Correlation Effects in Complex Spectra. II. Transition Probabilities for the Magnesium Isoelectronic Sequence*

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(Received 8 June 1967)

Absolute multiplet strengths have been calculated for electric dipole transitions involving the ground state and/or several lower-lying excited-state configurations of Mg I, Al II, Si III, P IV and Ca IX. Configuration mixing is taken into account by using linear combinations of Hartree–Fock–Slater (HFS) determinantal wavefunctions. Dipole length and dipole velocity expressions for the transition probability are evaluated, and in most cases these alternative formulations agree to within 25% of each other. Three modifications of the "universal" exchange potential used in the HFS self-consistent field method are investigated, and the differences in the calculated transition probabilities are found to be quite small, with perhaps a slight preference for the variational adjustment proposed by Lindgren. Calculated absolute multiplet strengths are compared with the available experimental measurements, and with other calculations.

INTRODUCTION

In recent years much work has been devoted to the calculation of atomic transition probabilities. Interest has been stimulated not only by the practical need to estimate oscillator strengths in such fields as astrophysics, plasma physics, and space research, but also by the fact that transition probabilities provide a quite sensitive measure of the reliability of approximate solutions to the many-electron problem of atomic structure. Most calculations[1] in the past are based on the use of the central-field approximation in which it is assumed that each electron moves *independently* in the field of the nucleus and in a central field made up of the spherically averaged potential fields of each of the other electrons. The solutions to the Schrödinger equation are then separable and are given by a set of one-electron wavefunctions $u_i(nlms)$, customarily called spin orbitals. The central-field Hamiltonian gives rise to a series of configurational energies E_k, each associated with a corresponding set ψ_k of spin orbitals. The most elaborate and well-known procedure of this type is the Hartree–Fock self-consistent field method[2] in which ψ_k is built up from determinantal wavefunctions of the spin orbitals so that the antisymmetry requirement is automatically satisfied. However, transition probabilities calculated by even the most accurate independent particle models appear to be unreliable and inconsistant in many instances,[1,3] especially for transitions originating from or terminating on energy levels which are strongly perturbed.

In this paper we report the calculation of atomic transition probabilities in which we take into account through the method of configuration interaction, the dynamical correlation in the motion of the electrons arising from their mutual Coulomb repulsion. In an earlier paper,[4] hereafter referred to as I, we investigated the effects of configuration interaction on the spacings of the energy levels, and the form of the wavefunctions for the ^1D and ^3D multiplets of the magnesium isoelectronic sequence. In I we used a variant to the Hartree–Fock procedure to generate a suitable basis set for the expansion of $\Psi-$, namely, the Hartree–Fock–Slater (HFS) procedure[5,6] in which the central-field potentials for different orbitals are replaced by a universal central-field potential found by treating the charge density of the atom as a free-electron gas. This paper is an extension of I to the $^1P^0$, $^3P^0$, ^1S, and ^3S multiplets for which we have also calculated over sixty absolute multiplet strengths for the ^1S–$^1P^0$, ^3S–$^3P^0$, ^1D–$^1P^0$, and ^3D–$^3P^0$ transitions occurring in Mg I, Al II, Si III, P IV, and Ca IX. We will show in several instances that the inclusion of correlation effects strikingly alters the predicted atomic transition probabilities.

Following a brief review of theory and method, we tabulate the calculated absolute multiplet strengths and compare them to measured oscillator strengths

[1] B. M. Glennon and W. L. Wiese, "Bibliography on Atomic Transition Probabilities," Natl. Bur Std. (U.S.), Misc. Publ. **278**, 1 (1966); W. L. Wiese, M. W. Smith and B. M. Glennon, "Atomic Transition Probabilities," NSRDS-NBS 4 (U.S. Government Printing Office, Washington, D.C., 1966), Vol. 1.

[2] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[3] R. H. Garstang, Intern. Astron. Union **26**, 57 (1966).

[4] R. N. Zare, J. Chem. Phys. **45**, 1966 (1966). Errata: In the second form of Eq. (17) replace $-\nabla^2$ by $-d^2/dr^2+l(l+1)/r^2$; in Eq. (18) replace

$$\begin{pmatrix} l_a & k & l_c \\ 0 & 0 & 0 \end{pmatrix}$$

by

$$-\begin{pmatrix} l_a & k & l_k \\ 0 & 0 & 0 \end{pmatrix}^2;$$

in Table I, entry B3, replace $A(n_cl_c, n_dl_d)$ by $A(n_bl_b, n_dl_d)$ and in entries B4 and B5 replace $E(n_al_a, n_bl_b; n_cl_c, n_dl_d)$ by $E(n_al_a, n_bl_b; n_dl_d, n_cl_c)$. Table I entries B2 and B3 are written for non-equivalent electrons; for equivalent electrons an additional factor of $\sqrt{2}$ must multiply I and A. A am indebted to Mr. Donald R. Beck, Department of Physics, LeHigh University, Bethlehem, Pa., for pointing out these corrections to me.

[5] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963).

that exist and to other calculations. Recently, Weiss[7] has completed a computation of some of the same transition probabilities, using a seemingly quite different procedure for including the effects of correlation. The close agreement of our results in many cases with his more extensive and more accurate calculations is quite heartening and encourages us to believe that the means are at hand for determining oscillator strengths to an accuracy of perhaps 20 or 30% for most strong transitions connecting low-lying levels of light atoms.

METHOD AND RESULTS

Russell–Saunders Multiplet Strengths

The basic theory of electric dipole radiation in atomic systems is given in Condon and Shortley,[8] and we follow their terminology closely. Using the assumption of Russell–Saunders coupling in a central-field potential, the energy levels of an atom are characterized by the set of quantum numbers αSLM_SM_L (or alternatively by $\alpha SLJM$, which is a linear combination of αSLM_SM_L with various M_SM_L). Here α denotes the electronic configuration, S the vectorial resultant of all the electron spins, L the vectorial resultant of all the electron orbital angular momenta, and M_S, M_L are the projections of S, L, respectively, on the axis of quantization. For an electric dipole transition connecting the multiplets αSL and $\alpha'SL'$, Condon and Shortley introduced the quantity $\mathcal{S}(\alpha SL; \alpha'SL')$, called the *absolute multiplet strength*. It is defined in terms of the electric dipole moment operator $\mathbf{P}$ by

$$\mathcal{S}(\alpha SL; \alpha'SL')$$
$$= \sum_{M_S,M_L} \sum_{M_{S'},M_{L'}} | (\alpha SLM_SM_L | \mathbf{P} | \alpha'SL'M_{S'}M_{L'}) |^2,$$
$$(1)$$

where from Eq. (1) the absolute multiplet strength is seen to be symmetrical in the indices for the upper and lower energy levels and to be independent of the wavelength of the emitted or absorbed radiation. The transition f value and Einstein A coefficient is related to $\mathcal{S}$ by

$$f(\alpha SL \rightarrow \alpha'SL') = (304/g\lambda) \mathcal{S}(\alpha SL; \alpha'SL'), \quad (2)$$

and

$$A(\alpha SL \rightarrow \alpha'SL') = (2.02 \times 10^{18}/g'\lambda^3) \mathcal{S}(\alpha SL; \alpha'SL'),$$
$$(3)$$

where in Eqs. (2) and (3) we measure wavelengths λ in Angstrom units (Å), and the absolute multiplet strength $\mathcal{S}$ in atomic units $(e^2a_0^2)$; g is the statistical degeneracy of the SL multiplet:

$$g = (2S+1)(2L+1). \quad (4)$$

The dipole moment operator is a one-electron tensor operator of the first rank which does not act on the spin coordinates. The following selection rules result: $\Delta S=0$, $\Delta L=0$, $\pm 1(0 \leftrightarrow 0)$, and electric dipole transitions are allowed only between those configurations of opposite parity which differ from each other by one electron. From matrix mechanics[9] we can readily obtain several different expressions for $\mathbf{P}$, of which the dipole length and dipole velocity forms are the most well known:

$$\mathbf{P}^{(L)} = \sum_i e\mathbf{r}_i, \quad (5)$$

and

$$\mathbf{P}^{(V)} = 2(E_I - E_F)^{-1} \sum_i e\boldsymbol{\nabla}_i. \quad (6)$$

The sum in Eqs. (5) and (6) is over all the electrons of the atomic system. In Eq. (5) $\mathbf{r}_i$ is the displacement vector of the ith electron measured from the center of the nucleus; in Eq. (6) $\boldsymbol{\nabla}_i$ is the gradient operator of the ith electron, and E_I and E_F are the initial and final energies, measured in Rydbergs, for the transition.

If exact electronic wavefunctions $\psi_{\alpha SL}$ and $\psi_{\alpha'SL'}$ were available for the multiplets αSL and $\alpha'SL'$, the absolute multiplet strength calculated by Eq. (1), using either expression for the dipole moment operator, would agree identically. For approximate wavefunctions unequal values of $\mathcal{S}$ result in general because the dipole length and dipole velocity operators $\mathbf{P}^{(L)}$ and $\mathbf{P}^{(V)}$ emphasize different regions of the electron coordinate space. From a theoretical viewpoint this presents us with some embarrassment, for if the calculated values of $\langle \mathbf{P}^{(L)} \rangle_{\alpha SL;\alpha'SL'}$ and $\langle \mathbf{P}^{(V)} \rangle_{\alpha SL;\alpha'SL'}$ disagree by the smallest amount, it is then possible to construct an expression for the dipole operator which still gives the correct result when exact wavefunctions are used, but which gives any numerical value of the absolute multiplet strength we desire, e.g.,

$$\mathbf{P} = n\mathbf{P}^{(L)} + m\mathbf{P}^{(V)}, \quad (7)$$

where $| n+m | = 1$. Thus if the calculated dipole length and dipole velocity expressions differ, we have no theoretical grounds for believing that the "true" absolute multiplet strength lies in between $\mathcal{S}^{(L)}$ and $\mathcal{S}^{(V)}$ or even close by. Nevertheless, if our electronic wavefunctions have been constructed in some nonpathological manner, the close agreement between the alternative dipole length and dipole velocity formulations provides us with a convenient means (although imperfect) for judging the accuracy and reliability of the approximate wavefunctions.

Explicit expressions for the absolute multiplet strength are derived in Condon and Shortley,[8] and tables of relative multiplet strengths compiled by Goldberg,[10] and Menzel and Goldberg[11] may also be found

[7] A. W. Weiss, J. Chem. Phys. **47**, 3573 (1967), following article.
[8] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One-and Two-Electron Atoms* (Academic Press Inc., New York, 1957); S. Chandrasekhar, Astrophys. J. **102**, 223 (1945).
[10] L. Goldberg, Astrophys. J. **82**, 1 (1935).
[11] D. H. Menzel and L. Goldberg, Astrophys. J. **84**, 1 (1936).

in a book by Allen.[12] More recently Rohrlich[13] has extended these tables and reformulated the calculation of absolute multiplet strengths by using the Racah algebra for angular momentum coupling. In this more compact notation the absolute multiplet strength for a transition between two configurations having the two electrons $nln'l'$ and $nln''l''$ outside a core of closed shells reduces to the simple form

$$\mathcal{S}(\alpha SL; \alpha' SL')$$
$$= |A(nln'l'SL; nln''l''SL')R(n'l'; n''l'')|^2. \quad (8)$$

Here the angular factor is given by

$$A(nln'l'L; nln''l''L') = (-1)^{l+l_>}$$
$$\times [l_>(2S+1)(2L+1)(2L'+1)]^{1/2}
\begin{Bmatrix} l' & L & l \\ L' & l'' & 1 \end{Bmatrix}, \quad (9)$$

where $l_>$ is the greater of (l', l'') and the expression enclosed in brackets is a 6-j symbol.[14] Equation (9) must be modified for transitions of the type $l^2 \rightarrow ll'$ by replacing l' by l, l'' by l' and multiplying the resultant expression by $\sqrt{2}$ to take into account the normalization of the wavefunction for equivalent electrons. The radial factor $R(n'l'; n''l'')$ in Eq. (8) is the radial matrix element of the dipole operator, and its form depends on the representation chosen for $\mathbf{P}$:

$$R^{(L)}(n'l'; n''l'') = \int_0^\infty P_{n'l'}(r) r P_{n''l''}(r) dr \quad (10)$$

is the dipole length expression; and

$$R^{(V)}(n'l'; n''l'') = \frac{2}{E_{\alpha SL} - E_{\alpha' SL'}}$$
$$\times \int_0^\infty P_{n'l'}(r) \left[\frac{d}{dr} + \frac{a}{r}\right] P_{n''l''}(r) dr \quad (11)$$

is the corresponding dipole velocity expression where

$$a = l'' + 1, \quad \text{if } l' = l'' - 1, \quad (12a)$$
and
$$a = -l'', \quad \text{if } l' = l'' + 1. \quad (12b)$$

In Eqs. (10) and (11) the $P_{nl}(r)$ are the radial parts of the nl spin orbitals and have the normalization and orthogonality properties

$$\int_0^\infty P_{nl}(r) P_{n'l'}(r) dr = \delta_{nl,n'l'}. \quad (13)$$

So far we have restricted our discussion to the assumption of a central-field potential. However, once independent-particle wavefunctions have been determined for some central-field model of the atom, we can improve upon our calculation of atomic properties by the so-called method of configuration interaction.[15] In this method we treat the mutual Coulomb repulsion among the electrons as a perturbation, calculate the nondiagonal matrix elements connecting configurations of the same parity, and diagonalize the atomic Hamiltonian $\mathcal{3C}$ within more than one configuration. Inclusion of these noncentral potential terms in $\mathcal{3C}$ results in displacing the energies of multiplets from the positions in which they would be found in the absence of such interaction. It also causes the wavefunction of each multiplet to become a linear combination of wavefunctions associated with the interacting configurations:

$$\Psi_{\alpha SL} = \sum_\beta c_{\alpha\beta} \psi_{\beta SL}. \quad (14)$$

Equation (14) can be viewed equally as well as arising from the expansion of the total wavefunction Ψ for the system in the configuration wavefunctions ψ as a basis set. The coefficients c are found by solving the set of simultaneous equations

$$\sum_\beta c_{\alpha\beta}(\mathcal{3C}_{\beta'\beta} - E\delta_{\beta'\beta}) = 0 \quad (15)$$

which result[16] when the expression for Ψ in (14) is substituted into the Schrödinger equation $\mathcal{3C}\Psi = E\Psi$. Explicit expressions for the electrostatic matrix elements of the atomic Hamiltonian operator between determinantal wavefunctions have been previously presented in I for atoms having two valence electrons outside a core of closed shells.

By substituting configuration interaction wavefunctions given by Eq. (14) into Eq. (1), the absolute multiplet strength may be rewritten in the generalized form[17]

$$\mathcal{S}(\alpha SL; \alpha' SL') = |\sum_\beta \sum_{\beta'} (-1)^{p_{\beta\beta'}} c_{\alpha\beta} c_{\alpha'\beta'}$$
$$\times A_{\beta\beta'}(nln'l'SL; nln''l''SL') R_{\beta\beta'}(n'l'; n''l'')|^2. \quad (16)$$

Each term in the summation describes a transition between a pair of configurations in which an electron "jumps" from the quantum state $n'l'$ in the configuration βSL to the quantum state $n''l''$ in the configuration $\beta' SL'$. The term $p_{\beta\beta'}$ is the number of permutations required to reorder the spin orbitals in the configur-

[12] C. W. Allen, *Astrophysical Quantities* (Athlone Press, London, 1955).

[13] F. Rohrlich, Astrophys. J. **129**, 441, 449 (1959).

[14] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (Technology Press, Cambridge, Mass., 1959).

[15] J. C. Slater, "Accurate Methods of Atomic Calculation," in *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. II, Chap. 18.

[16] Equation (15) may also be shown to be equivalent to variationally determining the constants $c_{\alpha\beta}$ in (14) so that the energy of the atomic system is made an extremum. See J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., New York, 1960), Vol. I, Appendix 9.

[17] An expression for the calculation of absolute multiplet strengths from configuration interaction wavefunctions was first given by (a) C. Froese, Astrophys. J. **140**, 361 (1964). A misprint in Froese's equation was corrected by (b) R. J. S. Crossley and A. Dalgarno, Proc. Roy. Soc. (London) **286A**, 510 (1965). Our Eq. (16) differs from Crossley and Dalgarno's in that it contains the phase factor $(-1)^{p_{\beta'\beta}}$ which is required when wavefunctions are used which do not belong to configurations built up from spin orbitals of the same principal quantum number.

ations β and β' so they stand in the same ordering.[18] Thus, the inclusion of correlation effects in the form of the wavefunction introduces interference terms which may either reinforce or cancel each other in the calculation of the absolute multiplet strength. Moreover, the noncentral character of the electron repulsion terms in the atomic Hamiltonian allows transitions, which ostensibly appear to occur only through the simultaneous jump of more than one electron, to take place between the multiplets αSL and $\alpha' SL'$. As first pointed out by Condon,[19] these transitions are made possible by the fact that the configuration names are no more than an approximation. With the help of Eq. (16) absolute multiplet strengths are calculated for the magnesium isoelectronic sequence. Their accuracy will depend on how rapidly the configuration interaction wavefunctions we use converge to the exact wavefunctions for the initial and final transition states.

Hartree–Fock–Slater Configuration Interaction Wavefunctions

In principle we can determine Ψ, and hence $\mathfrak{S}$, as accurately as we wish, provided the basis set ψ_β is a complete one. However, if the method of configuration interaction is to be a practicable procedure for including correlation effects in the form of the atomic wavefunction, we must be able to approximate Ψ rapidly by a truncated series in the functions ψ_β so that Eq. (15) reduces to the solution of a finite secular equation of modest size:

$$| \mathfrak{K}_{\beta'\beta} - E\delta_{\beta'\beta} | = 0. \quad (17)$$

Thus, it is more important to choose a set of independent-particle wavefunctions ψ_β for which the expansion of Ψ in that set is rapidly convergent than a set for which the first term in the expansion gives a better approximation to the total energy.

Consequently as in I, we use the Herman and Skillman version[6] of the HFS procedure.[5] The total wavefunction is then expanded in determinantal wavefunctions built up from the HFS spin-orbitals ϕ_i which are the "occupied" and "unoccupied" bound state solutions to the one-electron wave equation

$$[\nabla_i^2 + V(r)]\phi_i = \epsilon_i\phi_i. \quad (18)$$

Here

$$V(r) = V_0(r) + V_{\text{exch}}(r) \quad (19)$$

for $r < r_0$, and

$$V(r) = -2(Z - N + 1)/r \quad (20)$$

for $r \geq r_0$. In Eq. (18) $V(r)$ is a "universal" central-field potential in which *all* the electrons move, and $V_0(r)$

and $V_{\text{exch}}(r)$ are given in terms of the radial wavefunctions $P_{nl}(r)$ of the HFS spin orbitals by

$$V_0(r) = \frac{-2Z}{r} + \frac{2}{r}\int_0^r \sum_{nl}[P_{nl}(t)]^2 dt$$

$$+ 2\int_0^\infty \sum_{nl} \frac{[P_{nl}(t)]^2}{t} dt, \quad (21)$$

and

$$V_{\text{exch}}(r) = -\left\{\frac{81}{4\pi^2 r^2}\left[\sum_{nl} P_{nl}(r)\right]^2\right\}^{1/3}. \quad (22)$$

A Coulomb tail is joined to the potential at the critical distance r_0 for which Eq. (19) equals Eq. (20), so that $V(r)$ is forced to have the correct asymptotic behavior at large r.

In I we limited the extent of the basis set by and large to those configurations $nln'l'$ whose principal quantum numbers are $n = 3$ and $n' = 3$ or 4. The rationale for this choice was the hope that such orbitals would have a compact spatial extent over the region in which the electrons interact, and thus accelerate convergence. We follow the same procedure here by restricting the basis set to include (a) the ten configurations $3s3d$, $3s4d$, $3s5d$, $3s6d$, $3p^2$, $3p4p$, $3d^2$, $3d4d$, $3p4f$, and $3d4s$ which are solutions to the $V_{3s3d}(r)$ potential for the ^1D and ^3D multiplets; (b) the nine configurations $3s3p$, $3s4p$, $3s5p$, $3s6p$, $3p3d$, $3p4s$, $3p4d$, $3d4p$, and $3d4f$ which satisfy the $V_{3s3p}(r)$ potential for the $^1P^0$ and $^3P^0$ multiplets; (c) and the eight configurations $3s^2$, $3s4s$, $3s5s$, $3s6s$, $3p^2$, $3p4p$, $3d^2$, and $3d4d$ which satisfy the $V_{3s2}(r)$ potential for the ^1S and ^3S multiplets.

We have calculated in I the energy spacings and wavefunctions of the ^1D and ^3D multiplets of the magnesium isoelectronic sequence, using the configuration basis set constructed from spin orbitals which are self-consistent solutions to the central-field potential defined by Eqs. (19) and (20). Since then, two basic modifications to the HFS scheme have been proposed. These involve better approximations of the universal exchange potential given in Eq. (22). By introducing statistical considerations at an earlier stage in the derivation of the HFS variational equations, Kohn and Sham,[20] and Cowan *et al.*[21] have shown that the Slater exchange potential is then replaced by an exchange potential of two-thirds the magnitude

$$V'_{\text{exch}}(r) = \tfrac{2}{3} V_{\text{exch}}(r). \quad (23)$$

Numerical comparisons[21,22] of charge density integrals and total energies calculated with this modification and with the original HFS procedure appear to indicate that the use of Eq. (23) gives improved results.

[18] Reference 8, pp. 168–169. See Table I of I for explicit values of $(-1)^p\beta\beta'$ for atoms having two electrons outside a core of closed shells.
[19] E. U. Condon, Phys. Rev. **36**, 1121 (1930).

[20] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[21] R. D. Cowan, A. C. Larson, D. Liberman, J. B. Mann, and J. Waber, Phys. Rev. **144**, 5 (1966).
[22] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

Quite recently Lindgren[23] has investigated the use of a universal exchange potential of the general form

$$V''_{\text{exch}}(r) = -C(81/4\pi^2)^{1/3}r^{(n-3)/3}\left\{\sum_{nl}[P_{nl}(r)]^2\right\}^{m/3}. \quad (24)$$

The adjustable parameters C, n, and m, which equal unity for the Slater exchange potential, are varied to make the energy an extremum. Lindgren has carried out this variational procedure for the ground states of several atoms and reports that the parameter values are not particularly sensitive, since the energy minimum is quite flat. Furthermore, he found that the values of the adjustable parameters changed little from atom to atom. Accordingly, we have adopted the parameter set[24]

$$C = 0.8$$

$$n = 1.15$$

$$m = 1$$

for all the atoms of the magnesium isoelectronic sequence.

We might wonder which one of the modifications to the HFS procedure leads to a more rapidly convergent basis set for the method of configuration interaction. To help settle this question, transition probabilities have been calculated using the three different universal exchange potentials given in Eqs. (22)–(24), and the dipole length and dipole velocity values of the absolute multiplet strength are compared in Table I for some of the better known transitions occurring in Mg I and Al II. The remarkable thing about Table I is that the absolute multiplet strengths found by these methods agree among each other fairly well, so that it is quite difficult to choose between these alternative HFS procedures. However, on closer examination of these and other transitions, it appears that the variationally adjusted potential proposed by Lindgren gives results somewhat more consistent. Consequently we have used the universal exchange potential defined in Eqs. (24) and (25) in all subsequent calculations reported here.

In Table II we present calculated ^1S, ^3S, $^1P^0$, $^3P^0$, ^1D, and ^3D multiplet energies and compare them to the available spectroscopic data[25] for the first four members of the magnesium isoelectronic sequence and for Ca IX. Rather than calculate the total energy of the multiplet states, we have equated in Table II the calculated and observed lowest-lying ^3D, ^3P, and ^3S multiplets as

TABLE I. Comparison of the use of different universal exchange potentials in the configuration interaction calculation of absolute multiplet strengths. The first entry in each column is the dipole length value; the second entry is the dipole velocity value. The values of S given in atomic units $(e^2a_0{}^2)$ have been rounded to three significant figures.

Transition		$V_{\text{exch}}(r)$	$V'_{\text{exch}}(r)$	$V''_{\text{exch}}(r)$
Mg I	$3s3p\,^1P^0 - 3s^2\,^1S$	19.1	22.1	16.1
		10.7	12.0	12.2
Mg I	$3s3p\,^1P^0 - 3s4s\,^1S$	38.1	24.1	33.3
		9.18	16.1	5.69
Mg I	$3s3p\,^3P^0 - 3s4s\,^3S$	21.9	18.5	18.7
		19.4	18.3	19.0
Al II	$3s3p\,^1P^0 - 3s^2\,^1S$	10.6	11.4	10.1
		8.79	8.63	9.2
Al II	$3s3p\,^1P^0 - 3s4s\,^1S$	5.98	3.72	5.00
		3.75	3.95	2.81
Al II	$3s3p\,^3P^0 - 3s4s\,^3S$	7.25	6.08	7.02
		6.30	6.31	5.90

reference energies.[26] Inspection of Table II reveals that the agreement between the calculated and observed multiplet energies is better for multiplets arising from low-lying configurations than those arising from highly excited configurations. This is not surprising, since the choice of basis set configurations emphasized those configurations which might interact most strongly with the lower-lying configurations. However, this fact cautions us to regard with some reservation calculated transition probabilities involving higher-lying multiplets, especially those multiplets for which the calculated energies are in poor agreement with observation.

In Table III we present configuration interaction wavefunctions for several of the lower-lying multiplets of the magnesium isoelectronic sequence. The expansion coefficients listed in Table III have the property that the sum of their squares equals unity. Thus, we may regard the actual multiplet states as resonating between the different electronic configurations given in Table III. The probability of finding a certain multiplet associated with a particular configuration of electrons is given by the square of the corresponding expansion coefficient. This heuristic interpretation holds much charm for us by providing a simple means of visualizing the complex collective motion of the electrons that is easily identified with our traditional configurational viewpoint. Moreover, the configuration interaction wavefunctions can be written explicitly in terms of the interelectronic coordinates r_{ij}. The form of this relationship[15] is quite illuminating in understanding the manner in which spatial correlation is introduced by the method of configuration interaction into the properties of the wavefunction.

[23] I. Lindgren, Arkiv Fysik 31, 59 (1965).

[24] This parameter set was suggested by I. Lindgren and A. Rosén (private communication).

[25] Our sources of spectroscopic data are the following: (a) for the Mg I spectrum G. Risberg, Arkiv Fysik 28, 381 (1964); (b) for the Al II, P IV and Ca IX spectra, C. E. Moore, Natl. Bur. Std. (U.S.) Circ. 467, 1 (1949), and the references contained therein; and (c) for the Si III spectrum, Y. G. Toresson, Arkiv Fysik 18, 389 (1960). For the Si III spectrum see also C. E. Moore, "Selected Tables of Atomic Spectra" NSRDS-NBS 3 Sec. 1 (U.S. Government Printing Office, Washington, 1965).

[26] See J. E. Lennard-Jones and J. A. Pople, Phil. Mag. 43, 581 (1952); J. E. Lennard-Jones, Proc. Natl. Acad. Sci. (U.S.) 38, 496 (1952) for a general discussion of spatial correlation in two-electron atoms.

TABLE II. Comparison of calculated and observed ^1S, ^3S, $^1P^0$, $^3P^0$, ^1D, and ^3D multiplet energies for the magnesium isoelectronic sequence. We list here only those multiplets with energies which lie below the ionization continuum. The energies are given in Rydberg units.

Configuration	$^1S_{calc}$	$^1S_{obs}$	$^3S_{calc}$	$^3S_{obs}$
Mg I				
$3s^2$	−0.54585	−0.56177		
$3s4s$	−0.14556	−0.16574	−0.18665	−0.18665
$3s5s$	−0.07266	−0.08304	−0.08283	−0.08927
$3s6s$	−0.04261	−0.04986	−0.04674	−0.05265
Al II				
$3s^2$	−1.37276	−1.38385		
$3s4s$	−0.49364	−0.51498	−0.55213	−0.55213
$3s5s$	−0.26532	−0.27789	−0.28212	−0.28952
$3s6s$	−0.16619	−0.17391	−0.17346	−0.17904
$3p^2$	−0.32040		...	...
Si III				
$3s^2$	−2.44995	−2.46169		
$3s4s$	−0.98796	−1.01214	−1.06402	−1.06402
$3s5s$	−0.55367	−0.56740	−0.57468	−0.58288
$3s6s$	−0.35510	−0.36245	−0.36391	−0.36921
$3p^2$	−1.03386	−1.06340	...	...
$3p4p$	−0.05895	−0.10170	−0.19210	−0.19471
P IV				
$3s^2$	−3.76167	−3.77549		
$3s4s$	−1.62176	−1.64317	−1.70793	−1.70793
$3s5s$	−0.92564	−0.89017	−0.94998	−0.95874
$3s6s$	−0.60255		−0.61384	−0.61638
$3p^2$	−1.97839	−2.00227	...	...
$3p4p$	−0.43761		−0.59709	
Ca IX				
$3s^2$	−13.80115	−13.84214		
$3s4s$	−6.76982		−6.91649	−6.91649
$3s5s$	−4.00906		−4.10300	
$3s6s$	−2.70755		−2.73515	
$3p^2$	−10.21626		...	...
$3p4p$	−4.39291		−4.65015	
$3d^2$	−5.60838		...	...
$3d4d$	−1.27104		−1.70370	

Configuration	$^1P^0_{calc}$	$^1P^0_{obs}$	$^3P^0_{calc}$	$^3P^0_{obs}$
Mg I				
$3s3p$	−0.21457	−0.24256	−0.36249	−0.36249
$3s4p$	−0.10227	−0.11229	−0.12678	−0.12593
$3s5p$	−0.06067	−0.06351	−0.07014	−0.06758
$3s6p$	−0.04014		−0.04547	−0.04237
Al II				
$3s3p$	−0.80499	−0.83846	−1.04198	−1.04198
$3s4p$	−0.39873	−0.40043	−0.41626	−0.42289
$3s5p$	−0.22973	−0.23687	−0.23386	−0.23828
$3s6p$	−0.14988	−0.15440	−0.15028	−0.15350
$3p3d$	+0.11181		−0.00667	−0.04795
$3p4s$	−0.00536	−0.03516	−0.04088	−0.05435
Si III				
$3s3p$	−1.67661	−1.70639	−1.97886	−1.97886
$3s4p$	−0.84417	−0.85342	−0.85569	−0.86424
$3s5p$	−0.49822	−0.50673	−0.49719	−0.50254
$3s6p$	−0.35164	−0.37762	−0.32007	−0.32537
$3p3d$	−0.26584	−0.32579	−0.47842	−0.49116
$3p4s$	−0.28229	−0.31155	−0.38392	−0.39607

Configuration	$^1P^0_{calc}$	$^1P^0_{obs}$	$^3P^0_{calc}$	$^3P^0_{obs}$
P IV				
$3s3p$	−2.78831	−2.81693	−3.15232	−3.15232
$3s4p$	−1.42158	−1.42880	−1.42808	−1.43646
$3s5p$	−0.87167	−0.85886	−0.82776	−0.85854
$3s6p$	−0.53373	−0.56669	−0.54672	
$3p3d$	−0.90844	−1.05694	−1.20287	−1.21362
$3p4s$	−0.74937	−0.92252	−0.86551	−0.87638
$3p4d$	−0.21033		−0.27136	
$3d4f$	−0.09886		−0.16600	
Ca IX				
$3s3p$	−11.85849	−11.88758	−12.51384	−12.51384
$3s4p$	−6.26687		−6.27481	
$3s5p$	−3.70201		−3.77432	
$3s6p$	−2.56390		−2.56926	
$3p3d$	−7.83181		−8.40713	
$3p4s$	−5.14482		−5.25131	
$3p4d$	−3.86692		−3.87596	
$3d4f$	−3.32166		−3.45317	
$3d4p$	−2.28653		−2.42537	

Configuration	$^1D_{calc}$	$^1D_{obs}$	$^3D_{calc}$	$^3D_{obs}$
Mg I				
$3s3d$	−0.14007	−0.13913	−0.12497	−0.12497
$3s4d$	−0.07968	−0.07779	−0.07125	−0.06815
$3s5d$	−0.05118	−0.04887	−0.04738	−0.04285
$3s6d$	−0.03690	−0.03324	−0.03437	−0.02942
Al II				
$3s3d$	−0.36923	−0.38066	−0.51316	−0.51316
$3s4d$	−0.23586	−0.24667	−0.28414	−0.27684
$3s5d$	−0.16382	−0.16354	−0.18321	−0.17351
$3s6d$	−0.11621	−0.11458	−0.12915	−0.11891
$3p^2$	−0.62031	−0.60491	...	...
Si III				
$3s3d$	−0.92666	−0.95113	−1.15908	−1.15908
$3s4d$	−0.59752	−0.59969	−0.63424	−0.62459
$3s5d$	−0.39602	−0.38705	−0.40398	−0.39234
$3s6d$	−0.28235	−0.26964	−0.28463	−0.27197
$3p^2$	−1.37750	−1.34799	...	...
$3p4p$	−0.15227	−0.20234	−0.24088	−0.22960
P IV				
$3s3d$	−1.74895		−2.04965	−2.04965
$3s4d$	−1.08919	−1.07124	−1.11482	−1.10328
$3s5d$	−0.70837	−0.66803	−0.71633	
$3s6d$	−0.46938		−0.48143	
$3p^2$	−2.37316	−2.33443	...	...
$3p4p$	−0.56940		−0.65157	−0.68048
$3p4f$	−0.25080		−0.20705	
$3d^2$	−0.05850			
Ca IX				
$3s3d$	−9.56112		−10.09076	−10.09079
$3s4d$	−5.48962		−5.50469	−5.48717
$3s5d$	−3.48851		−3.42998	−3.47302
$3s6d$	−2.36215		−2.37344	
$3p^2$	−10.84801	−10.78762	...	...
$3p4p$	−4.55374		−4.73482	
$3p4f$	−3.39121		−3.56577	
$3d^2$	−6.09648		...	...
$3d4s$	−2.96846		−3.05486	
$3d4d$	−1.52183		−1.79490	

TABLE III. Configuration interaction wavefunctions for some low-lying ^1S, $^1P^0$ and ^1D multiplets of the magnesium isoelectronic sequence. An asterisk has been placed by those multiplets for which the spectral purity is less than 0.75 and two asterisks for those less than 0.50.

^1S Wavefunctions

Designation		Configurations							
		ψ_{3s^2}	ψ_{3s4s}	ψ_{3s5s}	ψ_{3s6s}	ψ_{3p^2}	ψ_{3p4p}	ψ_{3d^2}	ψ_{3d4d}
Mg I	$3s^2$	0.972	0.048	0.019	0.010	0.206	−0.095	−0.002	−0.001
Al II	$3s^2$	0.971	0.004	0.008	0.012	0.221	0.072	−0.012	−0.009
Si III	$3s^2$	0.975	0.027	0.005	0.017	0.214	0.052	−0.020	−0.013
P IV	$3s^2$	0.977	0.031	0.001	0.005	0.203	0.041	−0.025	−0.013
Ca IX	$3s^2$	0.983	0.019	0.007	0.003	0.179	0.017	−0.027	−0.004
Mg I	$3p^2$	0.217	−0.069	−0.063	−0.051	−0.953	−0.101	−0.121	−0.091
Al II	$3p^2$	0.213	0.003	0.006	0.020	−0.954	−0.000	0.176	−0.102
Si III	$3p^2$	0.205	−0.296	−0.001	0.003	−0.908	−0.044	−0.194	−0.085
P IV	$3p^2$	0.195	−0.065	−0.005	−0.001	−0.955	−0.009	−0.201	−0.069
Ca IX	$3p^2$	0.170	−0.023	−0.010	−0.002	−0.969	0.001	−0.176	−0.015

$^1P^0$ Wavefunctions

Designation		Configurations								
		ψ_{3s3p}	ψ_{3s4p}	ψ_{3s5p}	ψ_{3s6p}	ψ_{3p3d}	ψ_{3p4s}	ψ_{3p4d}	ψ_{3d4p}	ψ_{3d4f}
Mg I	$3s3p$	−0.930	0.286	0.113	0.066	−0.142	−0.093	−0.073	−0.034	−0.005
Al II	$3s3p$	−0.969	0.080	0.036	0.019	−0.206	−0.037	−0.089	−0.036	−0.013
Si III	$3s3p$	−0.972	0.035	0.018	0.009	−0.215	−0.021	−0.072	−0.030	−0.019
P IV	$3s3p$	−0.975	0.018	0.008	0.005	−0.212	−0.017	−0.054	−0.025	−0.022
Ca IX	$3s3p$	−0.982	0.001	−0.000	−0.000	−0.185	−0.007	−0.009	−0.011	−0.023
Mg I	$3p3d^*$	−0.098	0.049	0.016	0.014	0.755	0.320	−0.471	0.190	−0.240
Al II	$3p3d^*$	−0.165	0.040	0.018	0.018	0.859	0.265	−0.269	0.132	−0.270
Si III	$3p3d^*$	−0.180	0.047	0.063	0.194	0.835	0.402	−0.101	0.078	3.218
P IV	$3p3d$	−0.184	−0.111	−0.301	0.041	0.898	−0.164	−0.097	0.026	−9.136
Ca IX	$3p3d$	−0.183	0.063	0.021	0.001	0.978	0.020	0.003	−0.007	−0.066

^1D Wavefunctions

| Designation		Configurations									
		ψ_{3s3d}	ψ_{3s4d}	ψ_{3s5d}	ψ_{3s6d}	ψ_{3p^2}	ψ_{3p4p}	ψ_{3d^2}	ψ_{3d4d}	ψ_{3p4f}	ψ_{3d4s}
Mg I	$3s3d$	0.902	0.132	0.066	0.042	−0.401	0.028	−0.011	−0.027	−0.031	0.010
Al II	$3s3d^{**}$	0.664	−0.516	−0.160	−0.089	0.493	0.007	0.091	0.015	−0.077	0.046
Si III	$3s3d^*$	0.804	−0.222	−0.078	−0.039	0.514	−0.023	0.143	0.014	−0.095	0.038
P IV	$3s3d^*$	0.846	−0.103	−0.017	−0.021	0.488	−0.033	0.156	0.008	−0.093	0.025
Ca IX	$3s3d$	0.892	0.010	−0.000	0.007	0.426	−0.013	0.141	0.000	−0.061	−0.000
Mg I	$3p^{2*}$	0.306	0.268	0.228	0.193	0.817	−0.242	0.095	0.059	−0.052	0.051
Al II	$3p^{2*}$	−0.662	−0.112	−0.060	−0.036	0.731	0.012	0.056	0.061	0.022	−0.012
Si III	$3p^2$	−0.561	−0.082	−0.036	−0.021	0.816	0.026	0.077	0.059	0.012	−0.011
P IV	$3p^{2*}$	−0.513	−0.057	−0.018	−0.013	0.850	0.026	0.084	0.048	0.007	−0.011
Ca IX	$3p^{2*}$	−0.440	−0.013	−0.004	−0.000	0.894	0.002	0.084	0.015	−0.001	−0.011
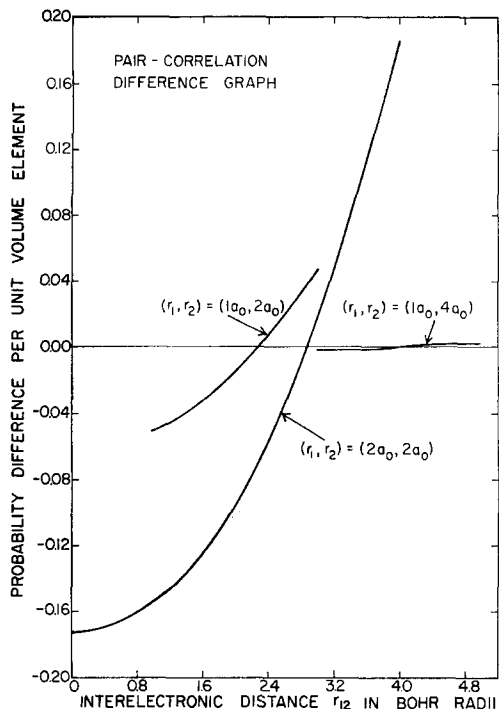
FIG. 1. Variation of the pair-correlation difference function $P(r_1, r_2, r_{12})$ for the ^1S ground multiplet of Si III as a function of interelectronic distance r_{12} of the valence electrons for fixed values of r_1 and r_2. Note that for $r_1 = r_2$, the valence electrons lie on the surface of a sphere and can only avoid each other through angular correlation terms.

For example, let us consider the expression for the spatial part of the ^1S multiplet wavefunction in which we ignore the position of the core electrons. Let the valence electrons denoted by 1 and 2 be located at r_1 and r_2 with the angle θ_{12} included between them and at a distance r_{12} from each other, given by

$$r_{12}{}^2 = r_1{}^2 + r_2{}^2 - 2r_1 r_2 \cos\theta_{12}. \quad (26)$$

The spatial part of the configuration interaction wavefunction $\psi_{CI}(^1S)$ can then be written in terms of the radial wavefunctions P_{nl} and expansion coefficients $c_{nln'l'}$ by

$$\psi_{CI}(^1S) = (1/4\pi)^{1/2}(c_{3s^2}\Xi_{3s^2} + c_{3s4s}\Xi_{3s4s} + c_{3s5s}\Xi_{3s5s}$$
$$+ c_{3s6s}\Xi_{3s6s}) P_0(\cos\theta_{12}) - (3/4\pi)^{1/2}$$
$$\times (c_{3p^2}\Xi_{3p3p} + _{3p4p}\Xi_{3p4p}) P_1(\cos\theta_{12}) + (5/4\pi)^{1/2}$$
$$\times (c_{3d^2}\Xi_{3d3d} + c_{3d4d}\Xi_{3d4d}) P_2(\cos\theta_{12}), \quad (27)$$

where the angular factors $P_l(\cos\theta_{12})$ are Legendre polynomials in the cosine of the included angle and the radial factors Ξ are given by

$$\Xi_{nlnl} = P_{nl}(1) P_{nl}(2) \quad (28a)$$

for equivalent electrons and

$$\Xi_{nln'l'} = 2^{-1/2}(P_{nl}(1) P_{n'l'}(2) + P_{n'l'}(1) P_{nl}(2)) \quad (28b)$$

for nonequivalent electrons. In Eq. (27) we can recog-

nize two rather different types of correlation, first pointed out by Lennard–Jones and Pople[26] with regard to the ^1S ground state of helium. First an angular correlation is brought about by the terms in $P_l(\cos\theta_{12})$ for $l > 0$. Here the electrons avoid each other by "hiding" on opposite sides of the nucleus for fixed values of r_1 and r_2. Second a radial correlation within each angular term is brought about by the radial factors $\Xi_{nln'l'}$ arising from the series configurations $nln'l'$. Here the electrons avoid each other by increasing the probability of finding one electron close to the nucleus if the other one is far away.

We can put this discussion on a more quantitative basis by introducing the concept of the *pair correlation difference function*, given by the square of the configuration interaction wavefunction in (27) minus the square of the central-field HFS wavefunction for the same multiplet:

$$P(r_1, r_2, r_{12}) = |\psi_{CI}(^1S)|^2 - |\psi_{HFS}(^1S)|^2. \quad (29)$$

Equation (29) is interpreted as giving the difference in probabilities with and without correlation in the dynamical motion of the electrons for finding electron 1 between r_1 and $r_1 + dr_1$, electron 2 between r_2 and $r_2 + dr_2$ with the interelectronic separation between r_{12} and $r_{12} + dr_{12}$. In Fig. 1 we have plotted $P(r_1, r_2, r_{12})$ as a function of r_{12} for several fixed values of r_1 and r_2 for the ^1S ground multiplet[27] of Si III. The negative values of $P(r_1, r_2, r_{12})$ in Fig. 1 correspond to electron deficient regions in $\psi_{CI}(^1S)$ over the results from the HFS procedure and vice versa. Figure 1 shows that the method of configuration interaction can lead to a smoothly varying correlation in the spatial position of the valence electrons and that by and large the most important form of correlation is angular correlation rather than radial "in-out" correlation.

Table III in conjunction with Table II can also be used to reassign certain multiplets to configurations which more appropriately classify the behavior[28] of the multiplet. As we discussed in I, the extent to which we are justified in assigning configuration labels to multiplets which simultaneously partake of the character of several different configurations may become a difficult problem, particularly when the same multiplets of two strongly interacting configurations would nearly coincide in the absence of configuration interaction. As in I it is then convenient to introduce the concept of the *spectral purity* of a multiplet term, given by the square of the leading coefficient in the expansion of the multiplet wavefunction in HFS determinants. If the spectral

[27] Table III indicates that the expansion coefficients $c_{nln'l'}$ change slowly in general along the isoelectronic sequence, so that the results shown in Fig. 1 for the ^1S ground state of Si III are quite similar to what is found for Mg I or Al II for example. Note in Fig. 1 for the curve $r_1 = r_2$ the formation of a so-called "Coulomb hole" due to the avoidance of the electrons.

[28] For example, the lowest-lying ^1D multiplet in the Ca IX spectra should be assigned to the configuration $3p^2$ and not to the configuration $3s3d$, as shown in Ref. 25(b). In Table II we have made the best assignments we could based on the configuration interaction wavefunctions. For further discussion see I.

purity is 0.9 or higher, there is no difficulty in making a meaningful configurational assignment. However, if the spectral purity of a multiplet drops below 0.9, there is substantial "contamination" from other interacting configurations; and if the spectral purity drops below 0.5, then it follows that the use of a single configuration label is a *fiction*, sanctioned by tradition but devoid of much significance. For such multiplets we can expect large deviations in the calculated oscillator strength from the values we would obtain using a central-field model.[29] Due to the extensive configuration mixing present in such multiplets, the calculation of absolute multiplet strengths also serves as a severe test of the validity of the limited basis set expansion we use.

CALCULATED TRANSITION PROBABILITIES

Using configuration interaction wavefunctions of the form of Eq. (14), we have calculated[30] with the help of Eq. (16) some 1395 absolute multiplet strengths for all transitions of the type $^1S-^1P^0$, $^3S-^3P^0$, $^1P-^1P^0$ and $^3D-^3P^0$ for Mg I, Al II, Si III, P IV and Ca IX which can occur between the configurations that constitute our basis sets. Most of these transitions involve either one or more states which lie above the ionization continuum, or belong to highly excited configurations for which correlation effects have been inadequately taken into account. Or they involve transitions between configuration labels which seemingly require the jump of more than one electron. Many of these transition probabilities are not expected to be of high reliability, but some of these transitions are of astrophysical interest.[31,32]

In Table IV we present dipole length and dipole velocity values for some of the electric dipole allowed transitions between multiplets belonging to the lower-lying configurations of the magnesium isoelectronic sequence. It is quite difficult to assess the accuracy of these calculated absolute multiplet strengths. As a check on the consistency of our results, it is useful to define a percentage error E between the dipole length $S^{(L)}$ and dipole velocity $S^{(V)}$ values:

$$E = 100 \times |\ S^{(L)} - S^{(V)}\ |/S_>, \qquad (30)$$

where $S_>$ is the greater of $(S^{(L)}, S^{(V)})$. In Table IV there are only 68 transitions for which a comparison can be made between $S^{(L)}$ and $S^{(V)}$ since experimental energy differences [see Eq. (11)] are lacking for the other transitions. For most of these transitions we find the agreement is better than 20%. In particular there are 23 transitions for which $0\% < E < 10\%$, 17 transitions for which $10\% < E < 20\%$, 9 transitions for which $20\% < E < 30\%$, 10 transitions for which $30\% < E < 40\%$, and an additional 10 transitions for which E exceeds 40%. As we have stressed before, this in itself does not demonstrate that the transition probabilities appearing in Table IV have been calculated to the same degree of accuracy. However, the closeness of agreement and the fact that intermediate calculations tend to show a somewhat smooth approach to these values of $S^{(L)}$ and $S^{(V)}$ encourage us to believe that the dipole length and dipole velocity results given in Table IV are converging to the actual absolute multiplet strength.

After such calculations the practical question always arises as to which value of $S^{(L)}$ or $S^{(V)}$ is to be preferred. It has been noted elsewhere[33] that the dipole length operator weights the portion of the wavefunction at relatively large distances from the nucleus. However, the dipole velocity operator emphasizes portions of the wavefunction closer to the nucleus in the region of the wavefunction's largest magnitude, but requires the calculation of the gradient of the wavefunction. At present we have little reason to believe that we can calculate more accurately the gradient of the wavefunction closer in or the wavefunction itself further out. Consequently, if we are pressed for a "best" value, we would suggest taking the mean

$$\langle S \rangle_{Av} = \tfrac{1}{2}(S^{(L)} + S^{(V)}) \qquad (31)$$

in the hope that $S^{(L)}$ and $S^{(V)}$ are converging equally as rapidly to $\langle S \rangle_{Av}$. However, when $S^{(L)}$ and $S^{(V)}$ differ by more than a factor of two, the assignment of a best value for S will be of doubtful significance.

Ideally, the most convincing check of our calculated transition probabilities would be a comparison with accurately determined values. Unfortunately there have been very few experimentally measured oscillator strengths reported for the magnesium isoelectronic sequence, and of these there is not wide agreement about which oscillator strengths represent first-class data.[1] Nevertheless we have collected in Table V the best experimental gf values known to the author for the magnesium isoelectronic sequence. These have been compared with calculated gf values found from Eq. (2), using the mean value $\langle S \rangle_{Av}$ derived from Table IV.

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[29] Indeed this is confirmed by this work and the work of Weiss (Ref. 7). In particular Weiss has given the Hartree–Fock values for many of the absolute multiplet strengths. In the case of the $3s3p\ ^1P^0-3p^2\ ^1D$ transition in Al II, the Hartree–Fock and configuration interaction values differ by over two orders of magnitude.

[30] A good portion of these programs have been documented in R. N. Zare, JILA Rept. No. 80 (Joint Institute for Laboratory Astrophysics, Boulder, Colorado, 1966). As an indication of the practicability of these calculations, it is worthwhile to mention some timing considerations. For example, the time required per element to calculate all energy levels, to find all wavefunctions and to compute dipole length and dipole velocity values of the absolute multiplet strengths for all possible transitions between the multiplets is about 10 min on a CDC-3600 computer.

[31] For example, see J. W. Swenson and G. Risberg, "Mg I lines in the Solar Spectrum," Arkiv Fysik 31, 237 (1965).

[32] Further information on correlated wavefunctions and oscillator strengths for the magnesium isoelectronic sequence may be obtained from the author on request.

[33] S. Chandrasekhar, Astrophys. J. 102, 223 (1945); S. S. Huang, *ibid.* 108, 354 (1948); D. R. Bates, J. Chem. Phys. 19, 1122 (1951); H. Shull, *ibid.* 20, 18 (1952); M. Wolfsberg *ibid.* 23, 793 (1955); G. Berthier, J. Chim. Phys. 51, 137 (1954); S. Ehrenson and P. E. Phillipson, J. Chem. Phys. 34, 1224 (1961); S. R. La Paglia and O. Sinanoğlu *ibid.* 44, 1888 (1966). I would like to thank Professor Paul Phillipson for suggesting to me the computation of the dipole length and dipole velocity forms of the absolute multiplet strength.

TABLE IV. Calculated absolute multiplet strengths for some of the low-lying transitions in Mg I, Al II, Si III, P IV, and Ca IX. The first entry is the value of $S(\alpha SL; \alpha' SL')$ calculated using the dipole length expression; the second entry is for the dipole velocity expression. All values of S, given in atomic units $(a_0^2 e^2)$ have been rounded to three significant figures. By writing "Forbidden" underneath them, we have marked those transitions which appear to require the simultaneous jump of two electrons and which thus can only occur through the noncentral nature of the potential.

Transition	Mg I	Al II	Si III	P IV	Ca IX
$3s3p\ ^1P^0 - 3s^2\ ^1S$	16.1	10.1	6.75	4.84	1.65
	12.2	9.22	6.26	4.55	1.52
$3s3p\ ^1P^0 - 3s4s\ ^1S$	33.3	5.00	0.591[a]	0.699	0.116
	5.69	2.81	0.357[a]	0.569	...
$3s3p\ ^1P^0 - 3p^2\ ^1S$		3.77	3.95	2.23	0.764
		...	3.85	2.29	...
$3s3p\ ^3P^0 - 3s4s\ ^3S$	18.7	7.02	3.23	1.83	0.436
	19.0	5.90	3.17	1.91	0.395
$3p3d\ ^1P^0 - 3p^2\ ^1S$			8.53	3.59	1.35
			8.33	4.36	...
$3s4p\ P^L - 3s^2\ ^1S$	1.65	0.0196	0.0377	0.0738	0.105
	1.20	0.00911	0.0324	0.0752	...
$3s4p\ ^1P^0 - 3s4s\ ^1S$	68.4	27.6	14.0	9.76	2.67
	54.3	22.5	13.6	10.1	...
$3s4p\ ^3P^0 - 3s4s\ ^3S$	209.	91.4	53.2	35.4	10.2
	182.	79.0	45.7	30.3	...
$3s4p\ ^1P^0 - 3p^2\ ^1S$ ("forbidden")		0.000185	1.20	0.0617	0.00569
		...	1.73	0.131	...
$3s3p\ ^1P^0 - 3s3d\ ^1D$	41.7	24.6	19.5	13.3	3.51
	16.9	19.3	17.8	...	...
$3s3p\ ^1P^0 - 3s4d\ ^1D$	7.02	8.00	1.05	0.0397	0.140
	4.25	6.27	0.894	0.0375	...
$3s3p\ ^1P^0 - 3s5d\ ^1D$	2.77	3.26	0.0794	0.0000	0.0654
	2.53	2.04	0.0532	...	...
$3s3p\ ^3P^0 - 3s3d\ ^3D$	72.4	46.2	29.2	19.5	5.99
	63.4	42.4	28.3	19.7	5.12
$3s3p\ ^3P^0 - 3s4d\ ^3D$	12.8	2.09	0.150	0.0490	0.832
	11.5	1.91	0.0990	0.0588	0.705
$3s3p\ ^3P^0 - 3s5d\ ^3D$	6.06	2.92[b]	0.00585	0.759	0.182
	4.47	0.283[b]	0.00414	...	0.107
$3s3p\ ^1P^0 - 3p^2\ ^1D$		0.0779	1.51	1.91	1.17
		0.0122	1.02	1.48	1.01
$3s4p\ ^1P^0 - 3p^2\ ^1D$ ("forbidden")		8.21	2.51[c]	1.14	0.129
		9.44	2.72[c]	1.13	...
$3p3d\ ^1P^0 - 3s3d\ ^1D$			5.94	1.81	1.40
			4.63	...	...
$3p3d\ ^3P^0 - 3s3d\ ^3D$		22.7	13.4	10.3	3.77
		15.2	8.34	7.00	...
$3p3d\ ^1P^0 - 3p^2\ ^1D$			0.000466	0.257	0.0142
			0.0588	0.138	...

[a] Using $V_{exch}(r)$ in the HFS procedure, we obtain instead $S^{(L)} = 0.142$ and $S^{(V)} = 0.333$.

[b] Using $V_{exch}(r)$ in the HFS procedure, we obtain instead $S^{(L)} = 0.551$ and $S^{(V)} = 0.420$.

[c] This "Forbidden" transition which we find to have a sizable oscillator strength has been observed by Y. G. Toresson (Ref. 25c) with a plate blackening of (9) on a scale of (0) to (10).

The general agreement shown in Table V is quite gratifying, although there are differences present. The poorest comparison is the gf value for the $3s3p\ ^1P^0$–$3s4d\ ^1D$ transition. For this transition our calculated values of gf range from 0.38 to 0.23 for $S^{(L)}$ and $S^{(V)}$, compared to the reported value of 0.18. For the same transition Trefftz[34] found the value $gf=0.02$ by using configuration interaction (but with a smaller basis set) and including a core polarization correction. This transition is thus quite sensitive to the calculational scheme. Further investigation shows that there is large cancellation present in the calculation of S, so that our accuracy must be considered low. This example illustrates a general failing in our computational technique; namely, small oscillator strengths tend to be inaccurate from the loss of significant figures due to the interaction of configurations causing heavy cancellation in the computation of the absolute multiplet strength.

From Table V we see that no experimental oscillator strengths have been determined for the higher stages of ionization along the magnesium isoelectronic sequence. For these transitions we have no means of directly verifying the validity of our calculations and must rely instead upon the results of other calculations as a check on the reasonableness of our methods. We are fortunate to have available the calculations of A. W. Weiss[7] who has computed absolute multiplet

TABLE V. Comparison of calculated and observed gf values. The calculated gf values given are a mean of the dipole length and dipole velocity results listed in Table IV and have been rounded to the same number of significant figures as the reported experimental values.

Atom	Transition	Wave-length	Observed gf values	Calculated gf values
Mg I	$3s^2\ ^1S$–$3s3p\ ^1P^0$	2852 Å	1.6[a] 1.2±0.3[b] 1.11±0.05[c] 1.85±0.007[d] 1.81±0.005[e]	1.55
	$3s3p\ ^1P^0$–$3s4s\ ^1S$	11828 Å	0.5[a]	0.5
	$3s3p\ ^3P^0$–$3s4s\ ^3S$	5183 Å	1.05[a]	1.11
	$3s3p\ ^1P^0$–$3s3d\ ^1D$	8806 Å	1.1[a]	1.0
	$3s3p\ ^3P^0$–$3s3d\ ^3D$	3838 Å	4.9[a]	5.4
	$3s3p\ ^1P^0$–$3s4d\ ^1D$	5528 Å	0.18[a]	0.31
	$3s3p\ ^3P^0$–$3s4d\ ^3D$	3096 Å	1.1[a]	1.2
	$3s3p\ ^1P^0$–$3s5d\ ^1D$	4702 Å	0.19[a]	0.18

[a] Quoted from C. W. Allen, *Astrophysical Quantities* (Athlone Press, London, 1963) in which proper reference citations are given.

[b] Yu. I. Ostrovskii, N. P. Penkin, and L. N. Shabanova, Dokl. Akad. Nauk SSSR **120**, 66 (1958) [English transl.: Soviet Phys.—Doklady **3**, 538 (1958)].

[c] W. Demtröder, Z. Physik **166**, 42 (1962).

[d] A. Lurio, Phys. Rev. **136**, A376 (1964).

[e] W. W. Smith and A. Gallagher, Phys. Rev. **145**, 26 (1966). Preference should be given to the experimental values reported in this and the preceding reference for the Mg I $3s3p\ ^1P^0$–$3s^2\ ^1S$ resonance line.

strengths for many of the same transitions given in Table IV. Weiss has used configuration superposition wavefunctions which consist of a set of pseudonatural orbitals generated by applying the Schmidt orthogonalization procedure to a linear combination of Slater-type orbitals that satisfy the Hartree–Fock equations for the atomic state in question. With this procedure he has effectively included in his calculations all configurations $nln'l'$ up to $n,\ n'=6$. Comparison of Table IV with the calculated absolute multiplet strengths of Weiss, which are probably the more accurate values, shows good agreement within the uncertainties of Table IV. A more detailed investigation shows that the agreement between Weiss' dipole length and dipole velocity values is closer in general than the agreement between our calculated values of $S^{(L)}$ and $S^{(V)}$, especially for transitions of Mg I. A possible explanation of this behavior is that the HFS procedure we use does not take into account electron exchange terms which differently affect the calculation of the $3s3p\ ^1P^0$ and $^3P^0$ multiplets, but treats as identical the radial wavefunctions (excluding configuration interaction) for both multiplets. However, the Hartree–Fock solutions for the $3s3p\ ^1P^0$ and $^3P^0$ multiplets of Mg I show appreciably different radial functions.[35] The result then is an extra burden on
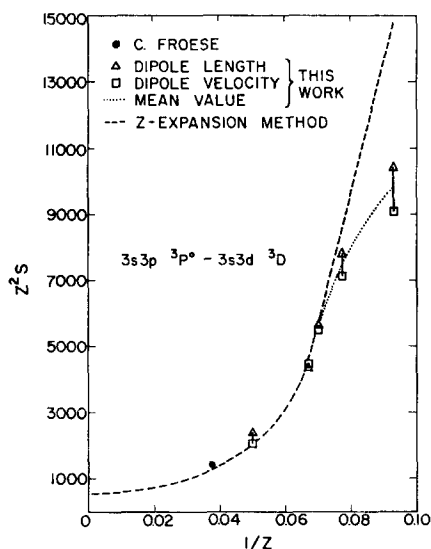

FIG. 2. Comparison of absolute multiplet strengths calculated by the Z-expansion method and by the dipole length and dipole velocity expressions using configuration interaction wavefunctions.

[34] E. Trefftz, Z. Astrophys. **28**, 67 (1950). Trefftz's work represents one of the earliest studies of correlation effects on the calculation of oscillator strengths, and she found significant deviations from Hartree–Fock values when configuration interaction wavefunctions were used. The calculated values of S by Trefftz and this paper are in reasonable agreement by and large, at least if one includes only the configurations Trefftz used as her basis set. Besides the $3s3p\ ^1P^0$–$3s4d\ ^1D$ transition, another exception is the $3s3p\ ^1P^0$–$3s5d\ ^1D$ transition for which Trefftz found $gf=0.06$ as compared to our value of $gf=0.18$ in Table V.

[35] A classic example of this effect is provided by the $^1P^0$ and $^3P^0$ states belonging to the configuration $1s^2\ 2s2p$ of the Be atom. If the self-consistent field problem is solved separately for each state, it is found that the peak for the $2p$ orbital for the $^1P^0$ state occurs at *twice* the distance that it occurs for the $^3P^0$ state. See D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A154**, 588 (1936).

our configuration interaction procedure which slows the rate of convergence. Evidently for Al II and higher stages of ionization these differential exchange effects on the multiplet wavefunctions are much less important.

Until the calculation of Weiss[7] and this paper, the Z-expansion method has offered the only guide to the behavior of transition probabilities along an isoelectronic sequence. In that procedure,[36] a perturbation solution to the Hartree–Fock radial equations is found in inverse powers of the nuclear charge Z. Here all the configurations which can be formed having the same principal quantum number n are included in the calculations. These configurations, called a complex by Layzer,[37] are degenerate in the limit of infinite Z and to a large extent are responsible for the angular correlation in the motion of the electrons. The absolute multiplet strength in the Z-expansion method can also be shown to have the form of a series in inverse powers of Z:

$$S = | \sum_{\nu} a_{\nu} Z^{-\nu} |^2, \qquad (32)$$

where the parameters a_{ν} depend upon the transition multiplets. Calculations of transition probabilities for L-shell electrons have been performed by Cohen and Dalgarno,[38] and the method has been extended to M-shell electrons by Crossley and Dalgarno.[39] In particular the latter authors have calculated, using an approximation to the first two terms of Eq. (32), absolute multiplet strengths for all transitions between multiplets belonging to the $n=3$ complex of the magnesium isoelectronic sequence.

There is little doubt that Eq. (32) should be an accurate representation of the absolute multiplet strength S when Z is large. For example Crossley and Dalgarno have compared their Z-expansion absolute multiplet strengths with those for Fe XV $(Z=26)$ found by C. Froese[40] who used numerical Hartree–Fock wavefunctions in which the mixing of the degenerate $n=3$

configurations was included. The agreement was found to be in general most satisfactory. The validity of the Z-expansion method for small Z has not been adequately investigated. However, we are in a position to determine quantitatively where along the isoelectronic sequence and by how much the Z-expansion absolute multiplet strengths deviate from the "correct" values.

In Fig. 2 we have plotted the values of Z^2S against $1/Z$ for the $3s3p\ ^3P^0$–$3s3d\ ^3D$ transition. A more complete set of curves of the same type as well as further discussion of the Z-expansion method is to be found in Weiss paper.[7] Figure 2 is typical of these plots showing excellent agreement between the configuration interaction calculations and the Z-expansion method at high Z but large departures for the first few stages of ionization. The reason for this discrepant behavior is not surprising if we look at the configuration interaction wavefunctions in Table III. Here we find the coefficients of the subordinate configuration wavefunctions not contained in the complex are largest for the first few stages of ionization. However they rapidly decrease with increasing stages of ionization as the configurations built up from spin orbitals of the same principal quantum number cluster together. Thus, we must be wary of the predictions of the Z-expansion method when it is applied to the neutral member or to the first few ionization stages of an isoelectronic sequence.[41] As we see from Fig. 2 this warning pertains as well to transitions among the triplets as well as the singlets. However, as shown in Fig. 2, we do find that our calculated absolute multiplet strengths approach the Z-expansion values for the higher stages of ionization. It remains to be shown, though, whether Russell–Saunder coupling calculations rather than intermediate coupling calculations will suffice for these heavier atoms.

ACKNOWLEDGMENT

[36] A. Dalgarno, Proc. Phys. Soc. (London) 75, 439 (1960); J. Linderberg and H. Shull, J. Mol. Spectry. 5, 1 (1960); J. Linderberg, Phys. Rev. 121, 816 (1961); M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) A261, 565 (1961).
[37] D. Layzer, Ann. Phys. (N.Y.) 8, 271 (1959).
[38] M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) A280, 258 (1964).
[39] Reference 17(b).
[40] Reference 17(a).

[41] For as an example of the misleading nature of the Z-expansion method for low Z, see E. Godfredson [Astrophys. J. 145, 308 (1966)] who calculated atomic term energies for atoms and ions with 11 to 28 electrons by the Z-expansion technique. In particular, Godfredson concludes that the lowest-lying ^1D of the Mg I spectra should be reassigned to the configuration $3p^2$. This is at variance with the findings of I.