Systematic trends in the line strengths of E1 transitions in the oxygen isoelectronic sequence

ANJU AGRAWAL and K L BALUJA

Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

Abstract. Line strengths S for the dipole allowed transitions within the $n = 2$ complex of the oxygen isoelectronic sequence have been fitted in the form $Z^2 S = A + B/(Z - C)$, where Z is the nuclear charge of a particular ion. The constants A, B and C are determined by using a non-linear least square method. The data for S are taken from the configuration interaction calculations which included internal, semi-internal and all external type correlations for ions in the range $Z = 8 - 25$. It is shown that the values of A obtained from the fit for all the transitions are in excellent accord with the ab-initio values obtained in the hydrogenic limit $Z \to \infty$ provided near degeneracy effects are included in the ground state multiplet $1s^2 2s^2 2p^4 \, {}^1S$.

1. Introduction

Accurate values of optical oscillator strengths of various transitions of ions are of interest in astrophysics [1] and fusion research [2]. They provide information on the abundance of elements in the spectrum of the solar corona and chromosphere. These important data are useful in establishing models for stellar atmospheres. The optical strengths are related to refractive index, the dipole polarizability and diamagnetic susceptibility of the system through sum rules [3–5]. It is well-known [6] that the generalized oscillator strength for a particular transition at zero momentum transfer is equal to the optical oscillator strength for that transition. An accurate knowledge of the optical oscillator strength can then be used as a correction factor for the entire range of momentum transfer to derive accurate electron collision cross-sections.

Beam-foil spectroscopy [7] is often employed to measure the lifetime of an excited state. A beam of fast ions from an accelerator is allowed to pass through a thin foil causing excitations in the ions due to collisions. However, other excited states often blend the decay curve of the state of interest. There may also be undetected systematic errors which may further compound the problem. There are various methods available [8] for the calculation of atomic transition probabilities. The calculations involve the modulus of the electric dipole transition matrix element which requires accurate knowledge of the wavefunctions of the states involved. The matrix element is extremely sensitive to the quality of the wavefunctions so it is important to obtain accurate wavefunctions. Fischer [9] has developed the numerical multi-configurational Hartree Fock (HF) method in which the orbitals of the configuration are all of HF type. The method of superposition of configurations was developed by Hibbert [10] in which

the reference function is an analytic HF function with each HF orbital expressed as a linear combination of Slater orbitals. When interacting configurations are included, the variational parameters of the reference function are not reoptimized. These configuration interaction methods include correlation which depends upon the span of the basis functions included in the calculation.

Particular applications may require oscillator strength data along an isoelectronic sequence or along a homologous series or along a Rydberg series [11]. Since each individual case requires a protracted calculation, it is natural that isoelectronic studies be made by methods with which we can extrapolate or interpolate. Smith *et al* [12] have given a general review of systematic trends in oscillator strengths. An interpolation curve based on the perturbation theory [13] may be employed to give information about the missing data. An interpolation curve for the line strength S is more convenient. In particular the form $Z^2 S = A + B/(Z - C)$, where Z is the nuclear charge and A, B and C are the parameters to be determined via a non-linear least square fit has been used by Trabert [14] to study the isoelectronic trends in the experimentally determined S values for the dipole allowed transitions in the Be sequence. This functional form was used by Baluja and Agrawal [15] for the isoelectronic study of S for the dipole allowed transitions in the carbon sequence. It was shown that the values of A obtained from the fit for all the transitions were in excellent accord with the ab-initio values obtained in the hydrogenic limit $Z \to \infty$ provided near degeneracy effects [16] were included. The present work is an extension of our previous work [15]. In the present work we have fitted the S values for the dipole allowed transitions in the $n = 2$ complex for O-sequence in the range $Z = 8 - 25$. In the O-sequence, the near degeneracy effects arise in the ground state multiplet $1s^2 2s^2 2p^4 \, {}^1S$. The two '2s' electrons are promoted to two '2p' electrons giving rise to the near degenerate configuration state $1s^2 2p^6 \, {}^1S$. The near degeneracy effect in the other ground state multiplets $1s^2 2s^2 2p^4 \, {}^3P, {}^1D$ is absent due to angular momentum coupling rules. The present work investigates the effect of near degeneracy on the value of A for the ${}^1S$ state. For the ${}^3P$ and ${}^1D$ states, the A values correspond to the single configurational value.

2. Theory

The multiplet line strength S between an initial bound state ϕ and a final bound state ϕ' is given by [9]

$$S = \left| \left\langle \phi \left| \sum_{i=1}^{N} \mathbf{r}_i \right| \phi' \right\rangle \right|^2 \tag{1}$$

where the summation is taken over all the electrons of the atom, $\mathbf{r}_i$ is the dipole operator for the ith electron. The corresponding oscillator strength is given by [9]

$$f = 2\Delta E \, S/(3g) \tag{2}$$

where ΔE is the excitation energy (in a.u.) and $g = (2L + 1)(2S + 1)$ is the statistical weight of the initial state.

According to the perturbation theory [13], the f value for a particular transition within an isoelectronic sequence may be expanded in inverse powers of Z

$$f = \sum_{i=0}^{\infty} f_i/Z^i. \tag{3}$$

The corresponding expansion for S is

$$Z^2 S = \sum_{i=0}^{\infty} S_i/Z^i. \tag{4}$$

Equation (4) can be rewritten in a more compact fashion as

$$Z^2 S = A + \frac{B}{(Z - C)} \tag{5}$$

where C is sometimes erroneously interpretted as a screening constant which takes into account the effect of higher terms. The nuclear charge Z now simply becomes a tuning parameter of the isoelectronic sequence. Equation (5) has been originally suggested by Edlen [17]. This form due to enhanced linearity permits extrapolative and interpolative predictions for missing data with high accuracy. It also reveals questionable data.

For the determination of the parameters A, B and C we minimized the sum of squares of residues given by

$$\sum_i \delta_i^2 = \sum_i (A + B/(Z_i - C) - Z_i^2 S_i)^2 \tag{6}$$

The data for S_i were taken from the CI calculations [18] for ions with Z in the range $Z = 8 - 25$. The minimization of $\sum_i \delta_i^2$ yielded the following equations for the coefficients A, B and C

$$\frac{\left(-\frac{1}{N} \sum_i Z_i^2 S_i \right) \left(\sum_i \frac{1}{Z_i - C} \right) + \sum_i \frac{Z_i^2 S_i}{(Z_i - C)}}{\left[-\frac{1}{N} \left(\sum_i \frac{1}{Z_i - C} \right)^2 \right] + \sum_i \frac{1}{(Z_i - C)^2}} =$$

$$\frac{\left(-\frac{1}{N} \sum_i Z_i^2 S_i \right) \left(\sum_i \frac{1}{(Z_i - C)^2} \right) + \sum_i \frac{Z_i^2 S_i}{(Z_i - C)^2}}{\left[-\frac{1}{N} \sum_i \frac{1}{(Z_i - C)^2} \right] \left(\sum_i \frac{1}{Z_i - C} \right) + \sum_i \frac{1}{(Z_i - C)^3}}. \tag{7}$$

$$B = \frac{\sum_i \frac{Z_i^2 S_i}{(Z_i - C)^2} - \left(\frac{1}{N} \right) \left(\sum_i \frac{1}{(Z_i - C)^2} \right) \left(\sum_i Z_i^2 S_i \right)}{\sum_i \frac{1}{(Z_i - C)^3} \left[\frac{1}{N} \sum_i \frac{1}{(Z_i - C)^2} \right] \left(\sum_i \frac{1}{Z_i - C} \right)} \tag{8}$$

$$A = -\frac{B}{N} \sum_i \frac{1}{Z_i - C} + \frac{1}{N} \sum_i Z_i^2 S_i \tag{9}$$

where N is the number of data points in the iso-electronic sequence. The parameter C was obtained by iteration using the bisection method [19]. The coefficients B and A were then determined from (8) and (9) respectively. We obtained excellent fits for

all the transitions. The resulting χ^2 is of the order of 10^{-4} or smaller for all the transitions studied here.

It is clear from (5) that the parameter A is the value of $Z^2 S$ when $Z \to \infty$. In this limit, all the Hartree Fock orbitals assume their hydrogenic character as the quantum defect vanishes. It is of interest to calculate the value of A ab-initio and compare with the corresponding fitted values. The ground state configuration of O-like ions is $1s^2 2s^2 2p^4$ which gives rise to three even parity multiplet states ^3P, ^1D and ^1S, the other states are forbidden due to Pauli exclusion principle. When two '2s' electrons are promoted to two '2p' electronic state we get the configuration $1s^2 2p^6$ which necessarily gives a ^1S state. This near degenerate, configuration mixes strongly with the HF state $1s^2 2s^2 2p^4\,^1S$ indicating a strong correlation. This effect increases with nuclear charge and is dependent upon the state. It influences the electronic charge distribution which affects the atomic properties. For ^1S state, we express the wavefunction $\phi(LS\pi)$ in the LS coupled representation as a linear combination of the HF wavefunction ϕ_1 and the near degenerate wavefunction ϕ_2

$$\phi(LS\pi) = c_1 \phi_1(1s^2 2s^2 2p^4\,^1S) + c_2 \phi_2(1s^2 2p^6\,^1S) \tag{10}$$

where L, S and π are the total orbital, total spin angular momentum and the parity of the state. For the states ^3P and ^1D there are no near degenerate states, so ϕ is a HF state for these cases. The configurational wavefunctions ϕ_i are constructed from the one-electron function

$$u_{nlm_l}(\mathbf{r}, m_s) = \frac{1}{r} P_{nl}(r)\, Y_{lm_l}(\theta, \phi) \chi(m_s) \tag{11}$$

where $\chi(m_s)$ is the spin wavefunction and $Y_{lm_l}(\theta, \phi)$ is a spherical harmonic. The ϕ_i satisfy the orthonormality condition

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \tag{12}$$

The expansion coefficients c_i can be calculated by solving a pair of simultaneous equations given by

$$\sum_{i=1}^{2} c_i (H_{ji} - E\delta_{ji}) = 0, \quad j = 1, 2 \tag{13}$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle . \tag{14}$$

where H is the Hamiltonian of the ion. The eigenvalues E_λ are calculated by diagonalizing the Hamiltonian matrix and we finally obtain

$$\frac{c_1}{c_2} = \frac{-2H_{12}}{[(H_{11} - H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}H_{21}}]}. \tag{15}$$

It is now trivial to calculate c_1 and c_2 by employing the normalization condition $c_1^2 + c_2^2 = 1$. All we need is the values of the Hamiltonian matrix elements.

Using Slater's approach [20], we obtain the following expressions for the Hamiltonian matrix elements of the two ^1S states of the oxygen sequence. The matrix element H_{11} corresponds to the HF state $1s^2 2s^2 2p^4\,^1S$ whereas H_{22} corresponds

to the near-degenerate $1s^2 2p^6 {}^1S$ state

$$H_{11} = 2I(1s, 1s) + 2I(2s, 2s) + 4I(2p, 2p) + F^0(1s, 1s)$$

$$+ 4F^0(1s, 2s) - 2G^0(1s, 2s) + F^0(2s, 2s) + 8F^0(1s, 2p)$$

$$- 4G^1(1s, 2p)/3 + 8F^0(2s, 2p) - 4G^1(2s, 2p)/3 + 6F^0(2p, 2p),$$

$$(16)$$

$$H_{22} = 2I(1s, 1s) + 6I(2p, 2p) + F^0(1s, 1s) + 12F^0(1s, 2p)$$

$$- 2G^1(1s, 2p) + 15F^0(2p, 2p) - 6F^2(2p, 2p)/5,$$

$$(17)$$

$$H_{21} = H_{12} = G^1(2s, 2p)/\sqrt{3}.$$

$$(18)$$

The integrals $I(nl, nl)$ are the one-electron integrals, $F^k(nl, n'l')$ and $G^k(nl, n'l')$ are the two-electron Slater's integrals [20]. For hydrogenic orbitals, these integrals can be easily evaluated. These energy integrals (for $Z = 1$) in atomic units are $I(1s, 1s) = -1/2, I(2s, 2s) = I(2p, 2p) = -1/8$; $F^0(1s, 1s) = 5/8$, $F^0(1s, 2s) = 17/81$, $F^0(2s, 2s) = 77/512$, $F^0(1s, 2p) = 59/243$, $F^0(2s, 2p) = 83/512$, $F^0(2p, 2p) = 93/512$, $F^2(2p, 2p) = 45/512$, $G^0(1s, 2s) = 16/729$, $G^1(1s, 2p) = 112/2187$, $G^1(2s, 2p) = 45/512$. It is now trivial to calculate c_1 and c_2 from (15). We obtain $c_1 = 0.979327757$, $c_2 = -0.202279866$. The zeroth order multiplet strength can now be written as

$$S(LS\pi \rightarrow L'S'\pi') = |\langle \phi(LS\pi)|\mathbf{r}|\phi_3(L'S'\pi')\rangle|^{2^*}$$

$$(19)$$

where $\phi(LS\pi)$ is the ground state wavefunction, $\phi_3(L'S'\pi')$ is the excited state wavefunction belonging to the configuration $1s^2 2s 2p^5$. For ${}^3P$ and ${}^1D$ multiplets of the ground state ϕ is simply a single configuration wavefunction whereas for ${}^1S$ state it is an admixture of HF $1s^2 2p^4 {}^1S$ state and the near degenerate state $1s^2 2p^6 {}^1S$. The $\mathbf{r}$ summed over all electrons is the position vector operator of tensorial rank one. We can now write

$$S_0(LS \rightarrow L'S') = c_1^2 S_1 + c_2^2 S_2 + 2c_1 c_2 \sqrt{S_1 S_2}$$

$$(20)$$

where

$$S_1 = |\langle \phi_1(1s^2 2s^2 2p^4; LS\pi)|\mathbf{r}|\phi_3(1s^2 2s 2p^5, L'S'\pi')\rangle|^2$$

$$(21)$$

$$S_2 = |\langle \phi_2(1s^2 2p^6; {}^1S)|\mathbf{r}|\phi_3(1s^2 2s 2p^5; L'S'\pi')\rangle|^2.$$

$$(22)$$

If we represent each ϕ_i as simply an antisymmetrized product of hydrogenic orbitals then we can express the LS line strength matrix in terms of Racah's reduced matrix elements [21]. Racah's algebra [21] can be used to decouple the wavefunctions until only the dipole integral between single electron orbitals remain. This decoupling allows us to write

$$S_i = \Lambda \sigma^2, \quad i = 1, 2$$

$$(23)$$

where Λ is the angular factor which depends upon the coupling of angular momenta of the electrons and σ is the hydrogenic transition integral

$$\sigma(2s \rightarrow 2p) = \int_0^\infty P_{2s}(r) P_{2p}(r) r \, dr = \sqrt{27}/Z.$$

$$(24)$$

The angular factors Λ for each transition can be worked out by using the standard

Racah algebra. This requires evaluation of Racah's coefficients and the fractional parentage coefficients. These angular factors are

$$\Lambda\,(2s^2 2p^4\,{}^3P \rightarrow 2s2p^5\,{}^3P^0) = 6,$$

$$\Lambda\,(2s^2 2p^4\,{}^1D \rightarrow 2s2p^5\,{}^1P^0) = 10/3,$$

$$\Lambda\,(2s^2 2p^4\,{}^1S \rightarrow 2s2p^5\,{}^1P^0) = 2/3,$$

and

$$\Lambda\,(2p^6\,{}^1S \rightarrow 2s2p^5\,{}^1P^0) = 2.$$

We now finally obtain the zeroth order multiplet strengths for various transitions in the hydrogenic limit

$$Z^2 S_0(2s^2 2p^4\,{}^3P \rightarrow 2s2p^5\,{}^3P^0) = 162,$$

$$Z^2 S_0(2s^2 2p^4\,{}^1D \rightarrow 2s2p^5\,{}^1P^0) = 90,$$

$$Z^2 S_0(2s^2 2p^4\,{}^1S \rightarrow 2s2p^5\,{}^1P^0) = 18,$$

$$Z^2 S_0(2p^6\,{}^1S \rightarrow 2s2p^5\,{}^1P^0) = 54,$$

$$Z^2 S_0(2s^2 2p^4 + 2p^6;\,{}^1S \rightarrow 2s2p^5\,{}^1P^0) = 7.12.$$

It is worth noting that for the transition ${}^1S \rightarrow {}^1P^0$, the effect of near-degeneracy is to reduce the hydrogenic value of $Z^2 S_0 = A$ from 18 to 7.12.

Results and discussion

We now compare the ab-initio values of A calculated above with the fitted values of A from the minimization procedure. The data used for S_i were taken from the configurational interaction calculation [18]. These elaborate calculations included internal, semi-internal and all external type correlation effects [22]. In the internal type corelation two 2s orbitals are promoted to two 2p orbitals within the Hartree–Fock sea which consists of 1s, 2s and 2p orbitals. In the semi-internal type correlation, one electron jumps outside the HF sea with $n \geqslant 3$ whereas the other electron shifts within the sea. In the all-external type correlation two electrons from the sea are shifted outside the sea with $n \geqslant 3$. Parity is conserved in all the shifts. All those correlating configurations were included which could be built from the orbitals $3l$. The internal type correlation is present only in the ${}^1S$ state of the ground state configuration, in the other transitions this is absent due to the property of parity conservation. These elaborate CI calculations for 17 ions in the O-sequence produced excellent values of the energies of all the atomic states involved for all the ions. It also yielded accurate values of the transition probabilities of various dipole allowed transitions within $n = 2$ complex. The agreement with the experimental values was excellent.

The values of the parameters A, B and C obtained for various transitions through the minimization procedure are listed in table 1 for full CI and HF calculations. The HF data were taken from the work of Gupta and Baluja [23]. We obtained excellent fits for all the transitions. This is reflected in the very small value of χ^2. We notice from table 1 that there is an excellent agreement with fitted values of A with the single configuration ab-initio values of $Z^2 S_0$ for the transitions ${}^3P \rightarrow {}^3P^0$ and ${}^1D \rightarrow {}^1P^0$. However for the transition ${}^1S \rightarrow {}^1P^0$, the fitted value of $A = 8.2856$ is less than half

of its single configuration value of $A_{HF} = 18$. This poor agreement is due to the absence of near degenerate effect in the single configuration scheme for ^1S state. But when this effect is included the ab-initio value $A = 7·12$ is in fair agreement with the fitted value. We also note that the single configuration fitted value of $17·46$ agrees closely with ab-initio value $18·0$. It is very important that where near degeneracy effects are present, they must be included in the zeroth-order calculation of line strengths for the correct interpretation of the hydrogenic limit. This limit checks the accuracy of the fitted values of A.

Table 1. Values of A, B, C, χ^2 and $Z^2 S_0$ for various transitions in the O-sequence.

Transition	A	B	C	χ^2	$Z^2 S_0$
$2s^2 2p^4\,^3P \to$ $\to 2s2p^5\,^3P^0$	161·6813 (157·06)	764·3139 (1292·98)	3.1936 (4·3953)	8·09(−6)* (8·09(−6))	162·0 (162·0)
$2s^2 2p^4\,^1D \to$ $\to 2s2p^5\,^1P^0$	87·3021 (87·27)	532·5121 (718·16)	3·4479 (4·3953)	4·40(−4) (4·79(−5))	90·0 (90·0)
$2s^2 2p^4\,^1S \to$ $\to 2s2p^5\,^1P^0$	8·2856 (17·46)	114·1842 (143·638)	−6·2861 (4·3953)	1·28(−4) (9·19(−6))	7·12 (18)

The values within the braces are those of single configuration (HF) case.
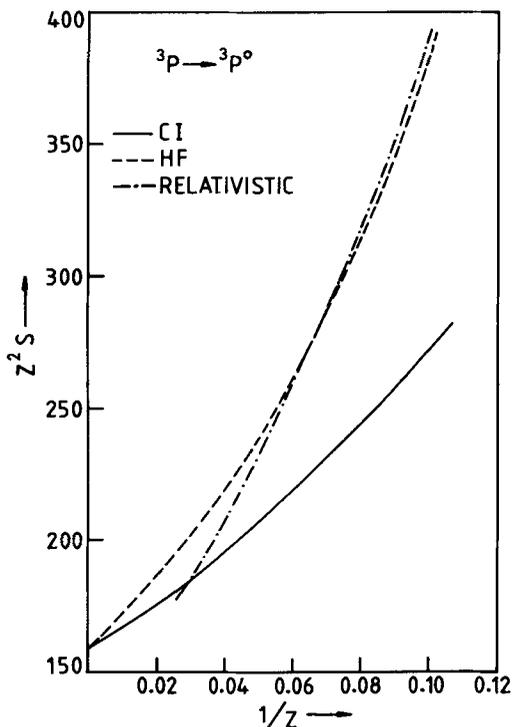*$a(-b)$ implies $a\,10^{-b}$

Figure 1. Variation of $Z^2 S$ with $1/Z$ for the transition $2s^2 2p^4\,^3P \to 2s2p^5\,^3P^0$ for ions in the oxygen isoelectronic sequence. —— Full CI (present results); ——— HF (present results); —·— Cheng *et al* (24). Relativistic.
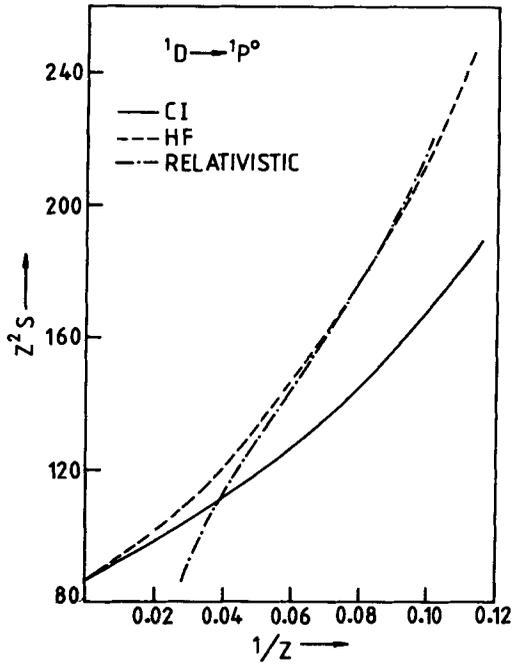
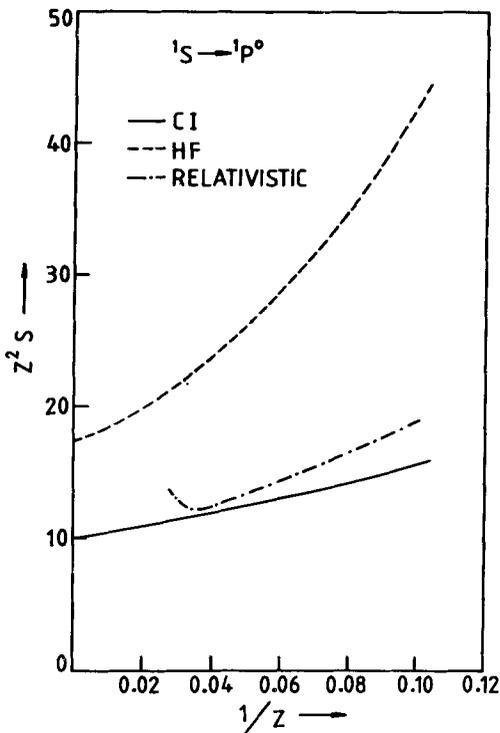**Figure 2.** Same as in figure 1 but for the transition $2s^2 2p^4 \, {}^1D \rightarrow 2s2p^5 \, {}^1P^o$.

Figure 3. Same as in figure 1 but for the transition $2s^2 2p^4 \, {}^1S \rightarrow 2s2p^5 \, {}^1P^o$.

In figure 1, we have displayed $Z^2 S$ values against $1/Z$ for the transition $^3P \rightarrow {}^3P^0$. The values of S correspond to the full CI and HF calculations. We have also shown the results obtained by Cheng et al [24] using the Dirac formalism which employed a restricted $j - j$ basis set including only the configurations within the $n = 2$ complex. It is well known that $j - j$ coupling scheme is inadequate near the neutral end where the LS coupling scheme prevails. Since our CI calculations included more correlation, our values lie lower than theirs for $Z \leqslant 25$ and our HF values. As Z increases the effect of correlation is diluted and both the curves tend to come nearer. However, since Cheng et al calculations included relativistic effects, it does not converge to the HF value of 162. Our non-relativistic curves for CI and HF cases converge extremely close to this value in the limit $Z \rightarrow \infty$. The relativistic effects increase with increasing Z. If we discard the higher $Z(> 20)$ values of Cheng et al, we notice that their curve apparently converges to the non-relativistic limit. This is a good check on their calculation and our CI calculation.

A similar trend is noticed in figure 2 for the transition $^1D \rightarrow {}^1P^0$. Figure 3 displays the results for the $^1S \rightarrow {}^1P^0$ transition. Since our HF results do not include near degenerate correlation, it lies above the other two curves. The results of Cheng et al [24] included near degeneracy effect within the relativistic formalism, it lies between HF and our full CI curve which included all types of correlation. The HF curve converges to the limiting value 17·46 which is extremely close to the ab-initio value of 18. However, this is not the correct limit when correlations are included.. Once again, if we extend the results of Cheng et al for values $Z \leqslant 20$, their curve and our full CI curves converge nearly to the correct limiting value.

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