

Correlation Effects in Complex Spectra. I. Term Energies for the Magnesium Isoelectronic Sequence*

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We present a method for the *ab initio* calculation of configuration interaction in many-electron spectra. It is based on the expansion of the total electronic wavefunction in terms of Hartree-Fock-Slater determinants, as calculated by the programs of Herman and Skillman. This procedure has been applied to several of the low-lying excited configurations of the magnesium isoelectronic sequence which are noted for the presence of violent perturbations causing term values arising from a single configuration to be distorted and/or inverted. Convergence to the observed energy separation between multiplet term values appears to be quite rapid, and the method offers promise as a means of including electronic correlation in the calculation of atomic properties. For example the calculated energy difference between the 1D and 3D terms arising from the $3s3d$ configuration differs from the observed energy difference by 24 cm^{-1} out of 1554 cm^{-1} for Mg I, 720 cm^{-1} out of $14\,540\text{ cm}^{-1}$ for Al II, and 1969 cm^{-1} out of $22\,820\text{ cm}^{-1}$ for Si III. Following a discussion of the nature and degree of configurational mixing with increasing nuclear charge along the magnesium isoelectronic sequence, an examination is made of the significance that can be attached to configurational assignments. An alternative nomenclature is proposed.

INTRODUCTION

TRADITIONALLY the analysis of atomic spectra has been based on the working assumption that a single configuration may be uniquely assigned to each atomic energy level. The theoretical positions of the term values arising from a given electron configuration are to be determined by diagonalizing the combined electrostatic and spin-orbit interaction energy matrices.^{1,2} For the simplest configurations, atomic theory predicts certain interval ratios which may be compared directly with observation. For other cases where there are more term values than radial integrals, it has become accepted practice to treat the latter quantities as adjustable parameters. Their values are determined to give the best least-squares fit to the experimental spectrum.

Agreement between theory and observation has been fairly successful, although there are glaring examples where the spectrum cannot be adequately fit.³ These departures have been attributed to perturbations arising from terms of nearby configurations. As early as 1930 it was stressed that the assignment of precise configurations to term levels was an approximation.⁴ By considering the nondiagonal matrix elements between configurations of the same parity, one can show that the energies of the terms may be displaced from the

positions where they would be found in the absence of such interaction and that the wavefunction of each term becomes a linear combination of wavefunctions associated with the interacting configurations.

To account for these effects additional adjustable parameters have often been introduced.⁵ Although much effort has been expended on theoretical justification, fundamental objections can be raised against this approach. The wide success of the first-order theory, in which all configuration-interaction effects are explicitly ignored, demonstrates that the parameters can be adjusted to accommodate much of the interaction effects. The inclusion of more parameters improves the agreement, but seldom gives insight into the correlated behavior of the electrons. Furthermore, the semiempirical character of this method tends to obscure the significance of a close fit with experimental data.

Instead, we have undertaken the *ab initio* calculation of the effects of configuration mixing. Using the Hartree-Fock-Slater procedure⁶ as modified by Herman and Skillman⁷ to obtain radial wavefunctions, the on-

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¹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), hereafter referred to as *QTAS*.

² J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Co., Inc., New York, 1960), Vols. 1 and 2, hereafter referred to as *QTAS*.

³ E. U. Condon and G. H. Shortley, *Phys. Rev.* **37**, 1025 (1931).

⁴ E. U. Condon, *Phys. Rev.* **36**, 1121 (1930).

⁵ A partial list of references follows: (a) R. F. Bacher and S. Goudsmit, *Phys. Rev.* **46**, 948 (1934); (b) D. R. Layzer, thesis, Harvard University, Cambridge, Mass., 1950 (unpublished); (c) R. E. Trees, *Phys. Rev.* **83**, 756 (1951); **84**, 1089 (1951); **85**, 381 (1952); *J. Res. Natl. Bur. Std. (U.S.)* **53**, 35 (1954); and C. K. Jørgensen, *Phys. Rev.* **123**, 278 (1961); **129**, 1220 (1963); *J. Opt. Soc. Am.* **54**, 651 (1964); (d) G. Racah, *Phys. Rev.* **85**, 381 (1952); *Lunds Univ. Arksskr. Avd. 2* **50**, 31 (1955); and Y. Shadmi, *Phys. Rev.* **119**, 156 (1960); (e) S. Meshkov, *ibid.* **91**, 871 (1953); **93**, 270 (1954); and C. W. Ufford, *ibid.* **94**, 75 (1954); (f) N. Sack, *ibid. Rev.* **102**, 1302 (1956); G. Racah and N. Spector, *Bull. Res. Council Israel* **9F**, 75 (1960); (g) K. Rajnak and B. G. Wybourne, *Phys. Rev.* **132**, 280 (1963); **134**, A596 (1964); *J. Chem. Phys.* **41**, 565 (1964); B. G. Wybourne, *Phys. Rev.* **137**, A364 (1965); K. Rajnak, *J. Opt. Soc. Am.* **55**, 126 (1965).

⁶ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁷ F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963) present a detailed documentation of these computer programs as well as the results of extensive tests on the ground-state energies of the elements of the periodic table.

and off-diagonal matrix elements of the Hamiltonian have been evaluated numerically and the resultant secular equation solved for its eigenvalues and eigenvectors. This approach, which is equivalent to expanding the total wavefunction in the complete set of Hartree-Fock-Slater determinants, differs in several respects from previous efforts.⁸ In order to assess the merits of this procedure we have applied it to one of the classic cases of perturbed spectra.

One of the earliest and perhaps most often cited examples of configuration interaction is the energy separation between the 1D and 3D terms of neutral magnesium, arising from the low-lying excited configuration Mg I $1s^2 2s^2 2p^6 3s3d$. Atomic theory predicts that the 1D lies above the 3D . The energy difference between the two terms is given by $\frac{2}{3}G^2(3s3d)$, where the Slater integral $G^2(3s3d)$ may be shown to be positive definite.⁹ In fact the reverse appears to be true. Observation places the singlet about 1554 cm^{-1} below the triplet's center of gravity.¹⁰ Indeed this inversion occurs not only for the configuration $3s3d$ but for the $3snd$ configurations for all n which are presently known ($n=13$).

Bacher¹¹ first suggested that the explanation for this term inversion was configuration interaction between the $3s3d$ and the $3p^2$ configurations, the latter lying above the ionization limit of the atom. Although it is difficult to doubt the essential truth of this conjecture, calculations to test this point have been hampered by the lack of reliable wavefunctions,¹² and it has never been made explicit what role other configurations of the same parity play in causing this term inversion.

⁸ A comprehensive review of the many-electron correlation problem up to the year 1959 has been given by P.-O. Löwdin, *Advan. Chem. Phys.* **2**, 207-322 (1959); H. Yoshizumi, *ibid.*, pp. 323-365. A discussion of some of the more current approaches is found in *Rev. Mod. Phys.* **35**, pp. 415-735 (1963).

⁹ G. Racah, *Phys. Rev.* **62**, 438 (1942).

¹⁰ Throughout this paper we compare calculated energies to the observed center of gravity of the multiplet levels. Our justification for this procedure is the assumption that the Russell-Saunders coupling scheme is valid for these light atoms. The position of the center of gravity, given by the average of the multiplet level energies, each one weighted by the factor $2J+1$, may then be shown to be unaffected by the spin-orbit interaction (E. U. Condon and G. H. Shortley, *TAS*, p. 195).

¹¹ R. F. Bacher, *Phys. Rev.* **43**, 264 (1933).

¹² Bacher calculated the energy difference between the Mg I 1D and 3D multiplet terms (Ref. 11) by taking the average configuration energies as given by experiment and using "truncated" Slater orbitals to estimate the radial parameter $R^1(3s3d; 3p3p)$ which connects the two configurations. He found at first $R^1(3s3d; 3p3p) = 25\,620 \text{ cm}^{-1}$, so that the 1D term was 4164 cm^{-1} below the 3D . The value of $R^1(3s3d; 3p3p)$ was later revised to $21\,387 \text{ cm}^{-1}$ [R. F. Bacher, *Phys. Rev.* **56**, 385 (1939)], which markedly improves the numerical agreement, placing the 1D 2234 cm^{-1} below the 3D term. However, L. Pincherle, *Phys. Rev.* **58**, 251 (1940), recalculated $R^1(3s3d; 3p3p)$ using Thomas-Fermi wavefunctions and found the value $23\,060 \text{ cm}^{-1}$, which would worsen the agreement. Although these calculations of the interaction between the $3p^2$ and $3s3d$ configurations show that this is of the right order of magnitude to account for the inversion of the 1D term, this does not quantitatively establish this point. Similarly, the earlier study of the 1D and 3D multiplet spacings in the Al II spectrum by L. Pincherle, *Nuovo Cimento* **10**, 37 (1933), appears to be more suggestive than conclusive.

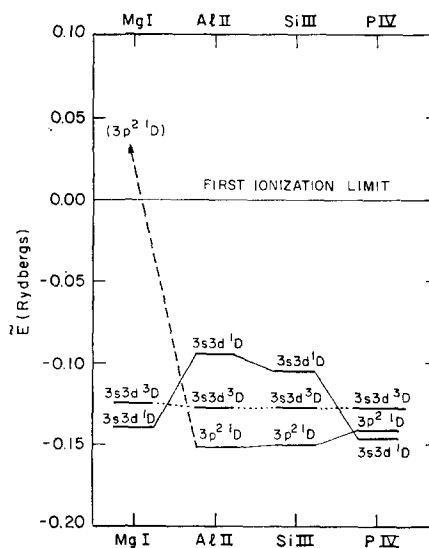


FIG. 1. Reduced 1D and 3D term energies (observed) in the magnesium isoelectronic sequence arising from the $3s3d$ and $3p^2$ configurations.

Furthermore, no attempt has been made to determine the related but more complicated splitting pattern of the entire $3snd$ series.

The regular variation of energy term values with increasing nuclear charge has long been to atomic spectroscopists a powerful tool for checking their assignments and predicting the location of energy levels in ions whose spectra have not yet been observed in the laboratory.¹³ We might imagine a power supply attached to the nucleus and inquire what happens to the energy levels as we slowly "turn up" the nuclear charge. As the electrons are pulled in more closely about the nucleus, the absolute energies of the term values are observed to increase almost quadratically with the "excess" nuclear charge $\zeta = (Z - N + 1)$, while the relative positions are often little changed. Thus a plot of the "reduced" term energy $\bar{E} = E/\zeta^2$ against the excess nuclear charge ζ should reveal a nearly linear variation of \bar{E} which runs almost parallel to the ζ axis. Yet when we examine the 1D terms arising from the $3s3d$ and $3p^2$ configurations, as shown in Fig. 1, we find that their behavior appears to be quite irregular and perplexing. This fact becomes particularly striking if we contrast this with the smooth variation of the $3s3d$ 3D term along the isoelectronic sequence. From the spectroscopic data¹¹ it would appear that the lowest-lying 1D term belongs to the $3s3d$ configuration for Mg I, the $3p^2$ configuration for Al II and Si III, but the $3s3d$ configuration once again for P IV. Thus the $3p^2$ 1D

¹³ B. Elden, "Atomic Spectra," *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1964), Vol. 27, p. 80.

¹⁴ Our sources of spectroscopic data are the following: (a) for the Mg I spectrum, G. Risberg, *Arkiv Fysik* **28**, 381 (1965); (b) for the Al II and P IV spectra, C. E. Moore, *Natl. Bur. Std. (U.S.) Circ. No. 467*, 1 (1949), and the references contained therein; and (c) for the Si III spectrum, Y. G. Toresson, *Arkiv Fysik* **18**, 389 (1960-1961).

term apparently descends from above the ionization continuum in Mg I to the lowest-lying 1D term found in the Al II spectra. This seemingly paradoxical behavior has caused grave questioning of the present spectral assignments, although these spectra have been studied by several observers. It was in an attempt to answer these questions and to gain deeper insight into the consequences of configuration interaction that these studies were undertaken.

THEORY

The approximate Hamiltonian for an N -electron atom with nuclear charge Z may be written as the sum over one-electron and two-electron operators

$$\mathcal{H} = \sum_{i=1}^N f_i + \sum_{i>j=1}^N g_{ij}, \quad (1)$$

where

$$f_i = -\nabla_i^2 - 2Z/r_i \quad (2)$$

describes (in Bohr units for distance and rydbergs for energy) the motion of the i th electron in the Coulomb field of the point nucleus, and

$$g_{ij} = 2/r_{ij} \quad (3)$$

expresses the instantaneous Coulomb repulsion of the i th and j th electrons. The fundamental problem in the theory of complex spectra is to solve Schrödinger's equation

$$\mathcal{H}\psi = E\psi \quad (4)$$

for the eigenvalues E and corresponding wavefunctions ψ of the many-electron atom. This task is rendered arduous by the presence of the interelectronic repulsion terms g_{ij} in (1) which prevent a separation of variables. In all but the simplest atoms, resort is made to further approximation.

Independent-Particle Model

In the one-electron model of the atom we introduce the fiction of a central field potential $V(r_i)$ to describe the forces experienced by the i th electron in the field of the nucleus and in the suitably averaged fields of every other electron. By this mathematical device we may replace the Hamiltonian (1) by an auxiliary Hamiltonian

$$H_{CF} = \sum_{i=1}^N [-\nabla_i^2 + V(r_i)], \quad (5)$$

whose solutions are separable and are given by a set of one-electron wavefunctions $u_i(nlms)$, customarily called spin orbitals, each of which is a product of a radial and an angular part:

$$u_i(nlms) = r^{-1} P_{nl}(r) Y_{lm}(\theta, \phi) \begin{cases} \alpha \\ \beta \end{cases}. \quad (6)$$

In Eq. (6) the radial function $P_{nl}(r)$ depends on the

form of the central field potential, the angular function $Y_{lm}(\theta, \phi)$ is a spherical harmonic, and the spin of the electron is taken into account by choosing either α or β corresponding to the two possible orientations $\pm\frac{1}{2}$ of the projection of the spin along the axis of quantization.

Configuration Mixing

The central-field Hamiltonian H_{CF} gives rise to a series of energy levels E_k , called configurations, each associated with a corresponding set A_k of spin orbitals. Once the set of spin orbitals has been determined for each configuration, we can, in principle, improve upon the solution to (5) by taking the difference potential $\mathcal{H} - H_{CF}$ into account. This is equivalent to expanding the total wavefunction ψ of the system in terms of the configuration wavefunctions A_k as a basis set

$$\psi = \sum_k c_k A_k. \quad (7)$$

We can then convert the problem of solving Schrödinger's equation (2) into that of finding the coefficients c_k of the expansion. By substituting Eq. (7) into Eq. (2) we obtain an infinite set of simultaneous equations:

$$\sum_k c_k (\mathcal{H}c_{nk} - E\delta_{nk}) = 0. \quad (8)$$

This procedure will be practicable only if ψ can be approximated rapidly by a truncated series in the function A_k so that our problem reduces to the solution of a finite secular equation of moderate size:

$$|\mathcal{H}c_{nk} - E\delta_{nk}| = 0. \quad (9)$$

In principle there is no limit to how accurately we can determine ψ , provided the basis set A_k is a complete one; in practice we are limited by our patience and computing facilities. Thus it is most important that we choose an orthonormal set A_k so that the expansion of ψ in that set is rapidly convergent.

Hartree-Fock-Slater Basis Set

The "best" one-electron wavefunctions for a many-electron system can be determined by the variation principle. One begins by constructing an approximate many-electron wavefunction A_k in terms of a set of spin orbitals u_i and varies the average energy of the atomic system with respect to each u_i . This leads in general to a set of coupled integrodifferential equations which may be solved iteratively in a self-consistent manner for the u_i that make the energy an extremum. The actual form of the variational equations depends upon the representation chosen for A_k . If A_k is given by a simple product of spin orbitals, we are led to the Hartree equations; if A_k is built up from determinantal wavefunctions of the spin orbitals so that the antisymmetry requirement of the total wavefunction is

automatically satisfied, the more complex but more accurate Hartree-Fock equations result.¹⁵

We have adopted the use of a variant to the Hartree-Fock procedure for the generation of a suitable basis set for the expansion of the total wavefunction. This is based on a suggestion by Slater^{2,6} that the essential features of the Hartree-Fock method could be retained by replacing the exchange potential for different orbitals by a universal exchange potential found by treating the charge density of the atom as a free-electron gas. This commonly called Hartree-Fock-Slater (HFS) procedure has been incorporated into a set of computer programs by Herman and Skillman⁷ who have added the important refinement of forcing the potential to have the correct asymptotic behavior at large r .

The resultant HFS variational equations have a simple appearance, the radial wave equations being given by

$$[-d^2/dr^2 + l(l+1)/r^2 + V(r)]P_{nl}(r) = \epsilon_{nl}P_{nl}(r), \quad (10)$$

where $V(r)$ is the single potential in which all the electrons move:

$$V(r) = -\frac{2Z}{r} + \frac{2}{r} \int_0^r \sum_{nl} [P_{nl}(t)]^2 dt + 2 \int_r^\infty \sum_{nl} \frac{[P_{nl}(t)]^2}{t} dt - \left\{ \frac{81}{4\pi^2} r^2 \sum_{nl} [P_{nl}(r)]^2 \right\}^{1/8} \quad (11)$$

for $r < r_0$, and

$$V(r) = -2(Z-N+1)/r \quad (12)$$

for $r \geq r_0$. The critical radius r_0 is the value of r for which Eq. (11) equals Eq. (12).

The solution to the HFS equations for a given configuration E_k is a single Slater determinant A_k built up from the occupied spin orbitals u_i ($i=1, 2, \dots, N$) which constitute the configuration. However there are other spin orbitals besides the occupied spin orbitals whose radial part satisfies the eigenvalue equation posed in (10). All such spin orbitals which are solutions to (10) will be orthogonal to each other. For $l \neq l'$, this follows at once from the properties of the spherical harmonics; for $l=l'$ (but $n \neq n'$), the spin orbitals are solutions of the same Schrödinger equation but for different energies. Determinants constructed from one or more of these "unoccupied" orbitals are referred to as excited-state solutions. The set A_k of determinants built up from all occupied and unoccupied spin orbitals which satisfy (10) form a complete orthonormal set for the expansion of an arbitrary N -electron wavefunction ψ , in particular the solution to the Schrödinger equation for the atomic system.

Due to the Coulomb form of the atomic potential at large r , $V(r)$ holds an unlimited number of discrete

¹⁵ Self-consistent-field methods are discussed at length in D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957). See also J. C. Slater, *QTAS*, Chaps. 9 and 18.

energy levels, of which an important consequence is the association of each Rydberg state of the atom (whether or not it lies above the ionization limit of other Rydberg series) with an excited state determinant A_k composed entirely of bound occupied and unoccupied spin orbitals. This is to be sharply contrasted with the more familiar Hartree-Fock procedure in which the unoccupied spin orbitals loosely correspond to negative ion states of the atom and have radial wavefunctions which are either unbounded or have a large, diffuse spatial extent.¹⁶

The practical advantages of using a basis set having discrete excited-state spin orbitals were stressed by Hylleraas¹⁷ in one of his earliest papers. We are trying to expand the total wavefunction $\psi(\mathbf{r}_i, \mathbf{r}_j)$ whose essential features are concentrated at small values of r_i and r_j . Any truly complete basis set will suffice for this expansion, but a basis set which requires fewer spin orbitals to span the electron space relevant to $\psi(\mathbf{r}_i, \mathbf{r}_j)$ will be more rapidly convergent. Thus, although the HFS procedure yields a total energy of the atom slightly inferior to the Hartree-Fock procedure, it may nevertheless prove to be a superior starting point for treating electronic correlation.

Matrix Elements of Electrostatic Interaction

The matrix components \mathcal{H}_{nk} which appear in the secular equation (9) are found from the general rules for calculating the diagonal and nondiagonal matrix elements of operators between determinantal wavefunctions.¹⁸ The form of the diagonal components, which split each configuration into multiplet terms characterized by a total orbital angular momentum L and spin angular momentum S , is well known; the form of the nondiagonal components, which mix together multiplet terms of the same L , S , and parity, does not appear to have been worked out in detail. Let the N electrons be divided into two groups: the core electrons, denoted by the index κ ; and the valence electrons, denoted by η . The total Hamiltonian (1) may be divided into three parts:

$$\mathcal{H} = \mathcal{H}(\text{core}) + \mathcal{H}(\text{core-valence}) + \mathcal{H}(\text{valence}), \quad (13)$$

where

$$\mathcal{H}(\text{core}) = \sum_{\kappa} f_{\kappa} + \sum_{\kappa' > \kappa} g_{\kappa'\kappa}, \quad (14)$$

$$\mathcal{H}(\text{core-valence}) = \sum_{\eta} f_{\eta} + \sum_{\eta} \sum_{\kappa} g_{\eta\kappa}, \quad (15)$$

and

$$\mathcal{H}(\text{valence}) = \sum_{\eta' > \eta} g_{\eta'\eta}. \quad (16)$$

This decomposition has the significance that $\mathcal{H}(\text{core})$

¹⁶ See, for example, H. P. Kelly, *Phys. Rev.* **131**, 684 (1963); **136**, B896 (1964), who uses excited-state Hartree-Fock solutions in an impressive *tour de force* calculation of the Be atom ground-state correlation energy.

¹⁷ E. A. Hylleraas, *Z. Physik* **48**, 469 (1928).

¹⁸ E. U. Condon and G. H. Shortley, *TAS*, pp. 169-183.

gives the electrostatic interaction of the core electrons with the nuclear charge and with the other core electrons, $\mathcal{H}(\text{core-valence})$ gives the electrostatic interaction of the valence electrons with the nuclear charge and with the core electrons, and $\mathcal{H}(\text{valence})$ represents the electrostatic interaction between the different valence electrons.

We wish to specialize our results to configurations

$$I(n_a l_a, n_c l_c) = \langle n_a l_a | -\nabla^2 - 2Z/r | n_c l_c \rangle \\ = \delta l_a l_c \langle P_{n_a l_a}(r) | -\nabla^2 - 2Z/r | P_{n_c l_c}(r) \rangle, \quad (17)$$

$$A(n_a l_a, n_c l_c) = \sum_{\kappa} \langle n_a l_a n_{\kappa} l_{\kappa} | g_{\kappa\kappa} | n_c l_c n_{\kappa} l_{\kappa} \rangle \\ = \delta l_a l_c \sum_{\kappa} [R^0(n_a l_a, n_{\kappa} l_{\kappa}; n_c l_c, n_{\kappa} l_{\kappa}) + \frac{1}{2} \sum_{k=0}^{\infty} \begin{pmatrix} l_a & k & l_c \\ 0 & 0 & 0 \end{pmatrix} R^k(n_a l_a, n_{\kappa} l_{\kappa}; n_{\kappa} l_{\kappa}, n_c l_c)], \quad (18)$$

and

$$E(n_a l_a, n_b l_b; n_c l_c, n_d l_d) = \langle n_a l_a n_b l_b | g_{\eta'\eta} | n_c l_c n_d l_d \rangle \\ = (-1)^{l_a+l_c} [4(2l_a+1)(2l_b+1)(2l_c+1)(2l_d+1)/N_{ab}N_{cd}]^{\frac{1}{2}} \\ \times \sum_{k=0}^{\infty} [(-1)^L \begin{Bmatrix} l_a & l_b & L \\ l_d & l_c & k \end{Bmatrix} \begin{pmatrix} l_a & k & l_c \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & k & l_d \\ 0 & 0 & 0 \end{pmatrix} R^k(n_a l_a, n_b l_b; n_c l_c, n_d l_d) \\ + (-1)^S \begin{Bmatrix} l_a & l_b & L \\ l_c & l_d & k \end{Bmatrix} \begin{pmatrix} l_a & k & l_d \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & k & l_c \\ 0 & 0 & 0 \end{pmatrix} R^k(n_a l_a, n_b l_b; n_d l_d, n_c l_c)], \quad (19)$$

where R^k is the generalized electrostatic radial integral

$$R^k(n_a l_a, n_b l_b; n_c l_c, n_d l_d) = 2 \int_0^{\infty} \int_0^{\infty} \frac{r_1^{<k}}{r_2^{>k+1}} P_{n_a l_a}(r_1) P_{n_b l_b}(r_2) P_{n_c l_c}(r_1) P_{n_d l_d}(r_2) dr_1 dr_2, \quad (20)$$

and the angular factors are expressed in terms of 3- j and 6- j symbols.¹⁹ The normalization factors N_{ab} and N_{cd} for the antisymmetrized electronic wavefunctions,

$$\langle n_a l_a n_b l_b | = \langle n_a l_a | \langle n_b l_b | + (-1)^{L+S+l_a+l_b} \langle n_b l_b | \langle n_a l_a |, \quad (21a)$$

$$| n_c l_c n_d l_d \rangle = | n_c l_c \rangle | n_d l_d \rangle + (-1)^{L+S+l_c+l_d} | n_d l_d \rangle | n_c l_c \rangle, \quad (21b)$$

have the value

$$N_{ab}=2, \quad n_a l_a \neq n_b l_b, \\ N_{ab}=4, \quad n_a l_a = n_b l_b, \quad (22a)$$

$$N_{cd}=2, \quad n_c l_c \neq n_d l_d, \\ N_{cd}=4, \quad n_c l_c = n_d l_d. \quad (22b)$$

We present in Table I general expressions for the matrix elements of the many-electron Hamiltonian \mathcal{H} in terms of the special quantities, I , A , and E , defined

¹⁹ M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3- j and 6- j symbols* (The Technology Press, Cambridge, Mass., 1959).

having two valence electrons outside a core of closed shells. Let A and B represent two different determinantal wavefunctions with valence spin orbitals denoted by $n_a l_a, n_b l_b$ and $n_c l_c, n_d l_d$, respectively. We suppose that the core electrons of A and B are the same, and that identical spin orbitals of A and B appear in the same order. It proves useful to introduce the following special notation for frequently encountered matrix elements:

in Eqs. (17)–(19). These results are obtained by considering the form of the matrix elements of the operators $\mathcal{H}(\text{core})$, $\mathcal{H}(\text{core-valence})$, and $\mathcal{H}(\text{valence})$ into which the total Hamiltonian can be factored. For example, the nondiagonal matrix components $\langle A | \mathcal{H}(\text{core}) | B \rangle$ vanish, since A and B are assumed to have identical core electrons. The diagonal components $\langle A | \mathcal{H}(\text{core}) | A \rangle$ and $\langle B | \mathcal{H}(\text{core}) | B \rangle$ are equal. Their value has been denoted in Table I by $E(\text{core})$, and explicit expressions for $E(\text{core})$ have been presented elsewhere.²⁰

The nondiagonal matrix components of $\mathcal{H}(\text{core-valence})$ vanish unless the configurations A and B differ only in regard to one set of spin orbitals $n_a l_a, n_b l_b$ and $l_a = l_b$. If this condition is met,

$$\langle A | \mathcal{H}(\text{core-valence}) | B \rangle \\ = I(n_a l_a, n_b l_b) + A(n_a l_a, n_b l_b), \quad (23)$$

where the values of the two terms in Eq. (23) are of roughly comparable magnitude but of opposite sign. The determinants A and B are almost eigenfunctions

²⁰ J. C. Slater, *QTAS*, Vol. 2, p. 18.

of the total Hamiltonian \mathcal{H} , and thus it is not surprising to find that the value of this matrix element is small compared to the total energy of the atomic system. However, it is to be emphasized that this does not mean the contribution of this term to the multiplet energy difference is always insignificant.²¹ The diagonal matrix components of \mathcal{H} (core-valence) are obtained from Eq. (23) by setting $n_{AlA} = n_{BlB}$. We introduce the abbreviated quantities $I(n_{AlA})$ for $I(n_{AlA}, n_{AlA})$ and $A(n_{AlA})$ for $A(n_{AlA}, n_{AlA})$ in Table I. Reference to Eqs. (14)–(15) for this special case shows that $I(n_{AlA})$ corresponds to the one-electron expectation value designated with the same name by Slater,²² and that $A(n_{AlA})$ corresponds to the “average interaction energy of a pair of nonequivalent electrons” summed over the closed

shells of core electrons.²³ The diagonal electrostatic interaction matrix elements of \mathcal{H} (core-valence) were first calculated by Shortley²⁴; the nondiagonal matrix elements by Ufford,²⁵ who gave the form of $A(n_{AlA}, n_{BlB})$ but did not mention the contribution $I(n_{AlA}, n_{BlB})$ from the one-electron operators.

The nondiagonal matrix components of \mathcal{H} (valence) are readily evaluated from the Wigner-Eckart theorem¹⁹ and can be shown to be identical to the expression $E(n_{Ala}, n_{Bb}; n_{c}, n_{d})$ given in Eq. (19). This differs from a previous result given by Wybourne.²⁶ The diagonal matrix elements of \mathcal{H} (valence) are written in Table I in the more concise form $E(n_{Ala}, n_{Bb})$. An explicit expression for $E(n_{Ala}, n_{Bb})$ is found from Eq. (19) by setting $n_{Ala} = n_{c}$ and $n_{Bb} = n_{d}$. The resulting equation agrees with an expression previously derived by Möller.²⁷

In Table I the spin orbitals of A and B are ordered in standard form, according to the convention adopted by Condon and Shortley.²⁸ However, in calculating the nondiagonal matrix elements of \mathcal{H} , sometimes it is necessary to reorder the spin orbitals so that identical spin orbitals of A stand in the same place as identical spin orbitals of B . The permutations required to produce the new reordering give rise to the phase factors appearing in Table I. These phase factors do not alter the energy values which are the roots of the secular equation, but they do affect the relative phases of the configuration interaction wavefunctions.

To illustrate the use of Table I, we give some examples of the matrix elements resulting from the interaction of 1D terms:

$$(3s3d | \mathcal{H} | 3s3d) = E(\text{core}) + I(3s) + I(3d) + A(3s) + A(3d) + R^0(3s3d; 3s3d) + \frac{1}{2}R^2(3s3d; 3d3s), \quad (24a)$$

$$(3s3d | \mathcal{H} | 3p^2) = 2/(15)^{1/2}R^1(3s3d; 3p3p), \quad (24b)$$

and

$$(3s3d | \mathcal{H} | 3s4d) = I(3d, 4d) + A(3d, 4d) + R^0(3s3d; 3s4d) + \frac{1}{2}R^2(3s3d; 4d3s), \quad (24c)$$

where we have denoted the configuration $1s^22s^23s3d$ by $3s3d$, etc. In such a manner explicit expressions are found for all the matrix elements of the secular equation.

CALCULATIONS AND DISCUSSION

Reference Energy

Computer programs have been written to perform the necessary integrals indicated in Eqs. (17)–(19) and

²³ *QTA S*, Vol. 1, p. 325.

²⁴ G. H. Shortley, *Phys. Rev.* **40**, 185 (1932).

²⁵ C. W. Ufford, *Phys. Rev.* **44**, 732 (1933).

²⁶ B. G. Wybourne, *Phys. Rev.* **137**, A364 (1965). Dr. Wybourne has confirmed (by private correspondence) that the sign of the second term of his Eq. (2) should be changed from minus to plus. Then Eq. (2) agrees with our Eq. (18) for the case of nonequivalent electrons.

²⁷ N. H. Möller, *Arkiv Fysik* **18**, 135 (1960–1961).

²⁸ E. U. Condon and G. H. Shortley, *TAS*, pp. 168–169.

TABLE I. Electrostatic-interaction matrix elements of the many-electron Hamiltonian.

A. Diagonal matrix elements

$$(A | \mathcal{H} | A) = E(\text{core}) + I(n_{Ala}) + I(n_{Bb}) + A(n_{Ala}) + A(n_{Bb}) + E(n_{Ala}, n_{Bb})$$

B. Nondiagonal matrix elements

1. $n_{Ala}, n_{Bb} \neq n_{c}, n_{d}$

$$(A | \mathcal{H} | B) = E(n_{Ala}, n_{Bb}; n_{c}, n_{d})$$

2. $n_{Bb} = n_{Ala}, n_{Ala} \neq n_{c}$

$$(A | \mathcal{H} | B) = I(n_{Ala}, n_{c}) + A(n_{Ala}, n_{c}) + E(n_{Ala}, n_{Bb}; n_{c}, n_{d})$$

3. $n_{Ala} = n_{c}, n_{Bb} \neq n_{d}$

$$(A | \mathcal{H} | B) = I(n_{Bb}, n_{d}) + A(n_{c}, n_{d}) + E(n_{Ala}, n_{Bb}; n_{c}, n_{d})$$

4. $n_{Bb} = n_{c}, n_{Ala} \neq n_{d}$

$$(A | \mathcal{H} | B) = (-1)^{L+S+I_c+I_d} [I(n_{Ala}, n_{d}) + A(n_{Ala}, n_{d}) + E(n_{Ala}, n_{Bb}; n_{c}, n_{d})]$$

5. $n_{Ala} = n_{d}, n_{Bb} \neq n_{c}$

$$(A | \mathcal{H} | B) = (-1)^{L+S+I_c+I_d} [I(n_{Bb}, n_{c}) + A(n_{Bb}, n_{c}) + E(n_{Ala}, n_{Bb}; n_{c}, n_{d})]$$

²¹ The literature appears to be unclear on this topic as a review of previous expressions for the interaction between the $3s3d$ and $3s4d$ configurations will show. For example, R. F. Bacher (Ref. 11, pp. 268–269) equates $(3s3d | \mathcal{H} | 3s4d)$ to $R^0(3s3d; 3s4d) + 1/5R^2(3s3d; 4d3s)$, and does not mention the matrix element of \mathcal{H} (core-valence). On the other hand L. Biermann and E. Trefftz, *Z. Astrophys.* **26**, 213 (1949); E. Trefftz, *ibid.*, p. 240; *ibid.* **28**, 67 (1950) in a study of the effects of configuration interaction on the Mg I $3s3d$ line intensities, using a Hartree-Fock calculation including an adjustable polarization potential, set the value of $(3s3d | \mathcal{H} | 3s4d)$ to zero without discussion. It is tempting to believe that this follows from Brillouin's theorem for Hartree-Fock singly excited states, L. Brillouin, *Act. Sci. et Ind. Nos.* **71**, 159, 160 (1933–1934); C. Möller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934). However, Brillouin's theorem states that this matrix element vanishes only up to second order in the total energy for the true Hartree-Fock wavefunction. Using our HFS basis set, we have calculated $(3s3d | \mathcal{H} | 3s4d)$ from Eq. (23c) and find for Mg I the value 0.01346 Ry. This is not a negligible quantity when compared to the value of the $(3s3d | \mathcal{H} | 3p^2)$ interaction matrix element, which is found from Eq. (23b) to be 0.07302 Ry.

²² J. C. Slater, *QTA S*, Vol. 1, p. 217.

to solve the resulting secular equation for its energy values and wavefunctions.²⁹ The atomic potential $V(r)$ used in all calculations has been constructed to be the "best" potential from the standpoint of the variational principle for the $3s3d$ configuration. Consequently the core electrons of all configurations are identical and the energy of the core electrons $E(\text{core})$ is common to all diagonal matrix elements of \mathcal{H} . Since the solutions to the HFS equations satisfy a variational principle, the calculated total energy is an upper bound to the true energy of the system. However, we choose to sacrifice this weak condition for a more convenient energy scale. Our primary interest is in the energy separation between different multiplets, rather than the absolute energy positions of the multiplets. Consequently we do not evaluate $E(\text{core})$, which would allow us to calculate the total energy required to strip off all the electrons of the atom to lay the nucleus bare, but we adopt instead as our reference energy the calculated ionization potentials of the $3s3d\ ^1D$ and $\ ^3D$ multiplet terms. From Koopmans' theorem³⁰ the eigenvalues ϵ_{nl} appearing in Eq. (10) are to a good approximation the differences between the average energy of the atom with and without the nl th electron. By average energy we mean the weighted average of the multiplet energies, each one counted $(2L+1)(2S+1)$ times.³¹ The ionization energies of the $3s3d\ ^1D$ and $\ ^3D$ terms are thus given by

$$E(3s3d\ ^1D) = \epsilon_{3d} + \frac{1}{10}R^2(3s3d; 3d3s) \quad (25a)$$

and

$$E(3s3d\ ^3D) = \epsilon_{3d} - \frac{3}{10}R^2(3s3d; 3d3s). \quad (25b)$$

Equations (25a) and (25b) have been used throughout for fixing the absolute energy values of the roots of the secular equation.

Solutions to the Secular Equation

For our configuration interaction calculations, we selected at first a small basis set consisting of the $3s3d$, $3s4d$, $3s5d$, and $3p^2$ configurations. This proves sufficient to demonstrate the major effects of configuration interaction on the $3s3d\ ^1D$ and $\ ^3D$ multiplet spacing. For example, the Mg I $3s3d\ ^1D$ term, which would lie about 1440 cm^{-1} above the $\ ^3D$ term in the absence of configuration interaction, is found, when using this limited basis set, to be 1199 cm^{-1} below the $\ ^3D$ term. This is to be compared with the observed term inversion which places the $\ ^1D$ term 1554 cm^{-1} below the $\ ^3D$ term. The basis set was then extended to include all those interacting configurations $nl'n'l'$ whose principal quantum numbers are restricted to $n=3$ and $n'=3$ or 4 . The rationale for this choice was the hope that such

orbitals would have a compact spatial extent and thus accelerate convergence. In addition the $3s6d$ member was also included so that we might better observe interactions with the entire $3snd$ series. The final composition of the basis set amounts to 10 difference configurations: $3s3d$, $3s4d$, $3s5d$, $3s6d$, $3p^2$, $3p4p$, $3p4f$, $3d^2$, $3d4s$, and $3d4d$. Using the basis set the Mg I $\ ^1D$ term is calculated to lie 1530 cm^{-1} below the $\ ^3D$ term, or within 24 cm^{-1} of the observed splitting. Due to numerical inaccuracies we estimate that our calculated multiplet separations should be no more accurate than 1 cm^{-1} , and perhaps off by as much as 10 cm^{-1} .

We have concentrated our attention so far on determining the energies of the $3s3d\ ^1D$ and $\ ^3D$ multiplets found by solving an $N \times N$ secular equation for each different multiplet term. It would be somewhat disheartening to solve a separate $N \times N$ secular equation for the wavefunction and energy value of each term of the atom having the same multiplet structure, but arising from a different configuration. Fortunately this appears to be unnecessary when the HFS determinantal wavefunctions constitute the basis set. As we noted before, we may identify the excited-state HFS determinants with the excited states of the atom. Thus, as we treat the $3s3d\ ^1D$ or $\ ^3D$ terms by configuration mixing, we solve simultaneously for the other energy terms of the atom corresponding to the same multiplet designation.

In Table II we compare the calculated $\ ^1D$ and $\ ^3D$ term energies with the spectroscopic data available¹⁴ for the magnesium isoelectronic sequence from Mg I to P IV. One might wonder whether the potential found to be "best" for the $3s3d$ configuration would be a prudent choice for calculating the term energies arising from other configurations. Equations (11) and (12) indicate, however, that the form of $V(r)$ is determined predominantly by the numerically preponderate core electrons. If these inner electrons change little from one configuration to another, it would be plausible to expect that $V(r)$ is a good starting point for subsequent configuration-interaction calculations, and that the N -term energies which are roots to the same secular equation might be of comparable accuracy. For the $\ ^1D$ and $\ ^3D$ terms of the magnesium isoelectronic sequence, numerical calculations presented in Table II largely substantiate this conjecture.

However, closer inspection of Table II reveals that the agreement between the calculated and observed term energies is better for those terms arising from low-lying configurations than from highly excited configurations. This is not surprising since the choice of basis-set configurations emphasized selecting those interacting configurations which would most affect the positions of the multiplet terms arising from the $3s3d$ configuration. We note in Table II that the calculated values of the higher members of the $3snd$ series lie above the observed values, indicating that we have neglected the presence of higher-lying configurations which would push downwards on these term values.

²⁹ These programs have been documented in R. N. Zare, JILA Rept. No. 80 (Joint Institute for Laboratory Astrophysics, Boulder, Colorado, 1966). The time required per element to calculate all the energy levels and wavefunctions for the different interacting configurations is less than 5 min on an IBM 7094 computer.

³⁰ T. A. Koopmans, *Physica* **1**, 104 (1933).

³¹ J. C. Slater, *QTAS*, Chap. 14.

TABLE II. Comparison of calculated and observed 1D and 3D energy term values of the Mg I isoelectronic sequence. The term values are designated by the traditional configuration assignments, and the energy units are in rydbergs, measured from the first ionization limit of the atom as zero.

Configura- tion	1D (calc)	1D (obs)	3D (calc)	3D (obs)
Mg I				
$3s3d^a$	-0.14022	-0.13913	-0.12628	-0.12497
$3s4d^a$	-0.08090	-0.07779	-0.07224	-0.06815
$3s5d$	-0.05383	-0.04887	-0.04874	-0.04285
$3s6d$	-0.03916	-0.03324	-0.03598	-0.02942
$3p^2^b$	+0.07263	c
$3p4p^a$	+0.24496	c	+0.16868	c
$3p4f$	+0.23520	c	+0.23550	c
$3d^2^a$	+0.52836	c
$3d4s^a$	+0.44766	c	+0.42852	c
$3d4d$	+0.60695	c	+0.57372	c
Al II				
$3s3d^b$	-0.37396	-0.38066	-0.51302	-0.51316
$3s4d^a$	-0.24329	-0.24667	-0.28752	-0.27684
$3s5d^a$	-0.16859	-0.16354	-0.18901	-0.17351
$3s6d^a$	-0.11983	-0.11458	-0.13620	-0.11891
$3p^2^a$	-0.61560	-0.60491
$3p4p^a$	+0.12330	c	+0.02663	c
$3p4f$	+0.20773	c	+0.20777	c
$3d^2^a$	+0.47314	c
$3d4s^a$	+0.56227	c	+0.46381	c
$3d4d$	+0.78637	c	+0.71669	c
Si III				
$3s3d^a$	-0.92861	-0.95113	-1.15450	-1.15908
$3s4d^a$	-0.60270	-0.59969	-0.63937	-0.62459
$3s5d$	-0.40525	-0.38705	-0.41316	-0.39234
$3s6d^d$	-0.29452	-0.26964	-0.29707	-0.27197
$3p^2^a$	-1.36471	-1.34799
$3p4p^a,d$	-0.14017	-0.20234	-0.25017	-0.22950
$3p4f$	+0.04702	c	+0.05133	c
$3d^2^a$	+0.30907	c
$3d4s^a$	+0.43841	c	+0.36714	c
$3d4d$	+0.86270	c	+0.75215	c
P IV				
$3s3d^a$	-1.75076	e	-2.04508	-2.04965
$3s4d$	-1.09927	-1.07124	-1.12549	-1.10328
$3s5d^a,d$	-0.72696	-0.66803(?)	-0.72990	e
$3s6d^a$	-0.47814	e	-0.49427	e
$3p^2^a$	-2.35828	-2.33443
$3p4p^a,d$	-0.57823	e	-0.66094	-0.68048
$3p4f^a$	-0.27492	e	-0.23381	e
$3d^2^a$	-0.07860	e
$3d4s$	+0.19848	c	+0.13156	c
$3d4d$	+0.80643	c	+0.65822	c

^a Spectral purity of the 1D wavefunction is below 90%.

^b Spectral purity of the 1D wavefunction is below 50%.

^c This term has not been observed; it is predicted to lie above the first ionization continuum of the atom.

^d Spectral purity of the 3D wavefunction is below 90%.

^e This term has not been observed; it is predicted to lie below the first ionization continuum of the atom.

TABLE III. Energy separation between the 1D and 3D terms arising from the $3s3d$ configuration of the Mg I isoelectronic sequence. We use throughout the conversion factor $1 \text{ Ry} = 109\,737.31 \text{ cm}^{-1}$.

Atom	$[^1D-^3D]_{\text{calc}}$	$[^1D-^3D]_{\text{obs}}$	$\Delta[\text{calc-obs}]$
Mg I	-1 530 cm^{-1}	-1 554 cm^{-1}	24 cm^{-1}
Al II	15 260	14 540	720
Si III	24 789	22 820	1969
P IV ^a	-31 251	-33 868	2617

^a The $(3s3d-3p^2)$ 1D term has not been observed; the calculated difference P IV ($^1D-^3D$) is $32\,298 \text{ cm}^{-1}$. We show instead the difference between the $3p^2$, $3s3d$ 1D term and the $3s3d$ 3D term of P IV.

For example, the $3p5p$ configuration might have a significant influence on the multiplet terms of the $3s5d$ configuration, but has not been included in our basis set.

Table II also shows that the energy differences between the calculated and observed 1D and 3D terms increase as we go from Mg I to P IV. This is illustrated in Table III for the 1D and 3D terms of the $3s3d$ configuration. However, the absolute energy positions of the terms grow nearly quadratically with effective nuclear charge, and a much fairer comparison is made between the calculated and observed reduced energies $\bar{E} = E/(Z-N+1)^2$, from which it is found that the agreement of term-energy differences is comparable along the isoelectronic sequence.

This comparison is pictured in Figs. 2(a), 2(b), 2(c), and 2(d) for the 1D and 3D terms arising from the $3s3d$, $3s4d$, and $3p^2$ configurations, for Mg I to P IV, respectively. The entries to the extreme left in each plot are the average energies of each configuration. The next entries result from "turning on" the electrostatic interactions which produce the multiplet structure of each configuration (for clarity the 1S and 3P terms of the $3p^2$ configuration have been omitted). The third set of entries result from "turning on" the electrostatic interaction between the configurations comprising the basis set. This is to be compared with the observed term energies shown on the extreme right. Figure 2 illustrates the remarkable manner in which the multiplet splitting pattern changes with configuration mixing.

We find on further examination of Table II that all term energies predicted to lie above the $3sEd$ ionization continuum, and hence subject to autoionization, have not been observed. Our calculations also predict the location of several unreported term values below the first ionization continuum. The analyses of the Si III and P IV spectra contained in Ref. 14(b) appear to be quite fragmentary and, in some instances, incorrect. For Si III this situation has been remedied by the recent, detailed work of Torreson,¹⁴ who has greatly improved our understanding of this spectrum. In particular he finds that the term called $3p^2$ 1D in Ref. 14(b) is spurious, and the term called $3s3d$ 1D should be renamed the $3p^2$ 1D . Our calculations given in Tables

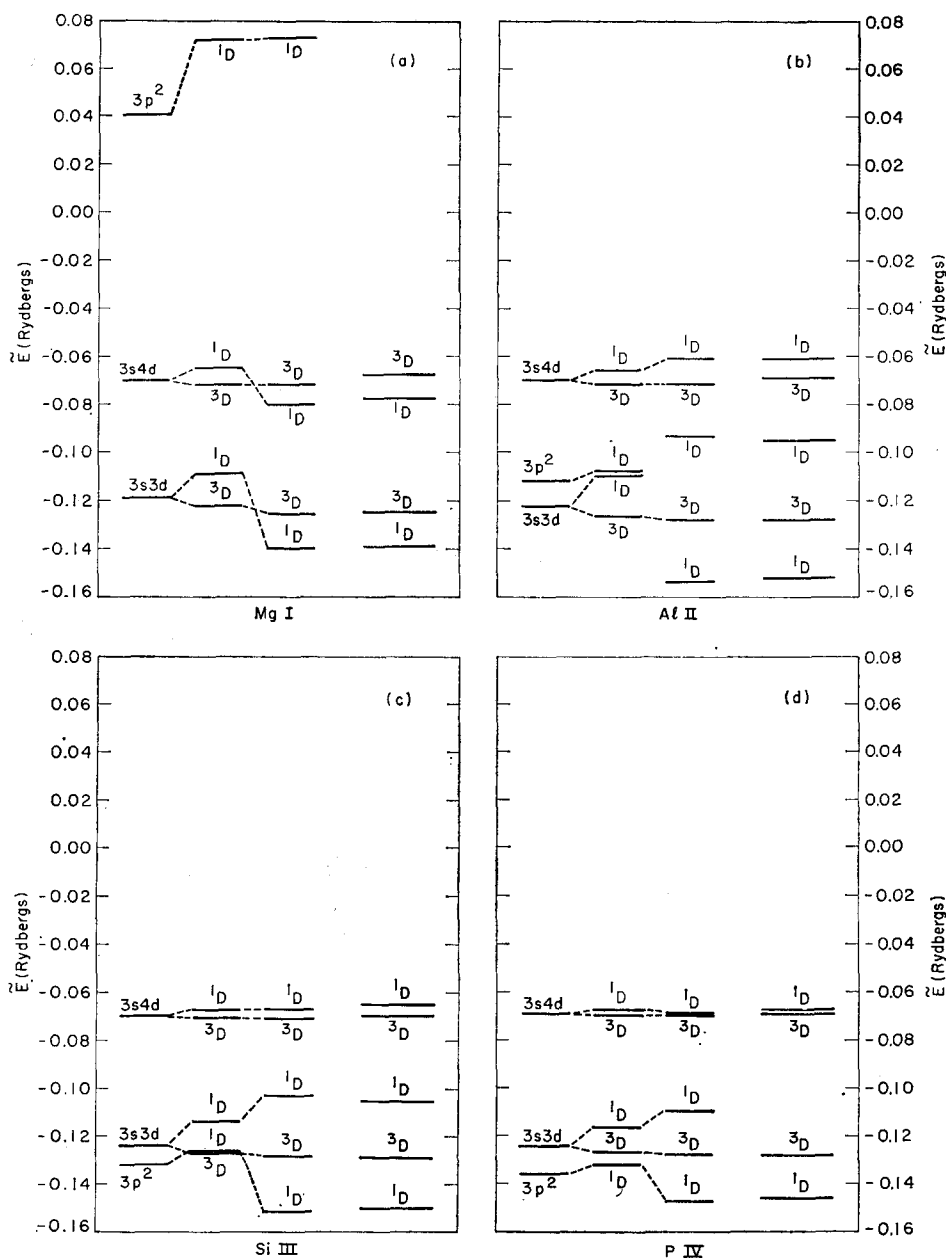


FIG. 2. Comparison between calculated and observed reduced energies of the 1D and 3D term values arising from the $3s3d$, $3s4d$, and $3p^2$ configurations. On the extreme left of each plot is shown the average energy of each configuration. The two center panels picture the calculated positions of the multiplet energies, neglecting and including configuration interaction, respectively. On the extreme right are the observed multiplet energy levels. The dashed lines are suggestive of the displacement the term values suffer due to mutual perturbations among like terms. For Al II these have been omitted for the low-lying 1D terms since the interaction is too violent to give this representation much meaning.

II and III are in close agreement with his observations and thus support his conclusions.

In the spectrum of P IV we find from our calculations that a similar reinterpretation is necessary: namely, the P IV $3p^2\ ^1D$ term given in Ref. 14(b) and pictured in Fig. 1 is not real; the $3s3d\ ^1D$ term should be more appropriately labeled the $3p^2\ ^1D$ term; and the true $3s3d\ ^1D$ term has not yet been identified. In Fig. 3 we have redrawn Fig. 1 to show the variation of the calculated reduced 1D and 3D energies of the $3s3d$ and $3p^2$ configurations along the isoelectronic sequence. On comparing Fig. 1 to Fig. 3 we observe that this removes several of the inexplicable kinks in the former plot.

Table II predicts that the unobserved P IV $3s3d\ ^1D$ term will be found $192\ 124\ \text{cm}^{-1}$ below the first ionization limit. By analogy to the Si III spectrum [Fig. 2(c)], we expect this calculated value is slightly too high, the actual $3s3d\ ^1D$ term energy lying about $2500\ \text{cm}^{-1}$ farther below the ionization continuum. Our calculations also give support to the assignment of the $3s5d\ ^1D$ term entered in Ref. 14(b) with a question mark. However the so-called $3s5d\ ^3D$ term in Ref. 14(b) is found to be rather the P IV $3p4p\ ^3D$ term; the true $3s5d\ ^3D$ term has not been observed but is calculated in Table II to lie $7565\ \text{cm}^{-1}$ above the $3p4p\ ^3D$ term. Thus it is apparent that these rapid programs²⁹ offer a powerful means of checking previous spectral

term assignments as well as predicting the location of term values which have not yet been identified.

Configuration Crossings

Figure 2 singles out the Al II spectrum as an outstanding example of the violent perturbations which arise among like multiplet terms when two interacting configurations draw close to each other. This occurs in the magnesium isoelectronic sequence when the $3p^2$ configuration crosses over the $3s3d$ configuration, as shown in Fig. 3. We call this event, which is a function of effective nuclear charge, a *configuration crossing* by analogy to potential-energy curve crossings of diatomic molecules³² which occur as a function of internuclear distance and hence also of effective nuclear charge. We wish to examine what happens to the multiplet term splitting pattern during a configuration crossing and why configuration crossings occur along an isoelectronic sequence.

An answer to the first question is given, in part, by Fig. 4, which illustrates the detailed manner in which the strong perturbation between the $3s3d$ and $3p^2$ 1D terms affects the entire Al II $3snd$ series. To the extreme left we picture the calculated average energies of the $3s3d$, $3p^2$, $3s4d$, $3s5d$, and $3s6d$ configurations. The next panel to the right shows the energy positions of the 1D terms arising from these configurations. The $3p^2$ 1D and $3s3d$ 1D terms are seen to be nearly resonant. We obtain the third panel by letting the $3s3d$ and $3p^2$ 1D terms interact, and the next panel by including the interaction of the $3s4d$ 1D term, and so forth for each higher member of the $3snd$ series. To the extreme right is placed the observed 1D term energies for comparison.

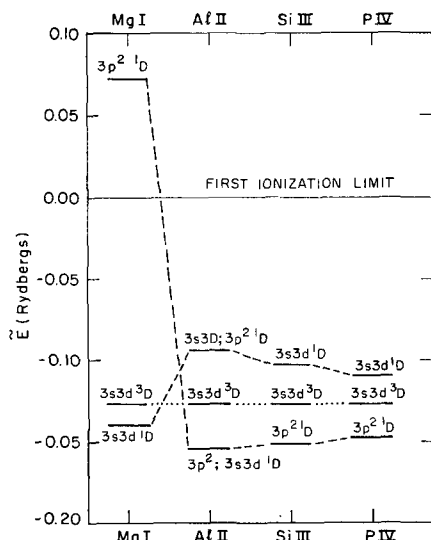


FIG. 3. Reduced 1D and 3D term energies (calculated) in the magnesium isoelectronic sequence arising from the $3s3d$ and $3p^2$ configurations.

³² G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950).

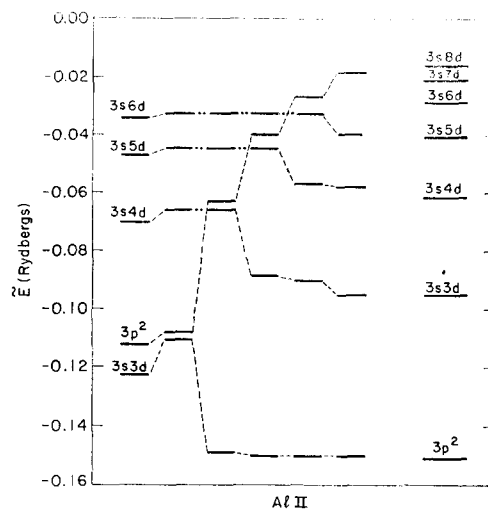


FIG. 4. Comparison between calculated and observed Al II 1D term energies. To the left is shown the effect of the different configurations progressively interacting with each other (see text). To the extreme right is the observed 1D multiplet energy levels.

We observe that the low-lying 1D terms rapidly converge to the correct splitting pattern whereas the higher members of the $3snd$ series require us to take into account still higher members before their positions are established. The identity of the $3p^2$ 1D term is thus absorbed and "swallowed up" by the $3snd$ series, each $3snd$ 1D term repelling the 1D term from the $3s(n+1)d$ member above it. Often the effect of a configuration crossing is not so far-reaching as in the Al II spectrum, but is only noticeable by the distortions in the multiplet splitting pattern of the two immediately neighboring configurations. Unlike the case of potential-energy curve crossings for molecules, the effective nuclear charge is not continuously variable and interacting energy levels are not always so nearly coincident as in the Al II spectrum.

The origin of configuration crossings along an isoelectronic sequence is somewhat more subtle³³ than might appear at first glance. In Fig. 5 we plot the reduced average energies of the $3s3d$, $3s4d$, $3p^2$, and $3p4p$ configurations against the effective nuclear charge. Both the $3p^2$ and $3p4p$ configurations are seen to descend from above the first ionization continuum, whereas the positions of the $3s3d$ and $3s4d$ configurations remain nearly unchanged along the isoelectronic sequence. We have marked on the extreme right of Fig. 5 the hydrogenic energies for the different principal quantum numbers n , which the configurations approach in the limit of infinite nuclear charge.³⁴ If the shielding of the nucleus is imperfect, the outermost electrons can penetrate the core electrons so that they experience more fully the attractive force of the nucleus, which in

³³ Compare N. G. Whitelaw, *Phys. Rev.* **44**, 544 (1933); J. H. Van Vleck and N. G. Whitelaw, *ibid.* p. 551. The author is embarrassed to admit he does not fully understand the latter article, but he assumes it must contain a correct explanation of this effect.

³⁴ D. Layzer, *Phys. Rev.* **132**, 735 (1963).

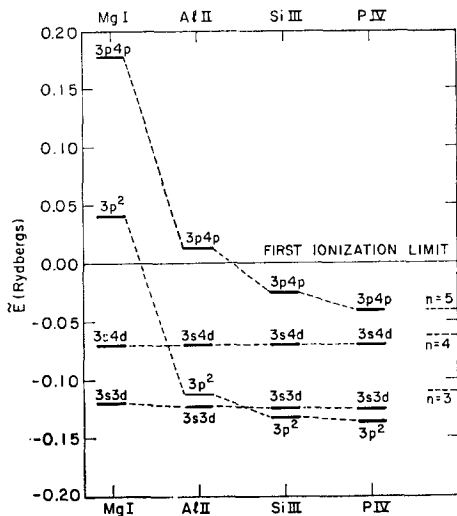


FIG. 5. Variation of configuration average energies with nuclear charge along the magnesium isoelectronic sequence. On the extreme right is placed the limiting hydrogenic energies for the different principal quantum numbers n , which the configurations approach with increasing nuclear charge.

turn increases the binding energy and hence makes the total energy more negative. From Fig. 5 it appears that the configuration crossings of the $3p^2$ and $3p4p$ configurations are due to the enhanced penetration ability of the $3p$ orbital.

However, we are in a position to sharpen the meaning of our intuitive notion of "penetration ability" and put configuration crossings on a more quantitative basis. Provided we disregard configuration mixing, the energy difference $E(A) - E(B)$ between two term values arising from the configuration A and B is given by the difference between the expectation values of the total Hamiltonian \mathcal{H} :

$$E(A) - E(B) = \Delta\mathcal{H}(\text{core-valence}) + \Delta\mathcal{H}(\text{valence}), \tag{26}$$

where

$$\Delta\mathcal{H}(\text{core-valence}) = \langle \mathcal{H}(\text{core-valence}) \rangle_A - \langle \mathcal{H}(\text{core-valence}) \rangle_B \tag{27a}$$

and

$$\Delta\mathcal{H}(\text{valence}) = \langle \mathcal{H}(\text{valence}) \rangle_A - \langle \mathcal{H}(\text{valence}) \rangle_B. \tag{27b}$$

Since $\langle \mathcal{H}(\text{core-valence}) \rangle$ gives the interaction of the valence electrons with the core electrons and with the nucleus, we identify $\Delta\mathcal{H}(\text{core-valence})$ as the penetration energy difference between the two configurations. Similarly we interpret $\Delta\mathcal{H}(\text{valence})$ to be the difference in interaction energy of the valence electrons

with each other for the two configurations. Thus the energy difference is in fact given by a sum of two quantities in Eq. (26), the first expressing the difference in penetrating ability, the second giving the difference in valence electron repulsion.

We present in Fig. 6 the variation of the quantities $E(A) - E(B)$, $\Delta\mathcal{H}(\text{core-valence})$ and $\Delta\mathcal{H}(\text{valence})$ with effective nuclear charge for the 1D terms of the $3s6d$, $3p4p$, and $3s3d$, $3p^2$ configurations, respectively. On comparing the $3s6d$ and $3p4p$ term-energy differences pictured in Fig. 6(a), we observe that $\Delta\mathcal{H}(\text{valence})$ remains nearly constant, ΔE follows the variation in $\Delta\mathcal{H}(\text{core-valence})$, and we conclude that the increased penetration ability of the $3p$ orbital fully accounts for the observed configuration crossing in the Si III spectrum.³⁵ For the more celebrated case of the $3s3d$, $3p^2$ configuration crossing, Fig. 6(b) reveals that this simple explanation is no longer sufficient. Instead we reach the somewhat unexpected conclusion that the variation in the penetration power and in the valence-electron repulsion share nearly equally the responsibility for causing the $3s3d$ and $3p^2$ configurations to cross.

This result may be explained, in part, by reference to Fig. 7 which compares the $3s$, $3p$, and $3d$ radial charge distributions from Mg I to P IV. As the effective nuclear charge increases, all three wavefunctions are pulled in more tightly about the nucleus, but from Fig. 7 it is evident that the $3p$ orbital is able to penetrate the core electrons almost as effectively as the $3s$ orbital. On the other hand, the electrostatic repulsion of the valence electrons depends in a complex manner [Eqs.

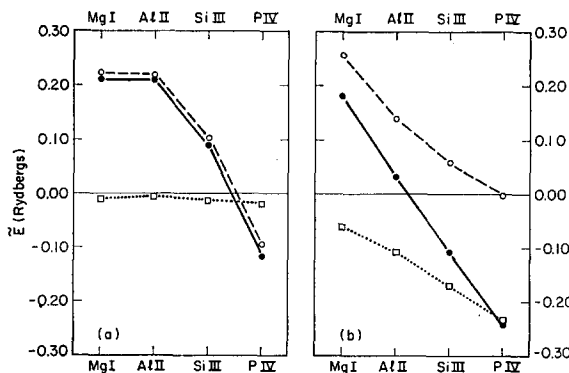


FIG. 6. Variation of the penetration ability $\Delta\mathcal{H}(\text{core-valence})$ and the valence electron repulsion $\Delta\mathcal{H}(\text{valence})$ which leads to the crossing of the 1D terms arising from (a) the $3p4p$ and $3s6d$ configurations, and (b) the $3p^2$ and $3s3d$ configurations. In (a): \circ , $\Delta\mathcal{H}(\text{core-valence})$; \bullet , $E(3p4p\ ^1D) - E(3s6d\ ^1D)$; \square , $\Delta\mathcal{H}(\text{valence})$. In (b): \circ , $\Delta\mathcal{H}(\text{core-valence})$; \bullet , $E(3p^2\ ^1D) - E(3s3d\ ^1D)$; \square , $\Delta\mathcal{H}(\text{valence})$.

³⁵ Torsson (Ref. 14) reports that the 1D and 3D terms of the Si III $3s6d$ configuration are badly perturbed by the neighboring $3p4p$ configuration. We predict that a similar situation will be observed in the P IV spectrum wherein a configuration crossing occurs between the $3p4p$ and the $3s5d$ configuration, rather than the $3s6d$ configuration (see Table II).

TABLE IV. Configuration-interaction wavefunctions for the 1D and 3D terms arising from the $3s3d$, $3s4d$, and $3p^2$ configurations of the Mg I isoelectronic sequence. All expansion coefficients have been rounded to three figures.

Wavefunction	A_{2s3d}	A_{3s4d}	A_{2s5d}	A_{3s6d}	A_{3p^2}	A_{3p^4p}	A_{3p^4f}	A_{3d^2}	A_{3d4s}	A_{3d4d}
Mg I										
$\psi_{2s3d;3p^2}(^1D)$	-0.912	-0.072	-0.032	-0.019	+0.385	-0.099	+0.034	+0.011	+0.041	+0.030
$\psi_{3s4d;3p^2}(^1D)$	-0.198	+0.932	+0.115	-0.057	-0.273	-0.038	+0.019	-0.014	-0.005	-0.004
$\psi_{3p^2;3p^4p;3s3d}(^1D)$	-0.319	-0.256	-0.213	-0.178	-0.691	+0.507	+0.056	-0.111	-0.042	-0.060
$\psi_{2s3d}(^3D)$	-0.992	+0.063	+0.035	+0.024	...	-0.074	+0.041	...	-0.048	-0.003
$\psi_{3s4d}(^3D)$	-0.056	-0.991	+0.109	+0.053	...	-0.022	-0.004	...	-0.013	-0.001
Al II										
$\psi_{3p^2;3s3d}(^1\bar{D})$	-0.677	-0.080	-0.034	-0.019	+0.720	-0.085	+0.024	+0.059	+0.027	+0.063
$\psi_{3s4d;3s4d;3p^2}(^1\bar{D})$	-0.615	+0.572	+0.160	+0.088	-0.489	-0.073	+0.077	-0.102	-0.011	-0.009
$\psi_{3s4d;3s5d;3p^2}(^1D)$	-0.271	-0.736	+0.493	+0.172	-0.282	+0.153	+0.032	-0.092	+0.000	-0.021
$\psi_{2s3d}(^3D)$	-0.995	+0.036	+0.024	+0.013	...	-0.060	+0.057	...	-0.038	-0.006
$\psi_{3s4d}(^3D)$	-0.037	-0.996	+0.055	+0.029	...	+0.038	-0.021	...	-0.023	-0.003
Si III										
$\psi_{3p^2;3s3d}(^1D)$	-0.573	-0.048	-0.017	-0.006	+0.809	-0.064	+0.014	+0.079	+0.018	+0.056
$\psi_{3s4d;3p^2}(^1D)$	-0.776	+0.290	-0.097	+0.054	-0.510	+0.093	+0.096	-0.153	+0.004	-0.000
$\psi_{3s4d;3p^4p}(^1D)$	-0.179	-0.930	+0.155	+0.068	-0.152	+0.204	+0.009	-0.096	+0.024	-0.012
$\psi_{2s3d}(^3D)$	-0.996	+0.028	+0.020	-0.000	...	-0.043	+0.055	...	-0.032	-0.005
$\psi_{3s4d}(^3D)$	-0.032	-0.993	+0.039	+0.021	...	+0.092	-0.034	...	-0.026	-0.003
P IV										
$\psi_{3p^2;3s3d}(^1D)$	-0.522	-0.027	-0.007	-0.002	+0.845	-0.051	+0.008	+0.086	+0.013	+0.044
$\psi_{3s4d;3p^2}(^1D)$	+0.830	-0.162	-0.061	-0.041	+0.488	-0.076	-0.105	+0.155	-0.017	-0.004
$\psi_{3s4d;3p^4p}(^1D)$	+0.105	+0.963	-0.072	-0.034	+0.074	-0.206	+0.015	+0.081	-0.036	+0.006
$\psi_{2s3d}(^3D)$	-0.997	+0.027	+0.017	+0.012	...	-0.022	+0.052	...	-0.028	-0.004
$\psi_{3s4d}(^3D)$	-0.030	-0.989	+0.031	+0.017	...	+0.129	-0.043	...	-0.027	-0.003

(18) and (19)] on the weighted overlaps of the radial wavefunctions. The two equivalent $3p$ electrons have the same spatial dependence. As the effective nuclear charge increases, their spatial extent is contracted and the electrostatic interaction increases, but not as rapidly as the electrostatic interaction between the $3s$ and $3d$ orbital, whose spatial extent is seen from Fig. 7 to be increasingly squashed together. Both these effects lower the $3p^2$ energy with respect to the $3s3d$ energy and together account for the observed configuration crossing.

Spectral Purity of the Term Values

We present in Table IV the configuration-interaction wavefunctions corresponding to the low-lying 1D and 3D terms arising from the $3s3d$, $3s4d$, and $3p^2$ configurations. These wavefunctions ψ are a linear combination of the HFS determinants $A_{nl'n'v}$ comprising the basis

set. The expansion coefficients [See Eq. (7)] have the property that they are normalized, i.e., the sums of their squares equal unity. Thus we may consider the actual electronic configuration as *resonating* between the different electronic configurations shown in Table IV. The probability of being in a particular configuration $A_{nl'n'v}$ is given by the square of the expansion coefficient. It is worthwhile questioning to what extent we are justified in assigning configuration labels to energy terms which simultaneously partake of the character of several different configurations. This problem becomes particularly acute when a configuration crossing is imminent.

Clearly we must introduce a more detailed description of the multiplet term values when extensive configuration mixing is present. We offer the following guidelines. Let us define a quantity, called the *spectral purity*, which we set equal to the square of the leading coeffi-

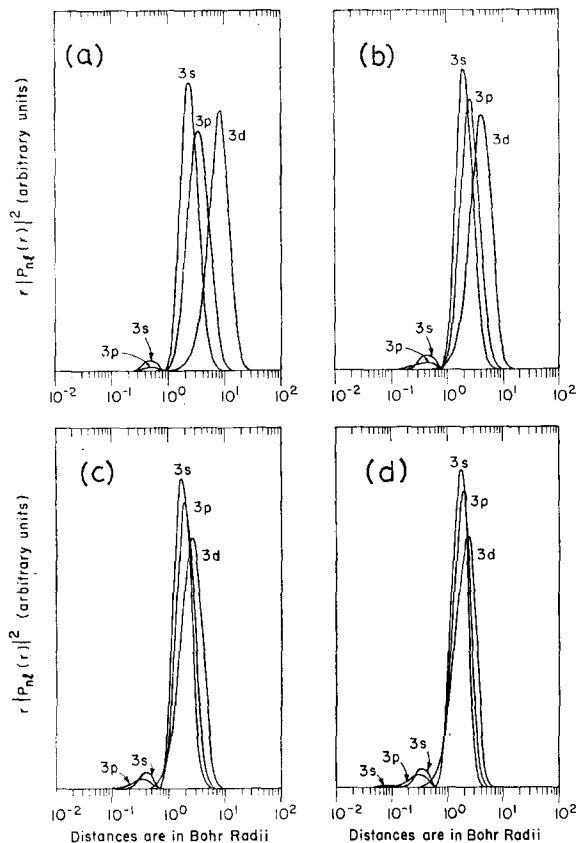


FIG. 7. Radial charge distributions of the $3s$, $3p$, and $3d$ spin orbitals. The square of the wavefunction times the distance is plotted against the logarithm of the distance. All plots are normalized so that the area under each curve is equal. The innermost "crest" of the $3s$ wavefunction is barely visible in P IV, but is lost along the base line in the other elements. (a) Mg I; (b) Al II; (c) Si III; (d) P IV.

cient in the expansion of HFS determinants. If the spectral purity exceeds 90%, the wavefunction is predominantly the character of the configuration belonging to the leading expansion coefficient, and the term energy should be designated by that configuration in the traditional manner. This case obtains for all the 3D terms shown in Table IV. When the spectral purity is less than 90% we cite those wavefunctions which are the chief constituents of ψ in the order of decreasing expansion coefficients, much as one might indicate the results of a chemical analysis for impurities. Thus we denote the lowest-lying 1D term of Mg by $3s3d$; $3p^2$ 1D . When the spectral purity drops below 50%, the wave-

function is heavily "contaminated" by other configurations and it is no longer very useful to regard the term value as arising from a single configuration. We indicate this by a superscript bar being placed above the term value. This situation occurs for some of the low-lying 1D terms of Al II, due to the $3s3d$, $3p^2$ configuration crossing.

We have marked in Table II those term values whose spectral purity is below 90% or below 50%. From Table II we see that moderately extensive configuration mixing is frequently present and makes us suspect that configuration crossings along an isoelectronic sequence are not an uncommon occurrence. This contention is borne out by a study of the variation of configuration energies with nuclear charge. We find, besides the crossings of the $3p^2$ and $3p4p$ configuration pictured in Fig. 6, that there are yet other configurations, e.g., the $3d^2$ and the $3p4f$, which will cut through the $3snd$ series causing serious term perturbations at still higher effective nuclear charge. Hence configuration crossing along an isoelectronic sequence appears to be a general phenomenon; and, whenever it occurs, not only are the energy levels displaced but the electronic wavefunctions associated with these energy levels become an appreciable mixture of the strongly interacting configurations. In Part I our emphasis has been on the term-energy positions. For many purposes, however, the configuration-interaction wavefunctions are the more important quantities, for they allow us to evaluate atomic properties which are in general more difficult to measure experimentally than the energy. The spectral purity of the wavefunction thus offers us a useful figure of merit for deciding when calculations of atomic properties which ignore configuration mixing can be relied upon, or when they should be viewed with reservation. We shall explore this aspect of the many-electron correlation problem in Part II, where the study of transition probabilities is undertaken.

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