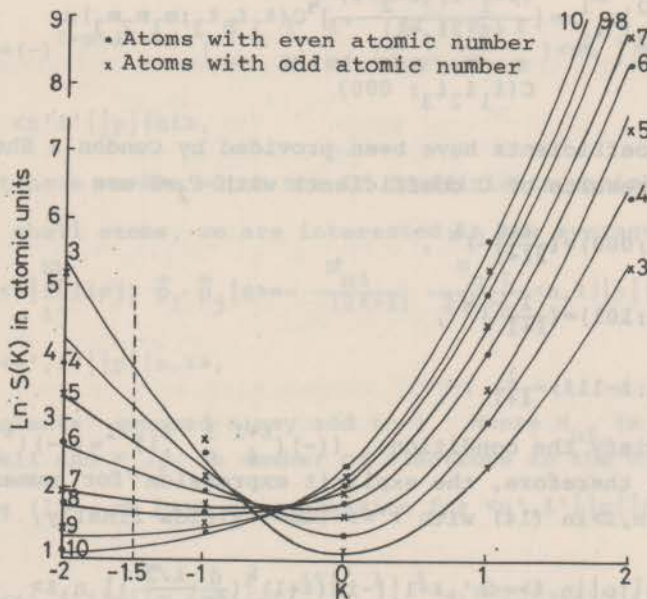


Fig. 1.  $\ln S(K)$  vs.  $K$  for atoms  $Z=3$  to 10

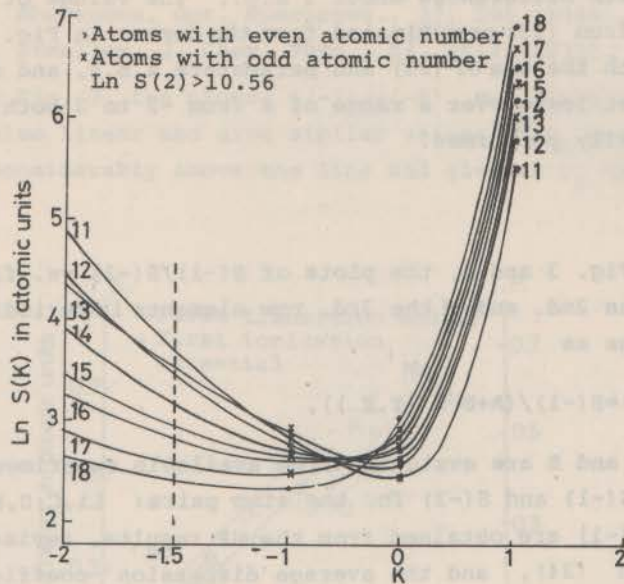


Fig. 2.  $\ln S(K)$  vs.  $K$  for atoms  $Z=11$  to 18.

A quantitative relation between  $S(K)$  and  $K$  are obtained,

$$\ln S(K) = a + bK + cK^2 + dK^3, \tag{23}$$

where the parameters  $a, b, c,$  and  $d,$  as listed in Table I, are found from the values of sums  $S(-2), S(-1), S(0),$  and  $S(1)$

Table I

Atom	$a$	$b$	$c$	$d$	$\ln S(-1.5)^*$	$\ln S(2)^*$
LI 2S	1.10	-0.52	1.39	0.32	3.92	8.19
BE 1S	1.39	-0.19	1.35	0.41	3.30	9.70
B 2P	1.60	0.31	1.26	0.35	2.80	10.03
C 3P	1.79	0.69	1.17	0.32	2.30	10.47
N 4S	1.94	0.98	1.14	0.32	1.95	11.03
O 3P	2.08	1.22	1.13	0.29	1.81	11.41
F 2P	2.20	1.47	1.10	0.28	1.53	11.73
NE 1S	2.30	1.72	1.05	0.24	1.27	11.92
NA 2S	2.40	1.05	1.79	0.32	3.77	14.23
MG 1S	2.48	1.16	1.78	0.36	3.54	14.78
AL 2P	2.56	1.11	1.87	0.44	3.62	15.76
SI 3P	2.64	1.32	1.80	0.41	3.30	15.76
P 4S	2.71	1.40	1.78	0.45	3.09	16.24
S 3P	2.77	1.45	1.80	0.47	3.06	16.68
CL 2P	2.83	1.64	1.73	0.45	2.74	16.65
AR 1S	2.89	1.83	1.66	0.42	2.46	16.51

\* Calculated from (23)

The values of  $\ln S(-1.5)$  calculated from (23) are about 0.15 a.u. smaller than those estimated directly from the curves in Fig. 1 and 2. The magnitudes

of  $\ln S(2)$  calculated from (23) give a similar trend as those obtained from HF results [3] with differences about 3 a.u.. The values of  $S(K)$  with  $K > 2.5$ , both calculated from (23) or estimated from the curves in Fig. 1 and 2, approach infinite. With the use of (23) and parameters  $a, b, c$ , and  $d$ , numerical evaluation of  $S(K)$  at least over a range of  $K$  from  $-2$  to  $2$  both integral or fractional can be easily performed.

## V. Discussion

As shown in Fig. 3 and 4, the plots of  $S(-1)/S(-2)$  vs. first transitional energy (T.E.) of the 2nd. and of the 3rd. row elements in periodic table suggest two linear regions as

$$S(-2) = S(-1) / (A + B \times (\text{T.E.})), \quad (24)$$

the parameters  $A$  and  $B$  are evaluated from available experimental or estimated values of both  $S(-1)$  and  $S(-2)$  for the atom pairs: Li, C; O, Ne; Na, Mg; and S, Ar. Values of  $S(-1)$  are obtained from the HF results, revised values of  $S(-2)$  are obtained from (24), and the average dispersion coefficient  $C_6$  listed in Table II are computed here by [12]

$$C_6 = \frac{3}{4} S(-1.5)^2, \quad (25)$$

where the improved values of  $S(-1.5)$  are also obtained from (23). Some available semiempirical values of  $C_6$  are listed in Table II too.

Table II  $C_6$  values

Atom	Semiempirical	This work
He 1S	1.4618	1.5145
Li 2S	1390	1349
Be 1S	218	476.46 (258.32)
B 2P		130.609
C 3P	40.9 ± 4.4	47.46
N 4S		23.079
O 3P	17.468	21.614
F 2P		9.797
Ne 1S	6.55 ± 0.87	7.67
Na 2S	1580	1239
Mg 1S	683 ± 35	647.72
Al 2P		717.624
Si 3P		324.542
P 4S		173.720
S 3P		260.100
Cl 2P		128.946
Ar 1S	66 ± 3	81.02

He, Ne, Ar: G. Starkschall & R.G. Gordon, *J. Chem. Phys.*, **54**, 663 (1971).

Li, Na: A. Dalgarno, *Advan. Chem. Phys.*, **12**, 143 (1967)

C: J.H. Miller & H. P. Kelley, *Phys. Rev.*, **A5**, 516 (1972).



O: H.P. Kelley, Internat. J. Quantum Chem., 38, 349 (1970).

Be: L.N. Shabanova, Opt. Spectrosc., 27, 205 (1969).

Mg: W.C. Stwalley, J. Chem. Phys., 54, 4517 (1971).

Also shown in Fig. 3, the plots  $S(-1)/s(-2)$  vs. first ionization potential (I.P.) are also linear and give similar values of  $C_6$  except that the point for Be lies considerably above the line and gives a  $C_6$  value of 258.32.

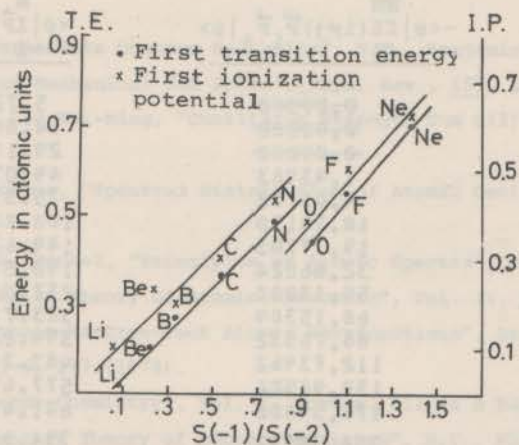


Fig. 3. Variations of  $S(-1)/S(-2)$  with first transition energies & first ionization potentials.

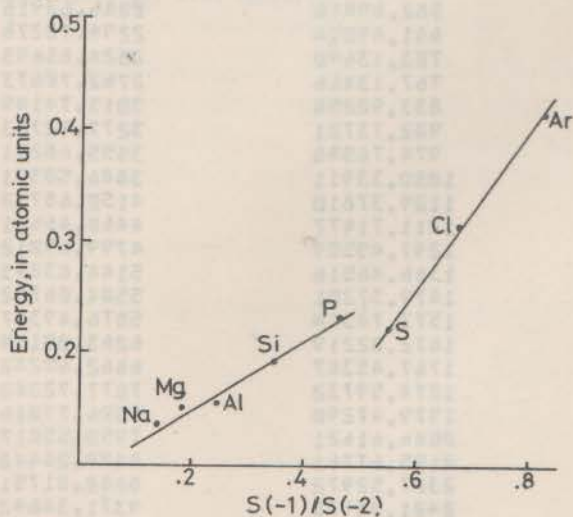


Fig. 4. Variations of  $S(-1)/S(-2)$  with transition energies.

## VI. Acknowledgment

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## Appendix

<u>Atom</u>	$-\langle \psi   \sum_{ij} \sum_{NN} (i \neq j) \vec{P}_i \cdot \vec{P}_j   \psi \rangle$	$\langle \psi   \sum_i^N \vec{P}_i^2   \psi \rangle$
HE 1S	<del>0.00000</del>	5.72363
LI 2S	<del>0.00000</del>	14.86567
BE 1S	<del>0.00000</del>	29.14561
B 2P	1.43983	49.05803
C 3P	4.81732	75.37584
N 4S	10.80150	108.80245
O 3P	19.77703	149.62025
F 2P	32.66024	198.81946
NE 1S	50.13088	257.09237
NA 2S	68.15389	323.71437
MG 1S	86.76532	399.22192
AL 2P	112.73962	483.74577
SI 3P	139.98504	577.69440
P 4S	170.59406	681.42689
S 3P	204.58072	794.96768
CL 2P	242.23511	918.93074
AR 1S	283.62971	1053.62335
K 2S	327.22479	1198.34421
CA 1S	374.00910	1353.49866
SC 2D	422.60054	1519.46652
TI 3F	473.47001	1696.80939
V 4F	527.00954	1885.75429
CR 5D	582.89416	2086.63916
MN 6S	641.49014	2299.72278
FE 5D	703.13690	2524.85693
CO 4F	767.13466	2762.70673
NI 3F	833.90254	3013.74149
CU 2S	902.73721	3277.92783
ZN 1S	974.76588	3555.68231
GA 2P	1050.33911	3846.50351
GE 3P	1129.37810	4150.68738
AS 4S	1211.71477	4468.46631
SE 3P	1297.45509	4799.69012
BR 2P	1386.46516	5144.83893
KR 1S	1479.37201	5504.06702
RB 2S	1573.74344	5876.49347
SR 1S	1672.02219	6263.00159
Y 2D	1767.45387	6662.60242
ZR 3F	1874.59732	7077.72040
NB 4F	1979.47290	7506.79016
MO 5D	2086.61621	7950.55017
TC 6S	2195.67761	8409.28442
RU 5D	2307.52972	8882.81751
RH 4F	2421.53778	9371.34692
PD 3F	2537.43799	9875.29785
AG 2D	2655.65735	10394.84400
CD 1S	2778.85236	10928.15300
IN 2P	2898.67459	11480.08940

Atom	$-\langle \Psi   \sum_{i,j} (i \neq j) P_i P_j   \Psi \rangle$	$\langle \Psi   \sum_i P_i^2   \Psi \rangle$
SN 3P	3026.56912	12045.80570
SB 4S	3156.32626	12626.75167
TC 3P	3288.84692	13223.32310
I 2P	3424.40918	13835.77260
XE 1S	3561.56989	14462.85080

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