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THE CALCULATION OF ENERGY LEVELS FOR ATOMS IN CONFIGURATIONS $1s^2 2s^2 2p^q nl$

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CONTENTS

Reactance matrices for electron collisions with ions in configurations $1s^22s^22p^q$ ($q = 1$ to 5), calculated by Saraph, Seaton & Shemming (1969), have been fitted to analytic functions of the energy and extrapolated to energies which give bound states with configurations $1s^22s^22p^q(S_iL_i)\,nl\,SL$. The positions of the bound states are calculated using methods of many-channel quantum defect theory. Allowance can be made for the fine-structure energy of the ion core, by using a representation $(S_iL_iJ_i)\,nlj\,J$ or a pair-coupling representation $(S_iL_iJ_i)\,nlK, J$.

The calculated level positions are compared with positions determined experimentally. The most detailed results are for the *n*p levels, but some results are given for *n*s and *n*d levels. Some semi-empirical adjustments are made in the calculated matrices, so as to obtain improved agreement between observed and calculated levels. In many cases the most serious source of error in the calculations is the neglect of interactions between configurations $2s^22p^qnl$ and $2s2p^{q+1}n'l'$. For the more highly ionized systems these interactions give rise to perturbed series. A discussion of results for valence-electron states in the neutral atoms, C I, N I, O I, F I and Ne I is followed by a discussion of the various iso-electronic sequences.

The results enable us:

(i) To assess the accuracy of the calculated reactance matrices.

(ii) To make identifications. In most cases, but not all cases, the assignments obtained for parentage, and for pair-coupling quantum numbers, agree with assignments which have been suggested previously. In some cases it is found that large admixtures of states occur and that no meaningful assignments of parentage or pair-coupling quantum numbers can be made.

(iii) To make predictions. Calculated positions of energy levels, and error estimates, are given for some levels which have not been observed.

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1. Introduction

A previous paper (Saraph, Seaton & Shemming 1969, to be referred to as paper I) was concerned with a study of excitation by electron impact of ions in configurations $1s^22s^22p^q$. The results obtained are used in the present paper as a basis for the calculation of energy levels for configurations $1s^22s^22p^q\,nl$.

The calculation of energy levels for atomic configurations $1s^22s^22p^q\,nl$, with $q = 1$ to 5 and $n \geqslant 3$, is complicated by the fact that the $1s^22s^22p^q$ ion core may have a number of different energy levels. Consider first the case in which fine structure is neglected. For $q = 2$, 3 and 4 the $2p^q$ core has three terms, ^3P, ^1D and ^1S for $q = 2$ and 4, and ^4S, ^2D and ^2P for $q = 3$. We denote these terms by $S_i L_i$, $i = 1$, 2 and 3, in order of increasing excitation energy. On adding a valence electron to the core, we may use a representation

$$\alpha = 1s^22s^22p^q(S_i L_i)\,nl\,SL. \tag{1.1}$$

It is usual to refer to $S_i L_i$ as the *parent term* of the ion core. However, for some values of lSL it is found that one can obtain several different states α, each having different values of $S_i L_i$. Since the Hamiltonian is not diagonal with respect to $S_i L_i$ it follows that, in such cases, a unique assignment of parent terms cannot be made. The valence electron levels form mutually perturbed series, converging to different terms of the ion core.

The fine structure energies of the core terms are generally much larger than the fine structure energies for the valence electron. When account is taken of fine structure it is therefore desirable to specify the total angular momentum J_i of the core. We may use a representation

$$\alpha = 1s^22s^22p^q(S_i L_i J_i)\,nljJ, \tag{1.2}$$

in which the angular momentum J_i is coupled to the total angular momentum j of the valence electron. It is sometimes more convenient to use a pair-coupling representation,

$$\alpha = 1s^22s^22p^q(S_i L_i J_i)\,nl\,KJ, \tag{1.3}$$

in which the angular momentum J_i is coupled to the orbital angular momentum l of the valence electron to give a resultant K, which is then coupled to the spin of the valence electron to give the total angular momentum J. For the ions with $q = 1$ and 5 we have a single core term, $S_1 L_1 = {}^2P$, but two fine-structure core levels, $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$.

Let us suppose that energy levels have been calculated neglecting fine structure. For the higher series members the calculated energy differences between neighbouring states will be small compared with the fine-structure energy differences in the ion core. Inclusion of fine structure will then modify profoundly the energy level structure for the high levels. We obtain mutually perturbed series converging to each of the fine-structure core levels.

Little work has been done previously on the calculation of energy levels for configurations $2p^q\,nl$. One approach would be to use standard methods of perturbation theory, but in many cases it would be difficult to decide which states α should be included for each energy level. A much better approach would to be solve the coupled equations of Hartree–Fock theory, taking all states of the ion core into account. The procedure which we adopt is, in essence, equivalent to the solution of the coupled Hartree–Fock problem, but the computations are greatly simplified by using techniques of generalized quantum defect theory. In this theory, which is summarized in § 2, one obtains expressions for the calculation of energy levels which involve certain analytic functions of the energy. These functions may be calculated for a few values of the energy and fitted to suitable interpolation and extrapolation formulae. A further advantage to be gained from the use of quantum defect theory is that it provides a convenient method for taking account of the fine-struture separations of the terms of the ion cores. In practice we use the results of paper I, obtained from approximate solutions of the coupled Hartree–Fock equations at energies corresponding to continuum states of the electron-ion systems. The techniques used for calculating and extrapolating the analytic functions of the energy are described in § 3, and methods used for the calculation of energy levels are discussed in § 4.

Comparisons between calculated and observed energy levels, discussed in § 5, enable us to:

(i) Assess the accuracy of the calculations.

(ii) Make identifications. For each energy level we obtain a wavefunction which is a linear combination of states in one of the representations, (1.1), (1.2) or (1.3). If one such state gives the dominant contribution, the quantum numbers for this state may be used as a label for the designation of the level concerned. In most cases our designations are in agreement with those which have been suggested previously, but there are some cases for which our work shows that the designations should be changed. We also find some cases for which there is a large admixture of states, and for which no meaningful assignment of quantum numbers can be made.

(iii) Make predictions. We are able to calculate the positions of levels which have not been observed and, from comparisons of theory and observations for other levels, estimate the probable error in the calculated positions.

The main approximation in all of our work is that we neglect interaction with configurations which are not of the type $1s^22s^22p^q\,nl$. In many cases the most important interacting configurations not taken into account will be of the type $1s^22s2p^{q+1}\,n'\,l'$. We have attempted to make some semi-empiricial corrections to the calculations, but always retaining a framework of algebraic theory which is consistent with the restriction of considering only $1s^22s^22p^q\,nl$ configurations.

Comparisons of observed with calculated energy levels allow us to make some assessment of the accuracy of the collision cross-section calculations of paper I. In some cases we can make semi-empirical adjustments to the cross-sections, using the results obtained in making similar corrections to the energy levels. These questions are discussed in § 6, which also includes some remarks on resonance structures in the cross-sections.

2. Summary of quantum defect theory

We summarize some results of quantum defect theory (Seaton 1966*a*, *b*, 1969*a*, to be referred to as QDT I, II and VII).

Let E be the total energy in Rydberg units of an ion core plus an added electron. Put

$$E = E_\alpha + z^2\epsilon_\alpha, \tag{2.1}$$

where α specifies a state of the system and where E_α is the energy of the ion core for this state and z is the charge on the ion core. When the ion core has energy E_α the added electron has an energy $z^2\epsilon_\alpha$. We say that α is an open channel if $\epsilon_\alpha > 0$ and a closed channel if $\epsilon_\alpha < 0$. For each closed channel α we define an *effective quantum number*

$$\nu_\alpha = (-1/\epsilon_\alpha)^{\frac{1}{2}} \quad (\epsilon_\alpha < 0). \tag{2.2}$$

For a bound state of the electron-ion system we have $\epsilon_\alpha < 0$ for all channels α.

2.1. *One-channel theory*

It is convenient to consider first the simple case of a system with only one channel α. If we drop the subscript α, the energy for a bound state of a valence electron is $z^2\epsilon_n$ where

$$\epsilon_n = -1/\nu_n^2. \tag{2.3}$$

The Rydberg formula is

$$\nu_n = n - \mu(\epsilon_n), \tag{2.4}$$

where n is an integer and where the *quantum defect*, $\mu(\epsilon)$, varies slowly as a function of ϵ.

For the continuum states, $\epsilon > 0$, the radial function for the added electron has an asymptotic phase $\delta(\epsilon)$ relative to the phase of the regular Coulomb function. It may be shown (Seaton 1955, 1958; QDT I) that $\pi\mu(\epsilon)$ is an analytic continuation of $\delta(\epsilon)$. If the phase $\delta(\epsilon)$ is known we may therefore calculate the quantum defect $\mu(\epsilon)$ by extrapolation and hence calculate the energies of the bound states.

Let us define $R(\epsilon)$ as

$$R(\epsilon) = \begin{Bmatrix} \tan\delta(\epsilon) & \text{for} & \epsilon > 0, \\ \tan\pi\mu(\epsilon) & \text{for} & \epsilon < 0. \end{Bmatrix} \tag{2.5}$$

The condition (2.4) for bound states may then be written

$$R + \tan\pi\nu = 0. \tag{2.6}$$

The advantage of this form is that it may be generalized to the many-channel case (§ 2.2).

Knowing $R(\epsilon)$, we may calculate the asymptotic form of the normalized bound-state radial functions. Let the radial function be $P(\rho)$ where $\rho = zr$ and put

$$P(\rho) = \mathscr{P}(\rho)\,Z, \tag{2.7}$$

where $\mathscr{P}(\rho)$ has asymptotic form

$$\mathscr{P}(\rho) \underset{\rho\to\infty}{\simeq} (2\rho/\nu)^{\nu}\,\mathrm{e}^{-\rho/\nu}K, \tag{2.8}$$

$$K = [\nu^2\,\Gamma(\nu+l+1)\,\Gamma(\nu-l)]^{-\frac{1}{2}}. \tag{2.9}$$

The normalization condition is

$$Z^2\zeta = 1 \tag{2.10}$$

where

$$\zeta = 1 + (2/\pi)\,\nu^{-3}\cos^2\pi\nu\,\mathrm{d}R(\epsilon)/\mathrm{d}\epsilon. \tag{2.11}$$

It may be noted that, for ν large, $\zeta \simeq 1$ and the normalization condition becomes $Z^2 = 1$.

In order to make accurate extrapolations, some further refinements must be introduced. Let us define

$$A = \prod_{p=0}^{l}(1+p^2\epsilon) \tag{2.12}$$

and

$$Y(\epsilon) = \begin{Bmatrix} (1-\exp(-2\pi/\surd\epsilon))\,R/A & \text{for} & \epsilon > 0, \\ R/A & \text{for} & \epsilon < 0. \end{Bmatrix} \tag{2.13}$$

In practice we usually consider energies such that $\exp(-2\pi/\surd\epsilon) \ll 1$, and the factor

$$(1-\exp(-2\pi/\surd\epsilon))$$

in (2.13) may then be neglected. The practical extrapolation procedure, which is justified in QDT I, is to put

$$Y = Y_1 Y_2^{-1} \tag{2.14}$$

and to fit Y_1 and Y_2 to polynomials in the energy. Accurate extrapolations can be made, over extended energy ranges, using polynomials of low order (some examples are given in QDT II).

Using Y we obtain the condition for bound states, in place of (2.6),

$$Y + (\tan \pi\nu)/A = 0. \tag{2.15}$$

That this equation is superior to equation (2.6) may be appreciated by considering the special case of hydrogenic systems, for which we have $R = Y = 0$. Equation (2.6) reduces to $\tan \pi\nu = 0$ giving, for the bound states, $\nu = n$ where $n = 1, 2, 3, \ldots$. Equation (2.15) reduces to $(\tan \pi\nu)/A = 0$. Putting $\epsilon = -1/\nu^2$ we see from (2.12) that $A = 0$ for $\nu = 1, 2, \ldots, l$. It follows that $(\tan \pi\nu)/A \neq 0$ for $\nu = 1, 2, \ldots, l$. The equation $(\tan \pi\nu)/A = 0$ gives $\nu = n$ where $n = (l+1), (l+2), \ldots$, which is obviously correct.

2.2. *Many-channel theory*

For energies such that all channels are open the asymptotic form of the wavefunction may be described in terms of a *reactance matrix* $\boldsymbol{R}$ with elements $R_{\alpha\alpha'}$, as defined in paper I.

We use the convention that quantities not in boldface type, and without subscripts, are diagonal matrices. Thus when all channels are closed we have a diagonal matrix $\tan \pi\nu$ with diagonal elements $\tan \pi\nu_\alpha$. On extrapolating $\boldsymbol{R}$ we obtain the equation for bound states (see QDT I),

$$|\boldsymbol{R} + \tan \pi\nu| = 0. \tag{2.16}$$

Define a matrix A with diagonal elements

$$A_\alpha = \sum_{p=0}^{l_\alpha} (1 + \epsilon_\alpha p^2). \tag{2.17}$$

For all channels open, but energies such that $\exp(-\pi/\surd\epsilon) \ll 1$, the matrix $\boldsymbol{Y}$ is defined by

$$\boldsymbol{Y} = A^{-\frac{1}{2}} \boldsymbol{R} A^{-\frac{1}{2}}. \tag{2.18}$$

We put

$$\boldsymbol{Y} = \boldsymbol{Y}_1 \boldsymbol{Y}_2^{-1}, \tag{2.19}$$

and fit $\boldsymbol{Y}_1$ and $\boldsymbol{Y}_2$ to polynomials in the energy (the exact procedures adopted are described in § 3). For bound states we obtain the many-channel generalization of (2.15):

$$|\boldsymbol{Y} + (\tan \pi\nu)/A| = 0. \tag{2.20}$$

The numerical methods used for solving this equation are described in § 4.

The theory allows us to obtain the amplitudes of the contributions to the bound state wavefunctions from each channel α. Let the radial function in channel α be

$$P_\alpha(\rho) = \mathscr{P}_\alpha(\rho)\, Z_\alpha, \tag{2.21}$$

where

$$\mathscr{P}_\alpha(\rho) \underset{\rho\to\infty}{\simeq} (2\rho/\nu_\alpha)^{\nu_\alpha} \, \mathrm{e}^{-\rho/\nu_\alpha} K_\alpha, \tag{2.22}$$

$$K_\alpha = [\nu_\alpha^2 \,\Gamma(\nu_\alpha + l_\alpha + 1)\, \Gamma(\nu_\alpha - l_\alpha)]^{-\frac{1}{2}}. \tag{2.23}$$

The vector $\boldsymbol{Z}$ with components Z_α is such that

$$\{\boldsymbol{Y} + (\tan \pi\nu)/A\}\, q A^{\frac{1}{2}} \boldsymbol{Z} = 0, \tag{2.24}$$

where

$$q = (-1)^l \,(2/\pi\nu^3)^{\frac{1}{2}} \cos \pi\nu. \tag{2.25}$$

Equation (2.24) has solutions other than $\boldsymbol{Z} = 0$ only when (2.20) is satisfied.

The normalization condition for the bound state wavefunction is

$$\sum_\alpha \int_0^\infty P_\alpha^2(\rho)\, \mathrm{d}\rho = 1. \tag{2.26}$$

It is shown in QDT I that this condition is satisfied if

$$\boldsymbol{Z}^T \boldsymbol{\zeta} \boldsymbol{Z} = 1, \tag{2.27}$$

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where $\boldsymbol{Z}^T$ is the transpose of $\boldsymbol{Z}$ and where

$$\boldsymbol{\zeta} = 1+q(\mathrm{d}\boldsymbol{R}/\mathrm{d}\epsilon)\,q. \tag{2.28}$$

The significance of the quantities Z_α may be understood as follows. The functions q are proportional to $\nu^{-\frac{3}{2}}$ and it therefore follows from (2.28) that $\zeta = 1+O(\nu^{-3})$. So long as ν is not too small, ζ is approximately equal to unity. In practice $\zeta \simeq 1$ for $\nu > (l+1)$. With $\zeta = 1$ the normalization condition (2.27) is $\mathbf{Z}^{\mathrm{T}}\boldsymbol{Z} = 1$. For one-channel cases we obtain $Z_\alpha = 1$ and it follows that the functions with asymptotic form (2.22), are normalized to

$$\int_0^\infty \mathscr{P}_\alpha^2(\rho)\,\mathrm{d}\rho = 1. \tag{2.29}$$

For the many-channel case it may also be assumed that the functions $\mathscr{P}_\alpha$ satisfy approximately the normalization condition (2.29), so long as ν_α is not too small. In this case we have the interpretation of Z_α that the total normalized wavefunction for the system is of the form

$$\Psi = \sum_\alpha \Psi_\alpha Z_\alpha, \tag{2.30}$$

where the functions Ψ_α for each channel are normalized to unity, $(\Psi_\alpha|\Psi_\alpha) = 1$.

The position is more complicated if the energy is such that, for some value of α, ν_α is less than $(l_\alpha+1)$. For $l_\alpha < \nu_\alpha < (l_\alpha+1)$, A_α is negative and K_α and Z_α are pure imaginary. In order to avoid complex numbers we introduce

$$V_\alpha = A_\alpha^{\frac{1}{2}} Z_\alpha, \tag{2.31}$$

which is always real. For ν_α large, A_α tends to unity and V_α tends to Z_α. We also introduce

$$W_\alpha = V_\alpha^2/(\sum_{\alpha'} V_{\alpha'}^2) \tag{2.32}$$

as a useful measure of the contribution of channel α to a given energy level.

2.3. *Limitations of the present form of quantum defect theory*

A rigorous mathematical development of quantum defect theory has been obtained on making the assumption that, beyond some finite radius r_0, all potentials other than pure Coulomb potentials can be neglected. This assumption cannot be strictly justified in practice, since one has interaction potentials $V_{\alpha\alpha'}(r)$ behaving for large r like r^{-m} with $m \geqslant 2$. In the equations solved in paper I there are potentials of quadrupole type ($m = 3$) but no dipole potentials ($m = 2$). We consider to what extent the presence of quadrupole potentials will invalidate the use of the theory which has been described.

For the smaller values of l the dominant interactions are of a short-range nature. For $l = 0$ and 1 it is found that no practical difficulties arise in using a theory which takes no explicit account of long-range interactions.

The difficulties which arise for larger values of l are best appreciated by first considering the one-channel case. For large l, R is small and the bound states occur at $\nu \simeq (l+1), (l+2), \ldots$. For the one-channel case the theory in which short-range potentials are assumed predicts that Y should remain finite at $\nu = 1, 2, \ldots, l$, and hence, since $R = AY$, that $R = 0$ at these values of ν. For functions having this behaviour, (2.15) does not give roots at $\nu \simeq 1, 2, \ldots, l$. We now consider the behaviour of R for a case in which long-range potentials are included. The quadrupole potentials are proportional to

$$V_q(r) = y_2(PP|r) \tag{2.33}$$

in the notation of paper I. Figure 1 shows R calculated for $l = 3$ in the $\mathrm{e}+\mathrm{O}^{2+}$ problem, by the use of the quadrupole potential V_q and the distorted wave approximation. It is seen that no reasonable extrapolation of this function will pass through zero at $\nu = 3$. If we calculate $Y = R/A$ and extrapolate Y in the usual way, we find that Y is singular at $\nu = 3$ and that (2.15) has a spurious root in the vicinity of $\nu = 3$. In order to check that the difficulty encountered is due to the long range of the potential V_q, R has been recalculated (Billings 1967) on replacing V_q by a continuous function V'_q such that $V'_q(r) = V_q(r)$ for $r < 5$, and $V'_q(r) = 0$ for $r > 7.5$. This gives the function R' shown in figure 1. It is seen that R' extrapolates to zero at $\nu = 3$.

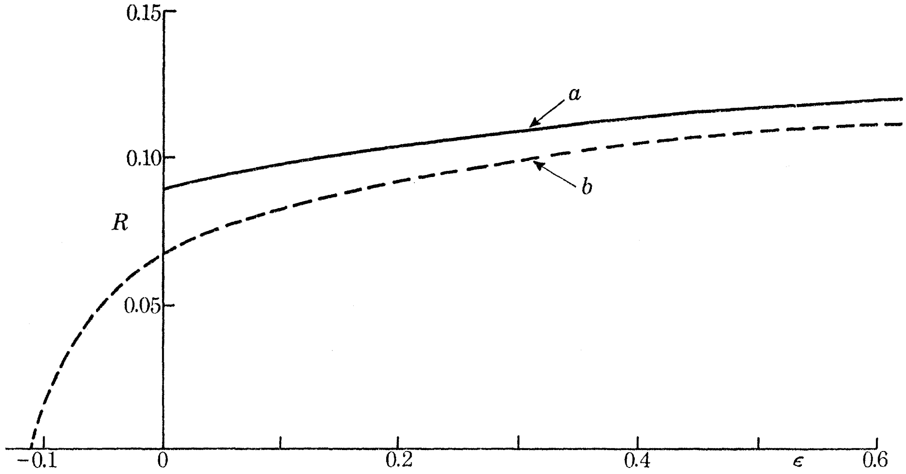

FIGURE 1. (*a*) The R-matrix for f-waves and the potential V_q (equation (2.33)), which behaves like r^{-3} for r large (*b*) The R'-matrix for f-waves and a potential V'_q such that $V'_q = V_q$ for $r \leqslant 6.5$, $V'_q = 0$ for $r \geqslant 7.5$.

If we are concerned only with one-channel cases, the difficulty encountered is not so serious, since we would not be interested in the region $\nu < (l+1)$. For many-channel problems, however, we have the further complications that the values of ν_α in some channels may be much smaller than the values in other channels, and also that there may be coupling between states of different l_α. In such situations the difficulties encountered using the short-range theory cannot be avoided. In principle, one could use a more general form of quantum defect theory, which takes long-range potentials explicitly into account, but this would involve numerical calculations of much greater complexity (Billings 1967). In the present work no attempt has been made to apply a more general form of the theory.

The function R' shown in figure 1 was calculated by Dr A. G. Billings, and we are indebted to him for permission to quote his results.

3. EXTRAPOLATION TECHNIQUES

3.1. *The calculations of paper I*

We summarize the results obtained in the course of the work described in paper I. Calculations were made for electron collisions with ions in configurations $1s^2 2s^2 2p^q$ with $q = 1$ to 5. The LS coupling representation (1.1) was used throughout. Since fine structure was not included, the ions with $q = 1$ and 5 were taken to have a single energy level, denoted by $i = 1$, and the ions with $q = 2$, 3 and 4 to have three levels, denoted by $i = 1$, 2 and 3 in order of increasing excitation energy. Energy-difference parameters Δ_i are defined as

$$\Delta_i = [E(S_i L_i) - E(S_1 L_1)]/z^2. \qquad (3.1)$$

The kinetic energy of the colliding electron, when the ion is in level i, is $k_i^2 = z^2\epsilon_i$. It follows from (2.1) that $\epsilon_1 = \Delta_i + \epsilon_i$. Calculated values of Δ_i were used in paper I; the numerical values used may be obtained from tables 3 and 9 and equation (2.40) of I.

Coupled integro-differential equations of Hartree–Fock type (equations (2.57) of I) were obtained for the calculation of the radial functions for the colliding electron, and approximate solutions of these equations were obtained by the methods described in §§ 2.7, 2.8 and 3.1 of I. Calculations were made for all partial waves by means of the distorted wave approximation, and more accurate solutions for the p-waves ($l = 1$) were obtained from the exact resonance approximation. The internal consistency of the results indicated that the errors in the collision strengths introduced by using the distorted wave approximation for $l > 1$ and the exact resonance approximation for $l = 1$ should not exceed a small percentage, and this has been confirmed by the work of Smith, Conneely & Morgan (1969) and of Henry, Burke & Sinfailam (1969), who have obtained exact solutions of the coupled equations. The distorted wave results for the s-waves ($l = 0$) are of a lower accuracy. The s-waves do not contribute significantly to the inelastic collision cross-sections and in consequence no attempt was made to improve the accuracy of the s-wave calculations. It is noted in § 2.3 that our extrapolation techniques may be unreliable for $l > 1$. The work of the present paper is therefore largely restricted to consideration of the p-waves.

The configuration $1s^22s^22p^q\,nl$ may interact with $1s^22s^22p^q\,n'\,l'$ where $l' = l \pm 2$. The calculations of paper I show that interaction between np and $n'f$ is generally small, and such interactions are therefore neglected in the present work. In some cases interaction between ns and n'd may be more important.

3.2. *Extrapolation procedures*

For all of the ions considered in the present paper the p-wave reactance matrices $\boldsymbol{R}$ have been calculated for five energies, $\epsilon_j = 0.00$, 0.05, 0.10, 0.25 and 0.50 where $j = 1$ for $q = 1$ and 5, and $j = 3$ for $q = 2$, 3 and 4. The $\boldsymbol{Y}$ matrices are calculated using (2.18) and fitted to functions of the energy variable ϵ_1. At this stage we use calculated energy differences Δ_i. We put $\boldsymbol{Y} = \boldsymbol{Y}_1\boldsymbol{Y}_2^{-1}$ where

$$\boldsymbol{Y}_1(\epsilon_1) = \boldsymbol{D}_1 + \boldsymbol{D}_2\epsilon_1 + \ldots + \boldsymbol{D}_s\epsilon_1^{s-1}, \tag{3.2}$$

$$\boldsymbol{Y}_2(\epsilon_1) = \boldsymbol{D}_{s+1} + \boldsymbol{D}_{s+2}\epsilon_1 + \ldots + \boldsymbol{D}_{m+1}\epsilon_1^{m-s}. \tag{3.3}$$

Given $\boldsymbol{Y}$ matrices calculated for m different values of the energy, one of the coefficient matrices $\boldsymbol{D}_n$ may be chosen arbitrarily and the remaining coefficient matrices may then be computed on solving a system of simultaneous linear equations. The choice of s in (3.2), (3.3) depends on the behaviour of $\boldsymbol{Y}(\epsilon_1)$. For the p-waves the $\boldsymbol{Y}$ matrices frequently have poles in the energy range of interest and it would therefore not be satisfactory to attempt to represent $\boldsymbol{Y}$ as a polynomial in ϵ_1 (that is, to take $\boldsymbol{Y}_2$ to be constant). We find that satisfactory results are obtained on taking $s = m-1$, which gives $\boldsymbol{Y}_2$ as a linear function of the energy.

It is convenient to arrange that $\boldsymbol{Y}_1$ and $\boldsymbol{Y}_2$ are never unreasonably large. Let us put

$$\boldsymbol{Y} = \tan \pi\boldsymbol{\eta}. \tag{3.4}$$

The matrix $\boldsymbol{\eta}$ may be computed as follows. We diagonalize $\boldsymbol{Y}$,

$$\boldsymbol{Y}\boldsymbol{X} = \boldsymbol{X}\tan \pi\bar{\eta}, \tag{3.5}$$

where $\tan \pi\bar{\eta}$ is diagonal. We then have

$$\boldsymbol{\eta} = \boldsymbol{X}\bar{\eta}\boldsymbol{X}^{-1}. \tag{3.6}$$

It has been noted that one of the coefficient matrices $\boldsymbol{D}_n$ in (3.2), (3.3) may be chosen arbitrarily. Our choice is to take, in (3.3),

$$\boldsymbol{D}_{s+1} = \cos \pi\eta_0 \tag{3.7}$$

where η_0 is the value of η calculated for $\epsilon_j = 0$. Since η varies fairly slowly with the energy, we then have

$$\boldsymbol{Y}_1 \simeq \sin \pi\eta, \quad \boldsymbol{Y}_2 \simeq \cos \pi\eta. \tag{3.8}$$

As a check on the extrapolation procedures we have made calculations with $m = 3$ and with $m = 4$, and with different choices for the m energies used for the determination of the coefficient matrices. We find in all cases that the different extrapolation procedures give results in close agreement, and we therefore conclude that the extrapolations should be quite reliable.

3.3. *Coupling schemes*

The $\boldsymbol{R}$ and $\boldsymbol{Y}$ matrices and the coefficient matrices $\boldsymbol{D}_n$ are first calculated in the representation S_iL_ilSL. In this representation all matrices are diagonal in SLM_SM_L and independent of M_SM_L. We shall also require the matrices in the representations $S_iL_iJ_iljJ$ and $S_iL_iJ_ilKJ$. In practice we transform the coefficient matrices. The transformation from S_iL_ilSL to $S_iL_iJ_iljJ$ is made by using 9-j recoupling coefficients,

$$D_n(S_iL_iJ_iljJ, S'_iL'_iJ'_il'j'J) = \sum_{SL}\{(S_iL_i(J_i), \tfrac{1}{2}l(j), J|S_i\tfrac{1}{2}(S), L_il(L), J)$$
$$\times D_n(S_iL_ilSL, S'_iL'_il'SL)\,(S'_i\tfrac{1}{2}(S), L'_il'(L), J|S'_iL'_i(J'_i), \tfrac{1}{2}l'(j'), J)\}, \tag{3.9}$$

and the transformation from $S_iL_iJ_iljJ$ to $S_iL_iJ_ilKJ$ is made by using 6-j recoupling coefficients,

$$D_n(S_iL_iJ_ilKJ, S'_iL'_iJ'_il'K'J) = \sum_{jj'}\{(J_il(K), \tfrac{1}{2}, J|J_i, l\tfrac{1}{2}(j), J)$$
$$\times D_n(S_iL_iJ_iljJ, S'_iL'_iJ'_il'j'J)\,(J'_i, l'\tfrac{1}{2}(j'), J|J'_il'(K'), \tfrac{1}{2}, J)\}. \tag{3.10}$$

The procedure of transforming coefficient matrices, rather than $\boldsymbol{R}$ or $\boldsymbol{Y}$ matrices, has the following advantages: (i) The size of the matrices in SL coupling is generally smaller than that of the matrices in the other representations, and it is therefore best to obtain the coefficient matrices before making transformations; (ii) once the coefficient matrices have been obtained in any representation, the $\boldsymbol{R}$ and $\boldsymbol{Y}$ matrices in this representation are easily calculated for all values of the energy; (iii) at energies close to poles in $\boldsymbol{R}$ and $\boldsymbol{Y}$ the elements of $\boldsymbol{R}$ and $\boldsymbol{Y}$ are large and big cancellation errors would result in attempting to make transformations. No such difficulty arises when transforming the coefficient matrices calculated using the methods described in § 3.2.

The 9-j and 6-j recoupling coefficients were calculated by using subroutines provided by the Atomic Physics group at the Meudon Observatory.

4. CALCULATION OF ENERGY LEVELS

4.1. *Energies of the ion core*

Table 1 gives experimental energy parameters

$$\Delta(S_iL_iJ_i) = [E(S_iL_iJ_i) - E(S_1L_1J_1)]/z^2 \tag{4.1}$$

for the first three ions in each isoelectronic sequence. In (4.1) $S_1L_1J_1$ is the ion ground state. In solving for the energies of the valence-electron states we usually take the independent energy parameter to be ν_1, the effective quantum number for the valence electron referred to the ion ground state. The effective quantum number referred to any other ion state is then

$$\nu_i = [\Delta_i + 1/\nu_1^2]^{-\frac{1}{2}}. \tag{4.2}$$

In solving (2.20) we use the experimental values of $\varDelta_i$. Some calculations are made neglecting fine structure. We then use parameters $\varDelta(S_i L_i)$ defined as

$$\varDelta(S_i L_i) = [E(S_i L_i) - E(S_1 L_1)]/z^2 \tag{4.3}$$

where

$$E(S_i L_i) = \frac{\sum_{J_i} (2J_i+1)\, E(S_i L_i J_i)}{(2S_i+1)\,(2L_i+1)}. \tag{4.4}$$

Table 1. Observed energies for ions in configurations $1s^2 2s^2 2p^q$

($\varDelta(S_i L_i J_i) = [E(S_i L_i J_i) - E(S_1 L_1 J_1)]/z^2$ where $S_1 L_1 J_1$ is the ground state and z is the charge on the ion. Energies $E(S_i L_i J_i)$ in Rydberg units.)

$q = 1$ ground state $^2P_{\frac{1}{2}}$

ion	$\varDelta(^2P_{\frac{3}{2}})$				reference
C II	0.000578	—	—	—	Johansson (1966)
N III	0.000397	—	—	—	Moore (1949)
O IV	0.000391	—	—	—	Moore (1949)

$q = 2$ ground state $^3P_0$

ion	$\varDelta(^3P_1)$	$\varDelta(^3P_2)$	$\varDelta(^1D_2)$	$\varDelta(^1S_0)$	reference
N II	0.000447	0.001196	0.139567	0.297867	Eriksson & Johansson (1961)
O III	0.000259	0.000699	0.046182	0.098383	Moore (1949)
F IV	0.000228	0.000621	0.025558	0.054216	Moore (1949)

$q = 3$ ground state $^4S_{\frac{3}{2}}$

ion	$\varDelta(^2D_{\frac{3}{2}})$	$\varDelta(^2D_{\frac{5}{2}})$	$\varDelta(^2P_{\frac{1}{2}})$	$\varDelta(^2P_{\frac{3}{2}})$	reference
O II	0.244496	0.244304	0.368788	0.368774	Moore (1949)
F III	0.077736	0.077651	0.117461	0.117461	Palenius (1969)
Ne IV	0.041741	0.041697	0.063167	0.063172	Tilford & Giddings (1965)

$q = 4$ ground state $^3P_2$

ion	$\varDelta(^3P_1)$	$\varDelta(^3P_0)$	$\varDelta(^1D_2)$	$\varDelta(^1S_0)$	reference
F II	0.003115	0.004471	0.190214	0.409344	Lidén (1949)
Ne III	0.001481	0.002112	0.058872	0.127004	Moore (1958)
Na IV	0.001120	0.001596	0.031309	0.06742	Moore (1949)

$q = 5$ ground state $^2P_{\frac{3}{2}}$

ion	$\varDelta(^2P_{\frac{1}{2}})$				reference
Ne II	0.007113	—	—	—	Litzén (1968)
Na III	0.003111	—	—	—	A. M. Crooker & C. N. Wu (1968) (priv. comm.)
Mg IV	0.002254	—	—	—	Moore (1949)

Our use of calculated ion energies in the first part of the calculations, and experimental ion energies in subsequent work, requires some further justification. We use calculated ion energies in obtaining $\boldsymbol{R}$ matrices, and in obtaining from them the $\boldsymbol{Y}$ matrices in terms of analytic functions of $\epsilon_1 = -1/\nu_1^2$. However, in order to make meaningful comparisons between theory and experiment for the energies of the valence-electron states it is necessary to use experimental energies for the ion cores; we therefore use experimental values of $\varDelta_i$ in solving (2.20). Some justification for the procedure adopted was obtained on making calculations, in the distorted wave approximation, with various assumed values of $\varDelta_i$. It was found that the $\boldsymbol{Y}$ matrices are generally less sensitive than the $\boldsymbol{R}$ matrices to the adopted energy differences, and vary more slowly as functions of the energy. The reason for this is that a considerable part of the energy dependence of the $\boldsymbol{R}$ matrices comes from the $A^{\frac{1}{2}}$ factors in the relation $\boldsymbol{R} = A^{\frac{1}{2}} \boldsymbol{Y} A^{\frac{1}{2}}$.

4.2. *Solutions for bound states*

Equation (2.20) is not in a form convenient for numerical computations. It is best to work with functions which are always finite. By using (2.19) it is readily shown that (2.20) is equivalent to

$$|\{(\sin \pi\nu)/A\}\, \boldsymbol{Y}_2 + (\cos \pi\nu)\, \boldsymbol{Y}_1| = 0. \tag{4.5}$$

This equation is solved by iterative numerical methods.

4.3. *Adjustment of Y matrices*

Our method of making semi-empirical adjustments in the $\boldsymbol{Y}$ matrices may best be understood by first considering a simpler method which has been used for many years (see, for example, Slater 1929). The configuration $2\mathrm{p}\,n\mathrm{p}$ gives six terms,

$$\alpha = 2\mathrm{p}\,n\mathrm{p}\,SL, \tag{4.6}$$

with $SL = {}^1\mathrm{S}, {}^1\mathrm{P}, {}^1\mathrm{D}, {}^3\mathrm{S}, {}^3\mathrm{P}, {}^3\mathrm{D}$. Assume that radial wavefunctions have been calculated by using a central potential. The variational expression for the energy is $E_\alpha = (\Psi_\alpha|\, \boldsymbol{H}\, |\Psi_\alpha)$. One obtains

$$E_\alpha = E_0 + f_2(\alpha)\, F_2 - g_0(\alpha)\, G_0 - g_2(\alpha)\, G_2, \tag{4.7}$$

where E_0, F_2, G_0 and G_2 are integrals involving the radial functions and $f_2(\alpha)$, $g_0(\alpha)$ and $g_2(\alpha)$ are known algebraic coefficients, given in table 2. The semi-empirical procedure is to adjust the four quantities E_0, F_2, G_0 and G_2 so as to obtain a best fit to the observed positions of the six terms. Our problem is to obtain a generalization of this method for use in many-channel quantum defect theory.

TABLE 2. COEFFICIENTS f_λ, g_λ IN EXPRESSION (4.7) FOR $E(2\mathrm{p}\,n\mathrm{p}\,SL)$

SL	f_2	g_0	g_2
${}^1\mathrm{S}$	$+0.4$	-1	-0.4
${}^3\mathrm{S}$	$+0.4$	$+1$	$+0.4$
${}^1\mathrm{P}$	-0.2	$+1$	-0.2
${}^3\mathrm{P}$	-0.2	-1	$+0.2$
${}^1\mathrm{D}$	$+0.04$	-1	-0.04
${}^3\mathrm{D}$	$+0.04$	$+1$	$+0.04$

A variational principle for the scattering phase matrix $\boldsymbol{\delta}$ has been described by Seaton (1967) and in § 2.2 of paper I. A similar variational principle is readily obtained for the matrix $\boldsymbol{\eta}$ defined in § 3.2. Consider a trial function $\boldsymbol{\Psi}^{\mathrm{t}}$ with asymptotic form which may be expressed in terms of a matrix $\boldsymbol{Y}^{\mathrm{t}}$. The variational principle gives a corrected $\boldsymbol{Y}$ matrix

$$\boldsymbol{Y}^{\mathrm{K}} = [\sin \pi\boldsymbol{\eta}^{\mathrm{t}} + (\cos \pi\boldsymbol{\eta}^{\mathrm{t}})\, \pi\delta\boldsymbol{\eta}]\, [\cos \pi\boldsymbol{\eta}^{\mathrm{t}} - (\sin \pi\boldsymbol{\eta}^{\mathrm{t}})\, \pi\delta\boldsymbol{\eta}]^{-1} \tag{4.8}$$

where $\delta\boldsymbol{\eta}$ is proportional to $(\boldsymbol{\Psi}^{\mathrm{t}}|\, H - E\, |\boldsymbol{\Psi}^{\mathrm{t}})$. In the distorted wave approximation one obtains an expression of the form

$$\delta\eta(\alpha, \alpha') = \sum_\lambda \{f_\lambda(\alpha, \alpha')\, \delta F_\lambda - g_\lambda(\alpha, \alpha')\, \delta G_\lambda\}, \tag{4.9}$$

where the coefficients f_λ and g_λ, for configurations $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^q nl$, are given in paper I. We use expressions of the form (4.9) for $\delta\boldsymbol{\eta}$, and take δF_λ and δG_λ to be variational parameters. Two further simplifications are made: (i) It is found that $\boldsymbol{\eta}$ varies slowly with energy and we therefore take $\delta\boldsymbol{\eta}$ to be independent of the energy. (ii) It was explained in § 3.2 that we take $\boldsymbol{Y} = \boldsymbol{Y}_1 \boldsymbol{Y}_2^{-1}$ where $\boldsymbol{Y}_1 \simeq \sin \pi\boldsymbol{\eta}$, $\boldsymbol{Y}_2 \simeq \cos \pi\boldsymbol{\eta}$. In place of (4.8) we take

$$\boldsymbol{Y}_1^{\mathrm{K}} = \boldsymbol{Y}_1 + \boldsymbol{Y}_2\, \pi\delta\boldsymbol{\eta}, \quad \boldsymbol{Y}_2^{\mathrm{K}} = \boldsymbol{Y}_2 - \boldsymbol{Y}_1\, \pi\delta\boldsymbol{\eta}. \tag{4.10}$$

5. Results for energy levels

5.1. *Sources of error in the calculations*

(*a*) *Ion wavefunctions*

We use Hartree–Fock wavefunctions for the ion cores, $1s^2 2s^2 2p^q$. Quadrupole interactions are neglected in the calculation of these functions, but are included in the calculation of the energies Δ_i of the ion core. In this approximation the same radial functions are obtained for each term $S_i L_i$ of the core.

The approximation used for the ion core functions is fairly crude, as may be seen on comparing observed and calculated core energies. Significantly different $\boldsymbol{R}$-matrices might be obtained by using more accurate core functions.

(*b*) *Accuracy of the solutions of the coupled integro-differential equations*

Results for s-waves, calculated in the distorted wave approximation, will be of low accuracy.

Reactance matrices for the p-waves calculated in the exact resonance approximation, should agree to within 1 or 2% with matrices obtained from exact solutions of the coupled integro-differential equations. Neglect of coupling between p-waves and f-waves will generally not lead to any important errors, but may be significant if a p-state happens to be very close to an f-state.

The use of distorted wave results for the d-states should not lead to important errors, except when s-states come close to d-states. It should be noted, however, that the quantum defects for the d-states are generally small and the quantum defects for the s-states are sometimes close to unity. It follows that one can get large interactions between states ns and $(n-1)$ d.

(*c*) *Other configurations not included in the calculations*

All of our calculations are for configurations of the type $1s^2 2s^2 2p^q nl$. The neglect of coupling to configurations of other types will in many cases be the main source of error in our work.

Table 3. Terms in configurations $1s^2 2s^x 2p^y$

	$x+y$				
x	3	4	5	6	7
2	${}^2P^o$	${}^3P$	${}^4S^o$	${}^3P$	${}^2P^o$
		${}^1D$	${}^2D^o$	${}^1D$	—
		${}^1S$	${}^2P^o$	${}^1S$	—
1	${}^4P$	${}^5S^o$	${}^4P$	${}^3P^o$	${}^2S$
	${}^2D$	${}^3D^o$	${}^2D$	${}^1P^o$	—
	${}^2S$	${}^3P^o$	${}^2S$	—	—
	${}^2P$	${}^1D^o$	${}^2P$	—	—
	—	${}^3S^o$	—	—	—
	—	${}^1P^o$	—	—	—
0	${}^4S^o$	${}^3P$	${}^2P^o$	${}^1S$	—
	${}^2D^o$	${}^1D$	—	—	—
	${}^2P^o$	${}^1S$	—	—	—

In table 3 we list the terms in configurations $1s^2 2s^x 2p^y$, in order of increasing excitation energy. Along an isoelectronic sequence the energy differences between these terms behave essentially as linear functions of z, whereas the binding energy of a valence electron varies essentially as z^2. This has a number of implications.

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Let us first consider the case of the np valence electron states for small values of z. In our work we calculate energies for configurations

$$1s^2 2s^2 2p^q \, np, \tag{5.1}$$

neglecting interaction with configurations such as

$$1s^2 2s 2p^{q+1} \, n's. \tag{5.2}$$

For small values of z the levels belonging to the configuration (5.2) will generally lie in the continuum, well above the $1s^2 2s^2 2p^q$ series limit. If we were to solve the collision problem allowing for collisional coupling between $1s^2 2s^2 2p^q$ and $1s^2 2s 2p^{q+1}$ we would obtain series of resonances in collision cross-sections, due to states of the type (5.2), at energies below the $2s2p^{q+1}$ limit. At continuum energies which are lower than the energy of the lowest resonance of the type (5.2) the effect of collisional coupling between $2s^2 2p^q$ and $2s2p^{q+1}$ will be to introduce an additional attractive polarization potential, behaving asymptotically like α/r^4 (Castillejo, Percival & Seaton 1960). The effect of such a potential will be to increase the scattering phase shifts, and to give larger binding energies for the valence electron states. The same conclusion may be reached from the standpoint of perturbation theory; high levels of the type (5.2) will produce a downward perturbation of the levels (5.1).

In the above discussion it is assumed that $n's$ in (5.2) is a valence electron, $n' \geqslant 3$. We could also consider the case of $n' = 2$, that is to say interaction of (5.1) with $1s^2 2s^2 2p^{q+1}$. Approximate allowance for interactions of this type have been made in the work of paper I.

Next, let us consider the np valence electron states for larger values of z. As z increases levels belonging to the configuration (5.2) will move down relative to the $2s^2 2p^q$ and $2s2p^{q+1}$ levels of the ion core, and will eventually become true bound states. The effect of such states will be to produce perturbations in the series of levels belonging to the configuration (5.1). The interactions which produce resonances in collision cross-sections for small values of z give rise to series perturbations for larger values of z. The case of the $q = 2$ isoelectronic sequence has been discussed in detail by Eissner, Nussbaumer, Saraph & Seaton (1969). For $q = 2$ the lowest state of the type (5.2) which interacts with (5.1) is

$$1s^2 2s 2p^3 (^5S) \, 3s \, ^4S. \tag{5.3}$$

For N I, the neutral atom in the sequence, this state lies above the $2s^2 2p^2 \, ^3P$ limit, for O II it is a bound state lying just below the ^3P limit, and for the higher members of the sequence it is more tightly bound. To summarize, we may say that interaction between the configurations (5.1) and (5.2) will have the following effects: for neutral atoms, to increase the binding energies for the valence–electron states belonging to the configuration (5.1); for more highly ionized atoms, to produce perturbations in the series belonging to (5.1). These effects are generally smallest for the neutrals. On comparing calculated and observed levels we therefore expect to find the largest discrepancies for the more highly ionized systems.

A further complication arises for the s- and d-valence electron states: the configurations $2s^2 2p^q \, ns$ and $2s^2 2p^q \, nd$ may be perturbed by $2s2p^{q+2}$. This type of perturbation, which has been discussed by Edlén (1964), is not allowed for in our calculations.

5.2. *Some illustrative results*

In the present section we discuss the results obtained for a few representative cases, with emphasis on the methods used in making the calculations; in § 5.3 we discuss more systematically the results obtained for neutral atoms, and in § 5.4 we discuss results for isoelectronic sequences.

(*a*) *Calculations neglecting fine structure*

Most of our work is concerned with the p-states. Neglecting fine structure, we use the representation

$$\alpha = 1s^2 2s^2 2p^q (S_i L_i)\, np\, SL. \tag{5.4}$$

The allowed values of $S_i L_i$ and SL are given in table 4. It is seen that for some values of SL only one value of $S_i L_i$ is allowed, giving simple one-channel cases. The results of the energy level calculations for these cases are most conveniently expressed in terms of the effective quantum numbers ν_i or the corresponding quantum defects

$$\mu_i = n - \nu_i,$$

where the principal quantum number n is assigned in the usual way. For other values of SL, two or three values of $S_i L_i$ are allowed. In these cases one has coupling between states belonging to different parent terms of the ion core. For each bound state energy level, we may obtain effective quantum numbers ν_i for each contributing ion term. The components V_i of the vectors $\boldsymbol{V}$ provide a useful measure of the relative contributions from the states of different parentage.

TABLE 4. STATES $p^q(S_i L_i)$ pSL

q	$S_i L_i$	SL									
1 and 5	^{2}P	^{1}S	^{1}P	^{1}D	—	^{3}S	^{3}P	^{3}D	—	—	—
2 and 4	^{3}P	^{2}S	^{2}P	^{2}D	—	—	^{4}S	^{4}P	^{4}D	—	—
	^{1}D	—	^{2}P	^{2}D	^{2}F	—	—	—	—	—	—
	^{1}S	—	^{2}P	—	—	—	—	—	—	—	—
3	^{4}S	—	—	—	—	—	—	^{3}P	—	—	^{5}P
	^{2}D	—	^{1}P	^{1}D	^{1}F	—	—	^{3}P	^{3}D	^{3}F	—
	^{2}P	^{1}S	^{1}P	^{1}D	—	—	^{3}S	^{3}P	^{3}D	—	—

In table 5 we give some illustrative results for the case of O II 2p^2 np. For SL = ^{2}S, ^{4}S, ^{4}P and ^{4}D we have simple one-channel cases, the parent term being the ^{3}P ground term of O III. For these cases it is seen that the quantum defect varies slowly with n, and that the vector $\boldsymbol{V}$ has only one component, which is close to unity. For SL = ^{2}F we have a one-channel case for which the parent term is the excited 2p^2 ^{1}D level of O III. This series contains only two bound states below the O III ^{3}P limit. The states above this limit may auto-ionize to the 2p^2(^{3}P) ϵf ^{2}F continuum. It should be noted that, when the effective quantum numbers of the bound ^{2}F levels are calculated relative to their proper parent state, O III ^{1}D, the quantum defects show the same pattern as those of the other one-channel cases.

For SL = ^{2}P we have a three-channel case, and for SL = ^{2}D a two-channel case. These are the angular momentum states of importance for the calculation of the $e + O^{2+}$ inelastic collision cross-sections, as described in paper I. In both the ^{2}P and ^{2}D series we obtain two levels, denoted by 3′p and 4′p in the conventional spectroscopic notation, for which the ^{1}D parent gives the dominant contribution; and in the ^{2}P series we obtain one level, 3″p, for which the contribution from the ^{1}S parent is dominant. It should be noted that, for all of the levels in the ^{2}P and ^{2}D series, there is a quite large admixture of states of different parentage.

It has already been mentioned in § 5.1 that the state 2s2p^3(^{5}S) 3s ^{4}S lies just below the 2s^{2}2p^2 ^{3}P limit. This state will therefore perturb the higher members of the 2s^{2}2p^2(^{3}P) np ^{4}S series, but in our calculations these perturbations are not taken into account. Eissner *et al.* show that the states

$2s2p^3(^3D)$ 3s ^2D and $2s2p^3(^3P)$ 3s ^2P lie, respectively, just above the $2s^22p^2$ ^1D and ^1S limits. They will produce some perturbations in the $2s^22p^2np$ ^2D and ^2P series, and it is shown by Eissner *et al.* that they produce important resonance effects in the inelastic collision cross-sections. Perturbations of this type are of less importance for the valence-electron states of N I, the neutral atom in the same isoelectronic sequence.

Table 5. Calculated effective quantum numbers and vectors V for O II $2p^2(S_iL_i)\,npSL$, neglecting fine structure

SL	n	ν_1	ν_2	ν_3	V_1	V_2	V_3
^2S	3	2.396	—	—	−0.923	—	—
	4	3.421	—	—	+0.960	—	—
	5	4.430	—	—	−0.976	—	—
	6	5.434	—	—	+0.984	—	—
	7	6.437	—	—	−0.988	—	—
^2P	3	2.550	2.239	1.993	+0.881	−0.229	+0.080
	3′	2.999	2.520	2.187	+0.295	+0.869	−0.001
	4	3.578	2.842	2.384	+0.897	−0.187	−0.264
	3″	3.896	2.994	2.471	−0.319	+0.022	−0.866
	5	4.592	3.277	2.623	+0.946	+0.190	−0.122
	4′	5.339	3.518	2.742	+0.518	−0.814	+0.027
	6	5.685	3.612	2.786	−0.871	−0.441	−0.046
	7	6.621	3.820	2.878	+0.977	−0.134	−0.040
^2D	3	2.505	2.209	—	−0.881	−0.253	—
	3′	2.939	2.484	—	+0.314	−0.864	—
	4	3.562	2.834	—	−0.936	−0.193	—
	5	4.535	3.256	—	−0.951	+0.211	—
	4′	5.242	3.490	—	+0.487	+0.833	—
	6	5.631	3.598	—	−0.896	+0.394	—
	7	6.578	3.812	—	+0.978	+0.134	—
^2F	3′	—	2.444	—	—	−0.920	—
	4′	—	3.470	—	—	+0.959	—

SL	n	ν_1	V_1
^4S	3	2.546	+0.914
	4	3.569	−0.957
	5	4.575	+0.974
	6	5.578	−0.983
	7	6.579	+0.988
^4P	3	2.446	−0.920
	4	3.467	+0.959
	5	4.475	−0.975
	6	5.478	+0.984
	7	6.480	−0.988
^4D	3	2.424	−0.921
	4	3.448	+0.960
	5	4.456	−0.976
	6	5.460	+0.984
	7	6.462	−0.988

(*b*) *Calculations including fine structure*

Fine structure in valence-electron states $2p^q\,nl$ is mainly due to the fine-structure separations in the $2p^q$ ion core. When fine structure is neglected in the calculations it is difficult to make any meaningful comparison of calculated and observed levels, particularly for the higher states. On transforming to the representation (1.2), or (1.3), and using experimental energies for the core, we make rather accurate allowance for the core contribution to the fine structure of the valence-electron states. We do not attempt to make any allowance for the spin-orbit interaction energy of the valence electron.

In comparing the calculations with experiment we adopt the following notation:

> Calculated quantities (energies, effective quantum numbers, quantum defects, etc.) are denoted by superscripts (c); Exact quantities, from experiment, are denoted by superscripts (e); and Adjusted quantities, obtained by the theory described in § 4.3, are denoted by superscripts (a).

In table 6 we give results for all $2p^2np$ levels which have been observed in O II. We give values of $\nu^{(c)}$, the effective quantum number calculated allowing for fine structure, and the differences between calculated and exact effective quantum numbers,

$$\delta\nu = \nu^{(c)} - \nu^{(e)}. \tag{5.5}$$

From table 6 we see that, for each term nSL, $\delta\nu(nSLJ)$ is practically the same for each value of J. We may therefore say that the calculated fine structure is in good agreement with the observed fine structure. This confirms our basic assumption, that the fine structure splitting in the valence-electron states is mainly due to the fine-structure of the ion core.

TABLE 6. CALCULATED EFFECTIVE QUANTUM NUMBERS FOR O II $2p^2np$ LEVELS, WITH FINE STRUCTURE, REFERRED TO THE O III $^3P_0$ LIMIT, AND DIFFERENCES BETWEEN CALCULATED AND OBSERVED EFFECTIVE QUANTUM NUMBERS

SL	n	J	$\nu^{(c)}$	$\nu^{(c)}-\nu^{(e)}$
^2S	3	$\frac{1}{2}$	2.3959	0.0432
^2P	3	$\frac{1}{2}$	2.5524	0.0316
		$\frac{3}{2}$	2.5545	0.0326
	3′	$\frac{1}{2}$	3.0044	0.0639
		$\frac{3}{2}$	3.0047	0.0628
	4	$\frac{1}{2}$	3.5862	0.0352
		$\frac{3}{2}$	3.5916	0.0365
^2D	3	$\frac{3}{2}$	2.5068	0.0330
		$\frac{5}{2}$	2.5097	0.0326
	3′	$\frac{3}{2}$	2.9425	0.0722
		$\frac{5}{2}$	2.9431	0.0733
	4	$\frac{3}{2}$	3.5659	0.0364
		$\frac{5}{2}$	3.5749	0.0365
	5	$\frac{3}{2}$	4.5462	0.0327
		$\frac{5}{2}$	4.5643	0.0327
^2F	3′	$\frac{5}{2}$	2.8787	0.0413
		$\frac{7}{2}$	2.8757	0.0408
^4S	3	$\frac{3}{2}$	2.5502	0.0652
^4P	3	$\frac{1}{2}$	2.4488	0.0280
		$\frac{3}{2}$	2.4496	0.0280
		$\frac{5}{2}$	2.4511	0.0280
	5	$\frac{1}{2}$	4.4896	—
		$\frac{3}{2}$	4.4933	0.0248
		$\frac{5}{2}$	4.5036	0.0257
^4D	3	$\frac{1}{2}$	2.4250	0.0299
		$\frac{3}{2}$	2.4259	0.0299
		$\frac{5}{2}$	2.4273	0.0299
		$\frac{7}{2}$	2.4293	0.0299
	4	$\frac{1}{2}$	3.4501	0.0278
		$\frac{3}{2}$	3.4523	0.0278
		$\frac{5}{2}$	3.4563	0.0278
		$\frac{7}{2}$	3.4622	0.0279
	5	$\frac{1}{2}$	4.4611	—
		$\frac{3}{2}$	4.4647	0.0266
		$\frac{5}{2}$	4.4732	0.0269
		$\frac{7}{2}$	4.4873	0.0271

(c) *Elimination of fine structure*

Since $\delta\nu(nSLJ)$ depends little on J we may conveniently define a quantity $\delta\nu(nSL)$ independent of J. We take the definition of this quantity to be

$$\delta\nu(nSL) = \frac{\sum\limits_J (2J+1)\,\delta\nu(nSLJ)}{(2S+1)\,(2L+1)}. \tag{5.6}$$

Let $\nu^{(c)}(nSL)$ be the effective quantum number calculated neglecting fine structure, and let $\nu^{(e)}(nSL)$ be defined by

$$\nu^{(e)}(nSL) = \nu^{(c)}(nSL) - \delta\nu(nSL). \tag{5.7}$$

We shall refer to $\nu^{(e)}(nSL)$ as the *exact effective quantum number, neglecting fine structure*. Since this quantity is used throughout much of our work, we recapitulate the steps involved in obtaining it:

(i) $\nu^{(c)}(nSLJ)$ is calculated allowing for fine structure.

(ii) $\nu^{(e)}(nSLJ)$ is obtained from experiment.

(iii) $\delta\nu(nSLJ) = \nu^{(c)}(nSLJ) - \nu^{(e)}(nSLJ)$ is insensitive to J and we form $\delta\nu(nSL)$ independent of J (using (5.6)).

(iv) $\nu^{(c)}(nSL)$ is calculated neglecting fine structure.

(v) $\nu^{(e)}(nSL)$ is defined by (5.7).

It is seen that $\nu^{(e)}(nSL)$ is a quantity deduced from experiment, but that some use is made of theory in eliminating fine-structure contributions to the energy.

In our calculations neglecting fine structure we obtain approximate solutions of a non-relativistic Schrödinger problem. It may be expected that exact solutions of this problem would give effective quantum numbers in close agreement with $\nu^{(e)}(nSL)$.

TABLE 7. DIFFERENCES, $(\nu_i^{(c)}-\nu_i^{(e)})$, BETWEEN CALCULATED AND EXACT EFFECTIVE QUANTUM NUMBERS FOR O II $2p^2(S_iL_i)\ np\,SL$

Calculations in the exact resonance (e.r.) and distorted wave (d.w.) approximations

			$(\nu_i^{(c)}-\nu_i^{(e)})$	
SL	n	S_iL_i	e.r.	d.w.
^2S	3	^3P	0.043	0.096
^2P	3	^3P	0.032	0.064
	3′	^1D	0.038	0.050
	4	^3P	0.036	0.066
^2D	3	^3P	0.033	0.067
	3′	^1D	0.045	0.060
	4	^3P	0.036	0.051
	5	^3P	0.033	0.058
^2F	3′	^1D	0.025	0.058
^4S	3	^3P	0.065	0.072
^4P	3	^3P	0.028	0.068
	5	^3P	0.025	0.052
^4D	3	^3P	0.030	0.075
	4	^3P	0.028	0.062
	5	^3P	0.027	0.057

As an example of the use of $\nu^{(e)}(nSL)$ we may consider the results for O II $2p^2np$ in two different approximations. Table 7 gives values of $(\nu^{(c)}-\nu^{(e)})$ obtained using the $\boldsymbol{R}$-matrices of paper I, as calculated in the exact resonance (e.r.) and distorted wave (d.w.) approximations. It is seen that the e.r. results are much superior to the d.w. results. In the remainder of the present paper we consider only e.r. results for np levels, but use the d.w. results for ns and nd levels.

(*d*) *Effective quantum numbers referred to different series limits*

Let us first consider the O II level $3'p\ ^2F$, for which the parent term is the first excited state of the ion core, $2p^2\ ^1D$. If we use effective quantum numbers referred to the $2p^2\ ^1D$ limit we obtain $\nu_2^{(c)} = 2.444$ in the e.r. approximation, and $\nu_2^{(e)} = 2.419$. The relation between ν_2 and ν_1 (the effective quantum number referred to the $2p^2\ ^3P$ limit) is

$$\frac{1}{\nu_1^2} = \frac{1}{\nu_2^2} - \Delta_2. \tag{5.8}$$

From table 1 we obtain, neglecting fine structure, $\Delta_2 = 0.0457$, and hence $\nu_1^{(c)} = 2.866$, $\nu_1^{(e)} = 2.826$. Putting $\delta\nu_i = \nu_i^{(c)} - \nu_i^{(e)}$, we have $\delta\nu_2 = 0.025$, $\delta\nu_1 = 0.040$. It is seen that $\delta\nu_1$ is larger than $\delta\nu_2$; from (5.8) we have the approximate relation

$$\delta\nu_1 \simeq (\nu_1/\nu_2)^3\,\delta\nu_2. \tag{5.9}$$

The accuracy of the calculations is, of course, best judged by considering the effective quantum numbers, ν_i, referred to the correct series limit.

Whenever one state of the ion core gives the dominant contribution to the wavefunction for a valence electron state, it is best to use the effective quantum number referred to that state of the core. This gives a fairly uniform basis for comparison of theory and experiment for all of the levels. For some cases, however, one can get contributions of comparable magnitude for two or more parent states; for these cases the selection of a series limit is essentially arbitrary.

In table 7, we have three levels, labelled 3′p ^{2}P, ^{2}D and ^{2}F, for which the dominant contribution comes from the excited state, 2p^2 ^{1}D, of the core (see table 5); for these levels we give effective quantum numbers, ν_2, referred to the ^{1}D limit. When this procedure is followed we see from table 7 that for O II 2p^2 *n*p the largest value of $(\nu_i^{(c)}-\nu_i^{(e)})$, in the e.r. approximation, occurs for 3p ^{4}S. This is the level for which we would expect the theory to be least accurate since, as noted in §§ 5.1 and 5.2 (*a*), the 2p^2*n*p ^{4}S series is perturbed by 2s2p^3 (^{5}S) 3s ^{4}S. The point which we wish to emphasize here is that if the effective quantum numbers for all of the levels in table 7 had been referred to the 2p^2 ^{3}P limit, we would have obtained $(\nu_1^{(c)}-\nu_1^{(e)}) = 0.073$ for the level 3′p ^{2}D, in place of $(\nu_2^{(c)}-\nu_2^{(e)}) = 0.040$; it would then not have been apparent that the theory was poorest for the ^{4}S series.

(*e*) *Semi-empirical adjustments of the calculated matrices*

It is seen from tables 6 and 7 that $\delta\nu$ is positive in all cases, which implies that the calculated valence-electron binding energies are smaller than the observed binding energies (see § 5.1). The effect of such systematic errors in the theory can be reduced on making semi-empirical adjustments to the matrices, using the methods described in § 4.3.

In making these adjustments, fine structure may be neglected; the adjustments are made so as to obtain better agreement between $\nu^{(c)}(nSL)$ and $\nu^{(e)}(nSL)$.

In § 4.3 it was stated that the correction matrices $\delta\boldsymbol{\eta}$ were taken to be independent of the energy. This may be justified by considering some simple one-channel cases. For these cases we can easily calculate the exact values of η; we put $\nu^{(e)} = n-\mu^{(e)}$ and $\tan(\pi\eta^{(e)}) = (\tan(\pi\mu^{(e)}))/A$ where, for p-states, $A = 1-1/\nu^2$. In table 8 we give values of $\eta^{(c)}$ and $\delta\eta = (\eta^{(c)}-\eta^{(e)})$ for the one channel cases O II 2p^2 *n*p ^{4}P and ^{4}D. For each series it is seen that $\eta^{(c)}$ varies slowly and that $\delta\eta$ is practically constant.

Table 8. Values of η for O II 2p^2(^{3}P) *n*p ^{4}P and ^{4}D

SL	n	$\eta^{(c)}$	$(\eta^{(c)}-\eta^{(e)})$
^{4}P	3	0.545	−0.023
	4	0.524	−0.024
^{4}D	3	0.563	−0.025
	4	0.548	−0.026
	5	0.542	−0.026

Let $E^{(a)}(nSL)$ be the energy of a term calculated using the adjusted matrices and let $E^{(e)}(nSL)$ be the exact energy (neglecting fine structure), as obtained from $\nu^{(e)}$, defined in § 5.2 (*c*). The four parameters in the expression (4.9) for $\delta\boldsymbol{\eta}$ are adjusted so as to minimize

$$D = \Sigma\{E^{(e)}(nSL)-E^{(a)}(nSL)\}^2, \tag{5.10}$$

where the summation is normally taken over all observed terms of the type considered. Typically we may use about 15 observed *n*p terms for the determination of four parameters. The minimization is effected by means of a computer subroutine written by Powell (1965), which we find to be very satisfactory.

In some cases it is found that the minimization of (5.10) gives an improved overall agreement between the exact energies $E^{(e)}$ and the adjusted energies $E^{(a)}$ but leads to a worse agreement for certain important energy differences. If it is required to improve the agreement for some particular energy difference, say $E(n'S'L') - E(n''S''L'')$, we may minimize

$$D = \Sigma\{E^{(e)}(nSL) - E^{(a)}(nSL)\}^2 + \{[E^{(e)}(n'S'L') - E^{(e)}(n''S''L'')] - [E^{(a)}(n'S'L') - E^{(a)}(n''S''L'')]\}^2 \tag{5.11}$$

In effect, this means that we give more weight to certain levels in the minimization procedure.

5.3. *Results for neutral atoms*

In § 5.1 it was argued that our method of calculation should be best for neutral atoms. The results for neutrals are discussed in some detail in the present section, and results for isoelectronic sequences are discussed in § 5.4.

(*a*) *Results for* C I 2p *n*p

A very thorough analysis of experimental data for C I is given by Johansson (1966).

(i) *Calculations for* C I 2p *n*p *neglecting fine structure.* Fine structure contributions to the experimental energies are eliminated using the method described in § 5.2 (*c*). Table 9 gives values of $\nu^{(c)}$, $(\nu^{(c)} - \nu^{(e)})$ and $(\nu^{(a)} - \nu^{(e)})$ for C I 2p*n*p. It is seen that the errors in the calculated results, $(\nu^{(c)} - \nu^{(e)})$, are fairly large. Adjustment of Y leads to a reduction in the systematic errors, but the residuals $(\nu^{(a)} - \nu^{(e)})$ are not as small as one would wish. It is worth discussing this simple case in greater detail.

TABLE 9. EFFECTIVE QUANTUM NUMBERS FOR C I 2p *n*p

SL	n	$\nu^{(c)}$	$(\nu^{(c)} - \nu^{(e)})$	$(\nu^{(a)} - \nu^{(e)})$
^{1}S	3	2.687	0.138	0.017
	4	3.689	0.120	0.006
	5	4.690	0.115	0.004
	6	5.691	0.113	0.003
^{1}P	3	2.286	0.053	−0.001
	4	3.313	0.049	−0.002
	5	4.323	0.048	−0.003
	6	5.327	0.045	−0.004
^{1}D	3	2.511	0.060	0.006
	4	3.533	0.060	0.013
	5	4.541	0.061	0.016
	6	5.545	0.063	0.018
^{3}S	3	2.389	0.054	0.029
	4	3.401	0.048	0.024
^{3}P	3	2.451	0.079	0.006
	4	3.475	0.082	0.018
	5	4.483	0.084	0.022
	6	5.486	0.085	0.024
^{3}D	3	2.321	0.043	−0.000
	4	3.344	0.040	−0.001
	5	4.352	0.040	−0.000
	6	5.355	0.040	+0.001

We use the expression (4.7) for the Hamiltonian matrix, with coefficients f_λ and g_λ given in table 2. In a simple perturbation theory treatment, based on a central-field model, we would use the same radial functions for each of the terms within a configuration 2p*n*p. We would then have four parameters, E_0, F_2, G_0 and G_2, for the determination of the energies of six 2p*n*p terms, SL = ^{1}S, ^{3}S, ^{1}P, ^{3}P, ^{1}D and ^{3}D. The exchange integrals G_λ may be eliminated on taking the arithmetic mean of singlets and triplets and, using the coefficients f_2 of table 2, we then obtain the ratio (S – D)/(D – P) = 1.5. The observed value of this ratio for C I 2p3p is (S – D)/(D – P) = 1.14. This illustrates the inherent limitation of the central-field model.

The exact resonance approximation should be more accurate than the simple central-field model, in that we calculate the radial functions allowing for the $\lambda = 0$ exchange term G_0 but neglecting F_2 and G_2. We then have two radial functions, one for $g_0 = +1$ and one for $g_0 = -1$. In practice it is found that the exact resonance approximation may give a less good value for the ratio (S – D)/(D – P); thus for C I 2p3p we obtain (S – D)/(D – P) = 2.22 using the values of $\nu^{(c)}$ given in table 9. The adjusted results give some improvement, (S – D)/(D – P) = 1.43, but not very close agreement with the observed value of 1.14.

These results for C I emphasize the nature of the limitation of using expressions for matrix elements of the form (4.7), obtained on restricting the wavefunction to a single configuration. Further improvement could be obtained only on making explicit allowance for interaction with other configurations.

Table 10. Fine structure results for C I 2p *n*p

		$(\nu^{(a)}-\nu^{(e)})$					
SL	*J*	$n = 3$	4	5	6	7	8
^{3}P	0	0.0060	0.0171	0.0219	0.0243	0.0254	—
	1	0.0061	0.0173	0.0221	0.0246	0.0258	—
	2	0.0060	0.0172	0.0220	0.0244	0.0254	—
^{3}D	1	–0.0004	–0.0011	–0.0008	–0.0002	+0.0019	+0.0068
	2	–0.0004	–0.0011	–0.0007	–0.0000	+0.0010	(0.0002)†
	3	–0.0005	–0.0012	–0.0008	–0.0006	–0.0004	–0.0002

† The term value for 2p 8p $^3D_2$ given by Johansson (1966) was obtained by extrapolation.

(ii) *Calculations for* C I 2p *n*p *including fine structure.* Table 10 gives results of calculations allowing for fine structure in the terms 2p *n*p ^{3}P and ^{3}D. The adjusted *Y* matrices have been used. It is seen that for the lower levels, $n = 3$, 4, 5 and 6, we obtain values of $(\nu^{(a)} - \nu^{(e)})$ for each term which are practically independent of *J*. The fine structure splitting of these terms is therefore given satisfactorily by the theory. The larger discrepancies in the fine structure results for the higher levels are a consequence of departures from *SL* coupling. This is illustrated in table 11 which gives the weights $W(\alpha)$, in the *SL* coupling representation $\alpha = 2\text{p}n\text{p}SLJ$, for the levels which are labelled 2p *n*p $^3D_1$. It is seen that *SL* coupling is a very good approximation for the lower levels but that no significant assignment of quantum numbers *SL* can be made for the higher levels. The level labelled 2p8p $^3D_1$ contains appreciable admixtures of $^3S_1$ and $^3P_1$. The error in the adjusted results, $\nu^{(a)} - \nu^{(e)}$, is fairly large for the ^{3}S and ^{3}P series, and in consequence the error for 8p $^3D_1$ is much larger than that for the lower *n*p $^3D_1$ levels. No such admixture of SL states occurs for 2p *n*p $^3D_3$, and for these levels the error in the adjusted results is seen to be much smaller and to vary slowly along the series.

(iii) *Calculations for* C I 2p *ns and* 2p *n*d. For C I the 2p *ns* levels have quantum defects close to unity and the 2p *n*d levels have quantum defects which are small. There is therefore significant interaction between *ns* and $(n-1)$ d. These interactions are allowed for in our calculations, which are made using the distorted wave results of paper I.

Results obtained with fine structure neglected are given in table 12. The terms ^{3}D, ^{3}P, ^{1}D and ^{1}P in the 2s^2 2p *ns* and *n*d series are perturbed by the 2*s* 2p^3 configuration, but these perturbations

TABLE 11. WEIGHTS $W(\alpha)$, IN THE SL COUPLING REPRESENTATION $\alpha = 2\mathrm{p}\,n\mathrm{p}\,SLJ$, FOR THE C I LEVELS LABELLED $2\mathrm{p}\,n\mathrm{p}\;{}^3\mathrm{D}_1$

	$W(\alpha)$			
n	$\alpha = {}^3\mathrm{S}$	$^1\mathrm{P}$	$^3\mathrm{P}$	$^3\mathrm{D}$
3	0.000	0.001	0.000	0.999
4	0.000	0.007	0.001	0.992
5	0.001	0.046	0.003	0.950
6	0.007	0.180	0.013	0.800
7	0.038	0.347	0.049	0.566
8	0.111	0.384	0.125	0.380

TABLE 12. EFFECTIVE QUANTUM NUMBERS FOR C I 2p ns AND 2p nd

SL	n	$\nu^{(c)}$	$\nu^{(e}$	$\nu^{(c)} - \nu^{(e)}$
$^1\mathrm{P}$	3s	2.049	1.951	0.098
	4s	3.074	2.965	0.109
	5s	4.087	3.976	0.111
	6s	5.104	4.992	0.112
	3d	3.017	3.013	0.004
	4d	4.025	4.021	0.004
	5d	5.037	5.035	0.002
$^3\mathrm{P}$	$2\mathrm{s}\,2\mathrm{p}^3$	—	2.650	—
	3s	2.029	1.899	0.130
	4s	3.049	2.941	0.108
	5s	4.059	3.946	0.113
	6s	5.053	4.955	0.098
	3d	3.004	3.089	−0.085
	4d	4.009	4.044	−0.035
	5d	5.042	5.047	−0.005
$^1\mathrm{D}$	3d	2.964	2.890	0.074
	4d	3.960	3.871	0.089
	5d	4.962	4.866	0.096
$^3\mathrm{D}$	$2\mathrm{s}\,2\mathrm{p}^3$	—	2.024	—
	3d	2.975	2.962	0.013
	4d	3.973	3.965	0.008
	5d	4.994	4.975	0.019
$^1\mathrm{F}$	3d	3.019	2.988	0.031
	4d	4.030	3.996	0.034
	5d	5.046	5.010	0.036
$^3\mathrm{F}$	3d	2.990	2.952	0.038
	4d	3.992	3.946	0.046
	5d	4.990	4.950	0.040

are not allowed for in our calculations. The experimental positions of $2\mathrm{s}2\mathrm{p}^3\;{}^3\mathrm{P}$ and $^3\mathrm{D}$ are given in table 12. Moore (1949) estimates that $2\mathrm{s}2\mathrm{p}^3\;{}^1\mathrm{P}$ and $^1\mathrm{D}$ lie just above the $2\mathrm{s}^2 2\mathrm{p}$ limit.

The $2\mathrm{s}^2 2\mathrm{p}\,n\mathrm{d}\;{}^1\mathrm{F}$ and $^3\mathrm{F}$ series are not perturbed by the ns levels or by $2\mathrm{s}2\mathrm{p}^3$. The calculated levels for these series are too high. This may be explained as a consequence of the neglect of coupling with higher states. We have already remarked in § 5.1 that the effect of such couplings will be to introduce an additional polarization potential; this is particularly important in calculating quantum defects for nd states.

The $2\mathrm{s}^2 2\mathrm{p}\,n\mathrm{d}\;{}^1\mathrm{D}$ and $^3\mathrm{D}$ series are not perturbed by the ns levels but are perturbed by $2\mathrm{s}2\mathrm{p}^3$ $^1\mathrm{D}$ and $^3\mathrm{D}$. The level $2\mathrm{s}2\mathrm{p}^3\;{}^1\mathrm{D}$ lies above the $2\mathrm{s}^2 2\mathrm{p}$ limit and perturbs all $2\mathrm{s}^2 2\mathrm{p}\,n\mathrm{d}$ levels downwards. This additional perturbation is not allowed for in our calculations and the difference between calculated and exact effective quantum numbers is therefore large. The level $2s2p^3\,{}^3D$, on the other hand, lies below the entire $2s^22p\,nd\,{}^3D$ series, and all levels in this series are therefore perturbed upwards. The neglect of both upward perturbations by $2s2p^3\,{}^3D$ and downward perturbations by higher levels causes the calculated effective quantum numbers to be in fortuitously good agreement with the experimental results.

For the ${}^1P$ and ${}^3P$ terms we have to consider both $2s^2\,2p\,ns$ series and $2s^2\,2p\,nd$ series. For the *n*s levels the calculated effective quantum numbers are too large by about 0.1, owing to the use of the distorted wave approximation. In consequence the calculated separations of the levels *n*s and $(n-1)$ d tends to be much smaller than the corresponding separations for the observed levels. Owing to *n*s and $(n-1)$ d being very close, the calculated results have large interactions between s and d states. For the ${}^3P$ series these interactions are so large that it is difficult to make assignments of *l* quantum numbers. A further interesting effect arises. The experimental positions for each *n*s level are always below the corresponding $(n-1)$ d levels, and the effect of s – d interactions is therefore to shift the s levels down and the d levels up. For the calculated levels the error in ν for the s levels is such as to bring the calculated *n*s levels above the calculated $(n-1)$ d levels. The calculated s – d interactions therefore work in the wrong direction, to depress the d levels and to raise the s levels. We can now understand the trend of the results in table 12. The experimental $nd\,{}^1P$ levels are depressed by interaction with $2s\,2p^3\,{}^1P$, which lies above the $2s^2\,2p$ limit, and the calculated $nd\,{}^1P$ levels are, incorrectly, depressed by s – d interactions: the close agreement between $\nu^{(c)}$ and $\nu^{(e)}$ for this series is therefore entirely fortuitous. The experimental $nd\,{}^3P$ levels are raised due to perturbation by $2s2p^3\,{}^3P$, and the values of $(\nu^{(c)}-\nu^{(e)})$ are therefore large and negative. The first member of the $2s^2\,2p\,ns\,{}^3P$ series is perturbed downwards by $2s2p^3\,{}^3P$, and all other members are perturbed upwards; the effect of these perturbations is seen in the irregular variation of $(\nu^{(c)}-\nu^{(e)})$.

(*b*) *Results for* N I $2p^2\,np$

We use the experimental energy level data quoted by Moore (1949), together with the later data of Eriksson & Johansson (1961). Fine structure is eliminated using the method described in § 5.2 (*c*). Table 13 gives calculated effective quantum numbers $\nu_i^{(c)}$ and values of $(\nu_i^{(c)}-\nu_i^{(e)})$ and $(\nu_i^{(a)}-\nu_i^{(e)})$.

TABLE 13. EFFECTIVE QUANTUM NUMBERS ν_i FOR N I $2p^2\,(S_iL_i)\,np\,SL$

SL	*n*	S_iL_i	$\nu_i^{(c)}$	$\nu_i^{(c)}-\nu_i^{(e)}$	$\nu_i^{(a)}-\nu_i^{(e)}$
${}^2S$	3	${}^3P$	2.215	0.065	0.012
	4	${}^3P$	3.238	0.054	0.007
${}^2P$	3	${}^3P$	2.409	0.038	0.026
	4	${}^3P$	3.403	—	—
	3′	${}^1D$	2.365	0.037	0.018
${}^2D$	3	${}^3P$	2.356	0.041	0.002
	4	${}^3P$	3.346	—	—
	5 or 3′	${}^3P$	4.214	0.190	0.011
	5 or 3′	${}^3P$	4.703	0.209	0.039
	6	${}^3P$	5.485	—	—
	7	${}^3P$	6.449	—	—
${}^2F$	3′	${}^1D$	2.276	0.034	−0.005
${}^4S$	3	${}^3P$	2.404	0.093	0.050
	4	${}^3P$	3.425	0.091	0.052
${}^4P$	3	${}^3P$	2.276	0.033	0.002
	4	${}^3P$	3.295	0.030	0.001
${}^4D$	3	${}^3P$	2.248	0.038	−0.002
	4	${}^3P$	3.270	0.033	−0.006

The ${}^2P$ series contains one level, $3'p\,{}^2P$, for which the ${}^1D$ parent gives the dominant contribution, but does not contain a bound state, $3''p$, of dominant ${}^1S$ parentage: at the first ionization limit, $\nu_1 \to \infty$, one has $\nu_3 = 1.835$; the $3''p$ level will lie in the continuum, at $\nu_3 \simeq 2.3$.

Our main interest in the N I results is in making parentage assignments for the ^{2}D series (in table 13 all effective quantum numbers for this series have been referred to the ^{3}P limit). Table 14 gives weights W, defined by (2.32), as obtained by using calculated matrices and adjusted matrices. Using the calculated matrices, we see that $W(^1\mathrm{D})$ is smaller than $W(^3\mathrm{P})$ for all of the levels, and that the largest value of $W(^1\mathrm{D})$ occurs for level number 4 in the table. Using the adjusted matrices the largest value of $W(^1\mathrm{D})$ occurs for level number 3. For this level $W(^1\mathrm{D})$ is nearly equal to $W(^3\mathrm{P})$ and there is little significance in attempting to make a parentage assignment. Using the adjusted results we may predict the positions of levels which have not been observed. The predicted positions of 4p ^{2}P and ^{2}D levels are given in table 15.

Table 14. Weights $W(S_i L_i)$ for $2\mathrm{p}^2\,n\mathrm{p}\ ^2\mathrm{D}$ series in N I

level number	calculated matrices $\nu_1^{(c)}$	calculated matrices $W(^3\mathrm{P})$	calculated matrices $W(^1\mathrm{D})$	adjusted matrices $\nu_1^{(a)}$	adjusted matrices $W(^3\mathrm{P})$	adjusted matrices $W(^1\mathrm{D})$
1	2.356	0.98	0.02	2.317	0.97	0.03
2	3.346	0.96	0.04	3.296	0.93	0.07
3	4.214	0.70	0.30	4.035	0.49	0.51
4	4.703	0.55	0.45	4.533	0.76	0.24
5	5.485	0.94	0.06	5.429	0.96	0.04
6	6.449	0.98	0.02	6.408	0.99	0.01

Table 15. Predicted term values for N I referred to the $2\mathrm{p}^2\ ^3\mathrm{P}_0$ limit at 117 214.0 cm^{-1}

level	predicted term value/cm^{-1}	estimated value of x/cm^{-1}
4p $^2\mathrm{P}_{\frac{1}{2}}$	$107\,681+x$	-400
$^2\mathrm{P}_{\frac{3}{2}}$	$107\,750+x$	-400
4p $^2\mathrm{D}_{\frac{3}{2}}$	$107\,165+x$	-30
$^2\mathrm{D}_{\frac{5}{2}}$	$107\,233+x$	-30

Note. $x = 0$ gives the term value obtained by using adjusted matrices. Estimated values of x are obtained from comparisons of adjusted and experimental results for other levels.

(c) *Results for* O I $2\mathrm{p}^3 n\mathrm{p}$

(i) *Fine structure.* In *SL* coupling the spin-orbit energy vanishes to first order for the 2p^3 configuration. The fine structure separations are therefore small for the 2p^3 ion core and for the valence-electron states with configuration $2\mathrm{p}^3 nl$. It is found that calculated fine-structure separations for the valence-electron states, obtained neglecting the spin-orbit energy of the valence electron, are not in good agreement with observed separations. To obtain any improvement it would clearly be necessary to take account of the spin-orbit energy of the valence electron. Since the observed fine-structure separations are small, we may average over fine structure and compare with results calculated neglecting fine-structure.

(ii) *Calculations neglecting fine structure.* An interesting feature of the O I spectrum is that a large number of $2\mathrm{p}^3 nl$ levels are observed above the 2p^3 ^{4}S limit (Moore 1949). When fine structure is neglected many of these levels are true bound states. Thus, for example, the $2\mathrm{p}^3 nl$ singlet levels cannot auto-ionize to the $2\mathrm{p}^3(^4\mathrm{S})\,\epsilon l'$ continuum without violation of spin conservation, and levels such as $2\mathrm{p}^3 n\mathrm{p}\ ^3\mathrm{S}$ and ^{3}D cannot auto-ionize without violation of parity conservation. The levels $2\mathrm{p}^2(^2\mathrm{D})\,n\mathrm{p}\ ^3\mathrm{F}$ can auto-ionize to $2\mathrm{p}^3(^4\mathrm{S})\,\epsilon f\ ^3\mathrm{F}$, but this level is observed spectroscopically which means that, even here, the auto-ionization probability must be small. A number of the levels above the ^{4}S limit will have finite, but very small, auto-ionization probabilities when fine-structure is taken into account.

TABLE 16. CALCULATED EFFECTIVE QUANTUM NUMBERS $\nu_i^{(c)}$ AND WEIGHTS $W(S_i L_i)$ FOR O I 2p^3 np

			$\nu_i^{(c)}$			$W(S_i L_i)$		
		$i =$	1	2	3	1	2	3
SL	n	$S_i L_i =$	^{4}S	^{2}D	^{2}P	^{4}S	^{2}D	^{2}P
^{1}S	3″		—	—	2.407	—	—	1.000
^{1}P	3′		—	2.220	1.748	—	0.910	0.090
	3″		—	3.612	2.230	—	0.125	0.875
^{1}D	3′		—	2.380	1.823	—	0.994	0.006
	3″		—	3.844	2.281	—	0.102	0.898
^{1}F	3′		—	2.250	—	—	1.000	—
^{3}S	3″		—	—	2.243	—	—	1.000
^{3}P	3		2.303	1.520	1.339	0.982	0.015	0.003
	4		3.315	1.727	1.475	0.993	0.006	0.001
	5		4.317	1.832	1.539	0.995	0.004	0.001
	6		5.308	1.890	1.573	0.989	0.009	0.002
^{3}D	3′		—	2.210	1.743	—	0.998	0.002
	4′		—	3.223	2.129	—	0.984	0.016
	3″		—	3.557	2.216	—	0.028	0.972
^{3}F	3′		—	2.238	—	—	1.000	—
^{5}P	3		2.206	—	—	1.000	—	—
	4		3.224	—	—	1.000	—	—

For states of the type 2p^3$(S_i L_i)$ np SL the allowed values of $S_i L_i$ and SL are listed in table 4. Table 16 gives some calculated effective quantum numbers $\nu_i^{(c)}$, and weights $W(S_i L_i)$. The only series with 2p^3 ^{4}S parentage are 2p^3 np ^{3}P and ^{5}P. The ^{5}P series is a simple one-channel case. The ^{3}P series has contributions from all three channels but the ^{4}S parentage contribution dominates for all levels below the ^{4}S limit. Above this limit the ^{3}P states will have large auto-ionization probabilities and are not observed spectroscopically.

TABLE 17. VALUES OF $(\nu_i^{(c)} - \nu_i^{(e)})$ AND $(\nu_i^{(a)} - \nu_i^{(e)})$ FOR O I 2p^3$(S_i L_i)$ np SL

SL	n	$S_i L_i$	$(\nu_i^{(c)} - \nu_i^{(e)})$	$(\nu_i^{(a)} - \nu_i^{(e)})$
^{1}S	3″	^{2}P	0.027	−0.011
^{1}P	3″	^{2}P	0.029	−0.005
^{1}D	3′	^{2}D	0.039	0.004
	3″	^{2}P	0.033	0.000
^{1}F	3′	^{2}D	0.049	0.008
^{3}P	3	^{4}S	0.028	−0.001
	4	^{4}S	0.028	−0.009
	5	^{4}S	0.029	−0.011
	6	^{4}S	0.021	−0.012
^{3}D	3′	^{2}D	0.042	0.004
	4′	^{2}D	0.047	0.004
	3″	^{2}P	0.034	−0.003
^{3}F	3′	^{2}D	0.051	0.011
^{5}P	3	^{4}S	0.031	−0.006
	4	^{4}S	0.028	−0.010

Table 17 gives values of $(\nu_i^{(c)}-\nu_i^{(e)})$ and $(\nu_i^{(a)}-\nu_i^{(e)})$ where, for each level, we select the value of i giving the dominant parentage contribution. It is seen that the calculated results are in fairly good agreement with experiment, and that the residuals are small after adjustments have been made.

Referring to tables 16 and 17, it is seen that all of the observed levels have well-defined parentage. The ^{3}P series is observed up to $n = 6$. From table 16 it is seen that the ^{4}S parentage contribution is dominant for $n \leqslant 6$.

Table 18 gives predicted term values for $2p^3(^2D)\,3'p\,^1P$ and $2p^3(^2P)\,3''p\,^3S$.

TABLE 18. PREDICTED TERM VALUES FOR O I $2p^3\,np$

level	T/cm^{-1}	x/cm^{-1}
$2p^3(^2D)\,3p\,^1P$	$113\,590+x$	± 100
$2p^3(^2P)\,3p\,^3S$	$128\,440+x$	-70

(*d*) *Results for* F I $2p^4\,np$

The energy level structure for F I $2p^4np$ is similar to that for N I $2p^2np$, discussed in § 5.4 (*b*) above. We use the experimental data of Lidén (1949). Table 19 gives calculated effective quantum numbers $\nu_i^{(c)}$ and values of $(\nu_i^{(c)}-\nu_i^{(e)})$ and $(\nu_i^{(a)}-\nu_i^{(e)})$. The general agreement between calculated and exact effective quantum numbers is fairly good, but adjustment of the matrices does not lead to any very marked improvement. No difficulty arises in making parentage assignments for the ^{2}D series; in particular the level designated $3'p\,^2D$ does not have much admixture of ^{3}P parentage. For the ^{2}P series, on the other hand, we find that a strong admixture of ^{1}D parentage occurs in several levels but does not dominate any one level. We therefore conclude that the assignment $2p^4(^1D)\,3p\,^2P$ cannot be given to any one level.

TABLE 19. EFFECTIVE QUANTUM NUMBERS FOR F I $2p^4(S_iL_i)\,np\,SL$

SL	n	S_iL_i	$\nu_i^{(c)}$	$(\nu_i^{(c)}-\nu_i^{(e)})$	$(\nu_i^{(a)}-\nu_i^{(e)})$
^{2}S	3	^{3}P	2.233	0.014	0.001
	4	^{3}P	3.249	0.021	0.009
^{2}P	3	^{3}P	2.296	0.049	0.030
	4	^{3}P	3.296	0.043	0.027
^{2}D	3	^{3}P	2.206	0.022	0.010
	4	^{3}P	3.224	0.024	0.012
	3′	^{1}D	2.219	0.019	0.006
^{2}F	3′	^{1}D	2.194	0.047	0.035
^{4}S	3	^{3}P	2.233	0.014	0.001
	4	^{3}P	3.249	0.019	0.006
^{4}P	3	^{3}P	2.154	0.046	0.034
	4	^{3}P	3.171	0.038	0.026
^{4}D	3	^{3}P	2.182	0.023	0.011
	4	^{3}P	3.199	0.022	0.010
	5	^{3}P	4.204	0.020	0.008

One further point may be noted. The algebraic coefficients in our formulation are identical for the ^{2}S and ^{4}S series, and the calculated positions of ^{2}S and ^{4}S levels therefore coincide exactly. When fine structure is eliminated, the values of $\nu^{(e)}(nSL)$ for ^{2}S and ^{4}S levels are very close, but not exactly coincident. In calculations allowing for the fine-structure energy of the ion core, we obtain larger differences between the ^{2}S and ^{4}S levels, in agreement with experiment.

TABLE 20. EFFECTIVE QUANTUM NUMBERS FOR Ne I $2p^5\,np$, REFERRED TO THE $2p^5\,{}^2P_{\frac{3}{2}}$ LIMIT, AND WEIGHTS $W(J_i, K)$ CALCULATED BY USING ADJUSTED MATRICES. QUANTUM NUMBER ASSIGNMENTS (J_i, K) FROM MOORE (1949)

							$W(J_i,K)$				
n	J	J_i	K	$\nu^{(e)}_{\frac{3}{2}}$	$\nu^{(c)}_{\frac{3}{2}}$	$\nu^{(a)}_{\frac{3}{2}}$	$J_i, K = \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}$	$\frac{3}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{5}{2}$
3	0	$\frac{3}{2}$	$\frac{1}{2}$	2.184	2.206	2.205	0.44	—	0.56	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	2.288	2.338	2.289	0.55	—	0.45	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	2.068	2.120	2.069	0.22	0.00	0.77	0.00	—
			$\frac{3}{2}$	2.147	2.170	2.150	0.00	0.40	0.00	0.59	—
		$\frac{1}{2}$	$\frac{3}{2}$	2.177	2.199	2.181	0.08	0.55	0.02	0.34	—
			$\frac{1}{2}$	2.190	2.212	2.207	0.68	0.04	0.21	0.07	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	2.134	2.156	2.135	—	0.08	—	0.05	0.88
			$\frac{3}{2}$	2.156	2.177	2.162	—	0.38	—	0.50	0.12
		$\frac{1}{2}$	$\frac{3}{2}$	2.181	2.203	2.196	—	0.54	—	0.45	0.00
	3	$\frac{3}{2}$	$\frac{5}{2}$	2.126	2.149	2.127	—	—	—	—	1.00
4	0	$\frac{3}{2}$	$\frac{1}{2}$	3.228	3.252	3.243	0.18	—	0.82	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	3.373	3.418	3.380	0 81	—	0.19	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	3.101	3.143	3.091	0.11	0.00	0.89	0.00	—
			$\frac{3}{2}$	3.170	3.189	3.173	0.01	0.03	0.00	0.97	—
		$\frac{1}{2}$	$\frac{3}{2}$	3.268	3.291	3.266	0.06	0.91	0.01	0.02	—
			$\frac{1}{2}$	3.276	3.300	3.287	0.82	0.06	0.11	0.01	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	3.154	3.174	3.152	—	0.01	—	0.03	0.96
			$\frac{3}{2}$	3.174	3.192	3.186	—	0.03	—	0.94	0.03
		$\frac{1}{2}$	$\frac{3}{2}$	3.277	3.298	3.279	—	0.96	—	0.04	0.01
	3	$\frac{3}{2}$	$\frac{5}{2}$	3.144	3.164	3.141	—	—	—	—	1.00
5	0	$\frac{3}{2}$	$\frac{1}{2}$	4.255	4.285	4.264	0.05	—	0.95	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	4.532	4.571	4.545	0.94	—	0.06	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	4.115	4.152	4.105	0.04	0.00	0.95	0.00	—
			$\frac{3}{2}$	4.177	4.194	4.179	0.00	0.00	0.00	0.99	—
		$\frac{1}{2}$	$\frac{3}{2}$	4.437	4.461	4.432	0.15	0.84	0.01	0.00	—
			$\frac{1}{2}$	4.438	4.466	4.445	0.80	0.15	0.04	0.00	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	4.161	4.180	4.158	—	0.00	—	0.02	0.98
			$\frac{3}{2}$	4.180	4.197	4.192	—	0.00	—	0.97	0.02
		$\frac{1}{2}$	$\frac{3}{2}$	4.446	4.469	4.446	—	0.99	—	0.01	0.00
	3	$\frac{3}{2}$	$\frac{5}{2}$	4.150	4.170	4.146	—	—	—	—	1.00
6	0	$\frac{3}{2}$	$\frac{1}{2}$	5.269	5.304	5.276	0.02	—	0.98	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	5.819	5.855	5.838	0.96	—	0.04	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	5.123	5.158	5.114	0.02	0.00	0.97	0.01	—
			$\frac{3}{2}$	5.180	5.197	5.182	0.00	0.00	0.00	0.99	—
		$\frac{1}{2}$	$\frac{1}{2}$	5.722	5.754	5.720	0.51	0.47	0.02	0.00	—
			$\frac{3}{2}$	5.728	5.760	5.728	0.45	0.53	0.02	0.00	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	5.164	5.183	5.161	—	0.00	—	0.02	0.98
			$\frac{3}{2}$	5.182	5.199	5.195	—	0.00	—	0.98	0.02
		$\frac{1}{2}$	$\frac{3}{2}$	5.738	5.763	5.737	—	0.99	—	0.00	0.00
	3	$\frac{3}{2}$	$\frac{5}{2}$	5.153	5.172	5.148	—	—	—	—	1.00
7	0	$\frac{3}{2}$	$\frac{1}{2}$	6.282	6.322	6.287	0.03	—	0.97	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	7.377	7.235	7.386	0.68	—	0.32	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	6.130	6.161	6.114	0.05	0.00	0.95	0.01	—
			$\frac{3}{2}$	6.182	6.199	6.184	0.00	0.00	0.01	0.99	—
		$\frac{1}{2}$	$\frac{3}{2}$	7.216	7.243	7.211	0.07	0.69	0.02	0.22	—
			$\frac{1}{2}$	7.230	7.258	7.247	0.67	0.05	0.23	0.05	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	6.166	6.185	6.162	—	0.00	—	0.01	0.99
			$\frac{3}{2}$	6.184	6.201	6.197	—	0.00	—	0.98	0.01
		$\frac{1}{2}$	$\frac{3}{2}$	7.226	7.253	7.232	—	0.73	—	0.25	0.02
	3	$\frac{3}{2}$	$\frac{5}{2}$	6.155	6.174	6.150	—	—	—	—	1.00

TABLE 20 (*cont.*)

							$W(J_i,K)$				
n	J	J_i	K	$\nu_{\frac{3}{2}}^{(e)}$	$\nu_{\frac{3}{2}}^{(c)}$	$\nu_{\frac{3}{2}}^{(a)}$	$J_i, K =$	$\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{3}{2}$	$\frac{3}{2},\frac{1}{2}$	$\frac{3}{2},\frac{3}{2}$	$\frac{3}{2},\frac{5}{2}$
8	0	$\frac{3}{2}$	$\frac{1}{2}$	7.231	7.435	7.236		0.31	—	0.69	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	9.083	9.119	9.113		0.81	—	0.19	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	7.099	7.143	7.075		0.24	0.00	0.76	0.00	—
			$\frac{3}{2}$	7.175	7.195	7.172		0.01	0.25	0.00	0.74	—
		$\frac{1}{2}$	$\frac{3}{2}$	—	9.012	8.943		0.80	0.02	0.19	0.00	—
			$\frac{1}{2}$	8.960	9.019	8.975		0.01	0.97	0.01	0.01	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	7.164	7.183	7.158		—	0.08	—	0.07	0.85
			$\frac{3}{2}$	7.183	7.201	7.187		—	0.18	—	0.69	0.13
		$\frac{1}{2}$	$\frac{3}{2}$	8.995	9.032	8.992		—	0.98	—	0.02	0.01
	3	$\frac{3}{2}$	$\frac{5}{2}$	7.156	7.174	7.150		—	—	—	—	1.00
9	0	$\frac{3}{2}$	$\frac{1}{2}$	8.275	8.310	8.282		0.02	—	0.98	—	—
		$\frac{1}{2}$	$\frac{1}{2}$	11.482	11.554	11.499		0.82	—	0.18	—	—
	1	$\frac{3}{2}$	$\frac{1}{2}$	8.127	8.159	8.114		0.02	0.00	0.98	0.00	—
			$\frac{3}{2}$	8.184	8.199	8.185		0.00	0.00	0.00	0.99	—
		$\frac{1}{2}$	$\frac{3}{2}$	—	11.302	11.245		0.06	0.83	0.02	0.10	—
			$\frac{1}{2}$	—	11.320	11.292		0.69	0.06	0.23	0.03	—
	2	$\frac{3}{2}$	$\frac{5}{2}$	8.173	8.186	8.163		—	0.00	—	0.02	0.98
			$\frac{3}{2}$	8.184	8.202	8.197		—	0.00	—	0.98	0.02
		$\frac{1}{2}$	$\frac{3}{2}$	11.268	11.319	11.275		—	0.88	—	0.10	0.02
	3	$\frac{3}{2}$	$\frac{5}{2}$	8.161	8.175	8.151		—	—	—	—	1.0

(*e*) *Results for* Ne I

The energy level structure for Ne I $2p^5(^2P)\,nl$ differs from that for C I $2p(^2P)\,nl$ in that the levels of the ^2P core are inverted for Ne and the separation of the core components is much larger. Our interest is mainly in the structure which results from the separation of the components of the $Ne^+\ ^2P$ core.

We have the following contributions to the energy:

(i) the energy of the core, $2p^5\,{}^2P_{J_i}$, $J_i = \frac{3}{2}$ and $\frac{1}{2}$.
(ii) the kinetic energy of the valence electron and the monopole electro-static interaction F_0.
(iii) the quadrupole direct electrostatic interaction F_2.
(iv) the exchange electrostatic interaction G_λ, $\lambda = l \pm 1$.
(v) the spin-orbit energy of the valence electron.

We shall assume that (v) is small and may be neglected. For large n, (iii) and (iv) are small compared with the fine structure of the core and a representation involving the quantum number J_i must be used. For large l it may be assumed that (iv) is small compared with (iii). In this case the pair coupling representation (J_i, K) is appropriate (see § 3.3); it should be noted that the interactions (ii) and (iii) are diagonal with respect to K. For smaller values of l it is less obvious that the pair coupling representation is appropriate. It so happens, however, that for most values of J the exchange interaction (iv) is diagonal with respect to K.

(i) *Results for* Ne I $2p^5(^2P)\,np$. In table 20 we give:

(α) From Moore (1949), quantum numbers n, J, J_i and K and effective quantum numbers $\nu_{\frac{3}{2}}^{(e)}$ referred to the $2p^5\,{}^2P_{\frac{3}{2}}$ limit. The assignment of quantum numbers J_i and K will be discussed below.

(β) Effective quantum numbers $\nu_{\frac{3}{2}}^{(c)}$ obtained using calculated matrices.

(γ) Results obtained by using adjusted matrices, effective quantum numbers $\nu^{(a)}_{\frac{3}{2}}$ and weights $W(J_i, K)$.

It is seen that the agreement between $\nu^{(e)}$ and $\nu^{(a)}$ is generally good and we may therefore have some confidence in the use of the adjusted results for a discussion of quantum number assignments. Using the representation (J_i, K), we obtain large admixtures of states for the levels with $n = 3$; for these levels a representation $2p^5(^2P)\,3p\ SLJ$ would be more appropriate.

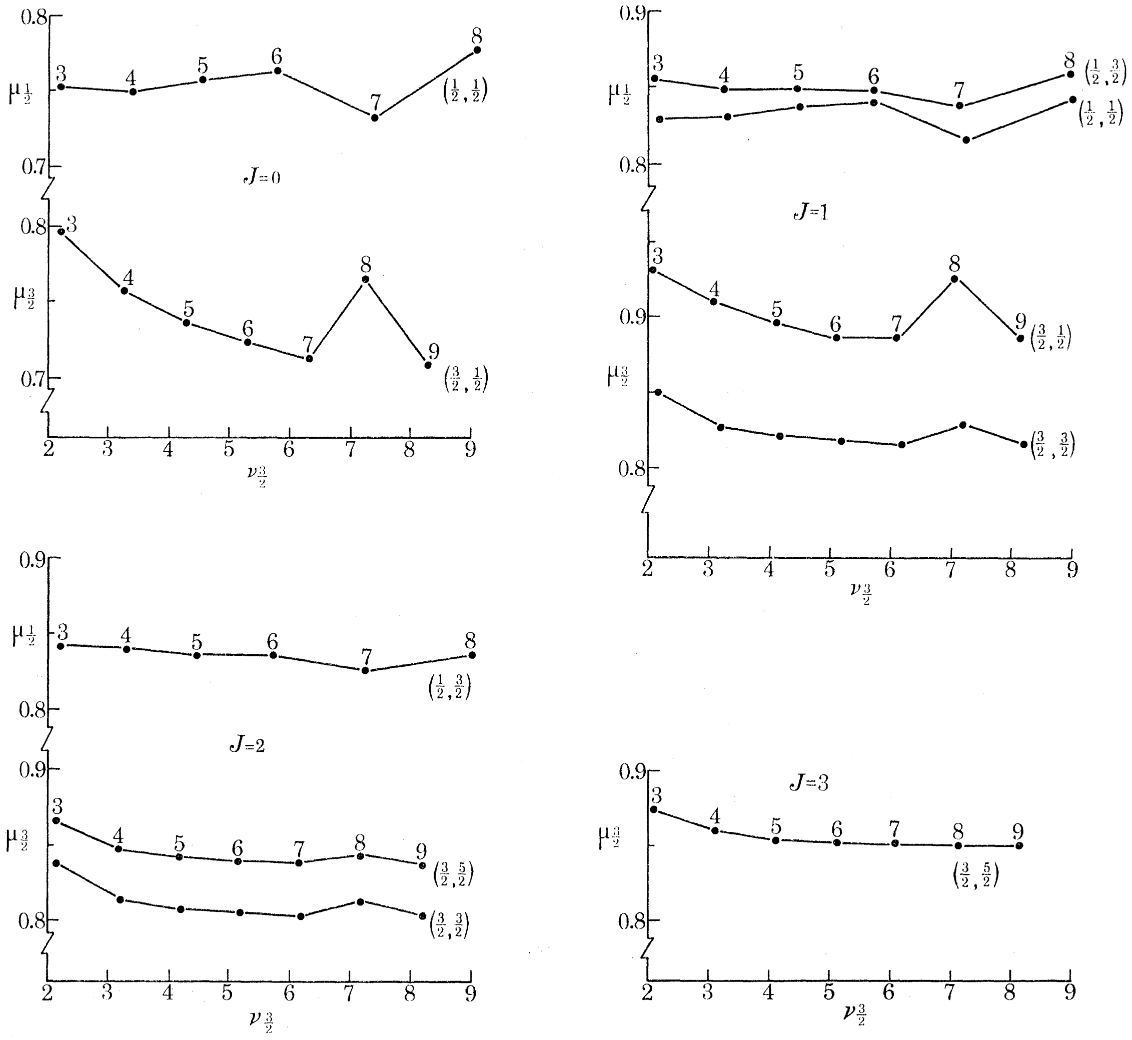

FIGURE 2. Quantum defects μ_{J_i} for Ne I $2p^5\,np$ levels, against $\nu_{\frac{3}{2}}$. A pair coupling notation, (J_i, K), is used. For these levels, experimental results are in very close agreement with results obtained by using adjusted matrices (see table 20).

In figure 2 we plot quantum defects $\mu_{\frac{3}{2}}$, referred to the $^2P_{\frac{3}{2}}$ limit, for levels $np(\frac{3}{2}, K)\,J$ and quantum defects $\mu_{\frac{1}{2}}$ for levels $np(\frac{1}{2}, K)\,J$, in both cases as functions of $\nu_{\frac{3}{2}}$. We discuss separately the series for different J values.

$J = 0$. From figure 2 it is seen that there is a strong perturbation between $8p(\frac{3}{2}, \frac{1}{2})$ and $7p(\frac{1}{2}, \frac{1}{2})$. The effect of this perturbation is seen in the weights W of table 20.

$J = 1$. For $J = 1$ the matrix of the electro-static energy has the form

$$(J_iK|\,\boldsymbol{H}\,|J_{i'}K') = \{E_0+G_0+0.4G_2\}\,\delta(J_iK, J_{i'}K') + f_2(J_iK, J_{i'}K')\,F_2, \qquad (5.12)$$

where the coefficient matrix $f_2(J_iK, J_{i'}K')$ is given in table 21. A curious feature of these results is that the states $(J_i, K) = (\frac{1}{2}, \frac{3}{2})$ and $(\frac{1}{2}, \frac{1}{2})$ are completely degenerate so long as one neglects coupling between states with $J_i = \frac{1}{2}$ and $J_i = \frac{3}{2}$. The separations between the levels $(\frac{1}{2}, \frac{3}{2})$ and $(\frac{1}{2}, \frac{1}{2})$ shown in figure 1 are entirely due to the coupling, through the coefficient f_2, to states with $J_i = \frac{3}{2}$. This coupling is weakest for 6p$(\frac{1}{2}, \frac{3}{2})$ and 6p$(\frac{1}{2}, \frac{1}{2})$, which lie about midway between the 6p and 7p states in the series $(\frac{3}{2}, \frac{1}{2})$ and $(\frac{3}{2}, \frac{3}{2})$. A consequence of the near-degeneracy of the 6p levels for $J_i = \frac{1}{2}$ is to give a large admixture of states, as is shown by the weights W in table 20; for this case assignment of quantum numbers (J_i, K) has little significance.

Table 21. The coefficient $f_2(J_iK, J_{i'}K')$ for $2p^5\,np$, $J = 1$

Values of $25f_2$.

$J_i'K'$	J_iK: $\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{3}{2}$	$\frac{3}{2}$ $\frac{1}{2}$	$\frac{3}{2}$ $\frac{3}{2}$
$\frac{1}{2}$ $\frac{1}{2}$	0	0	$-5\sqrt{2}$	0
$\frac{1}{2}$ $\frac{3}{2}$	0	0	0	$\sqrt{5}$
$\frac{3}{2}$ $\frac{1}{2}$	$-5\sqrt{2}$	0	-5	0
$\frac{3}{2}$ $\frac{3}{2}$	0	$\sqrt{5}$	0	4

A further feature of the $J = 1$ results is a large interaction between the 7p $J_i = \frac{1}{2}$ levels and the 8p $J_i = \frac{3}{2}$ levels.

$J = 2$. The results of table 20 and figure 2 show a fairly weak perturbation between 7p$(\frac{1}{2}, \frac{3}{2})$, 8p$(\frac{3}{2}, \frac{5}{2})$ and 8p$(\frac{3}{2}, \frac{3}{2})$.

$J = 3$. For this case there is only one series and the quantum defect varies quite smoothly.

In summary we may say that our results confirm the pair coupling quantum number assignments quoted by Moore for all levels with $n > 3$, with the exception of the 6p levels for $J_i = \frac{1}{2}$ and $J = 1$, for which the quantum number assignments have little significance.

(ii) *Results for* Ne I $2p^5(^2P)\,nd$. Energy levels for Ne I $2p^5\,nd$ have been calculated from distorted wave R matrices, allowing for interaction with $2p^5\,n's$. The results obtained are shown in figure 3. Our assignments of pair-coupling quantum numbers, $(J_i, K)\,J$, are in agreement with the assignment quoted by Moore (1949). In figure 3(*b*) we plot calculated quantum defects $\mu_{\frac{3}{2}}$ for levels $(\frac{3}{2}, K)\,J$ and $\mu_{\frac{1}{2}}$ for levels $(\frac{1}{2}, K)\,J$, in both cases as functions of $\nu_{\frac{3}{2}}$. Figure 3*a* gives similar plots of the experimental data. It is seen that the complicated pattern, which results from interactions between series converging to the two Ne^+ limits, is reproduced quite accurately by the calculations. Interactions with $2p^5\,ns$ are responsible for small perturbations near $n = 9$ and for structure in the $(\frac{3}{2}, \frac{1}{2})$ 0 series. The absolute values of the calculated quantum defects are too small by about 0.01. This may be explained as a consequence of the neglect of a polarization potential, which will be approximately the same for all nd levels.

(iii) *Results for* Ne I $2p^5(^2P)\,ns$. For the ns levels we may use quantum numbers $(J_i)\,J$. Figure 4 shows experimental results for quantum defects μ_{J_i} and results calculated in the distorted wave approximation. For the s-states the error in the d.w. results is large, $\delta\nu \simeq 0.06$. There are some perturbations between the series $(J_i)\,J = (\frac{3}{2})\,1$ and $(\frac{1}{2})\,1$. Perturbations in the ns series $(J_i)\,J = (\frac{3}{2})\,2$ and $(\frac{1}{2})\,0$ are due to interactions with nd states.

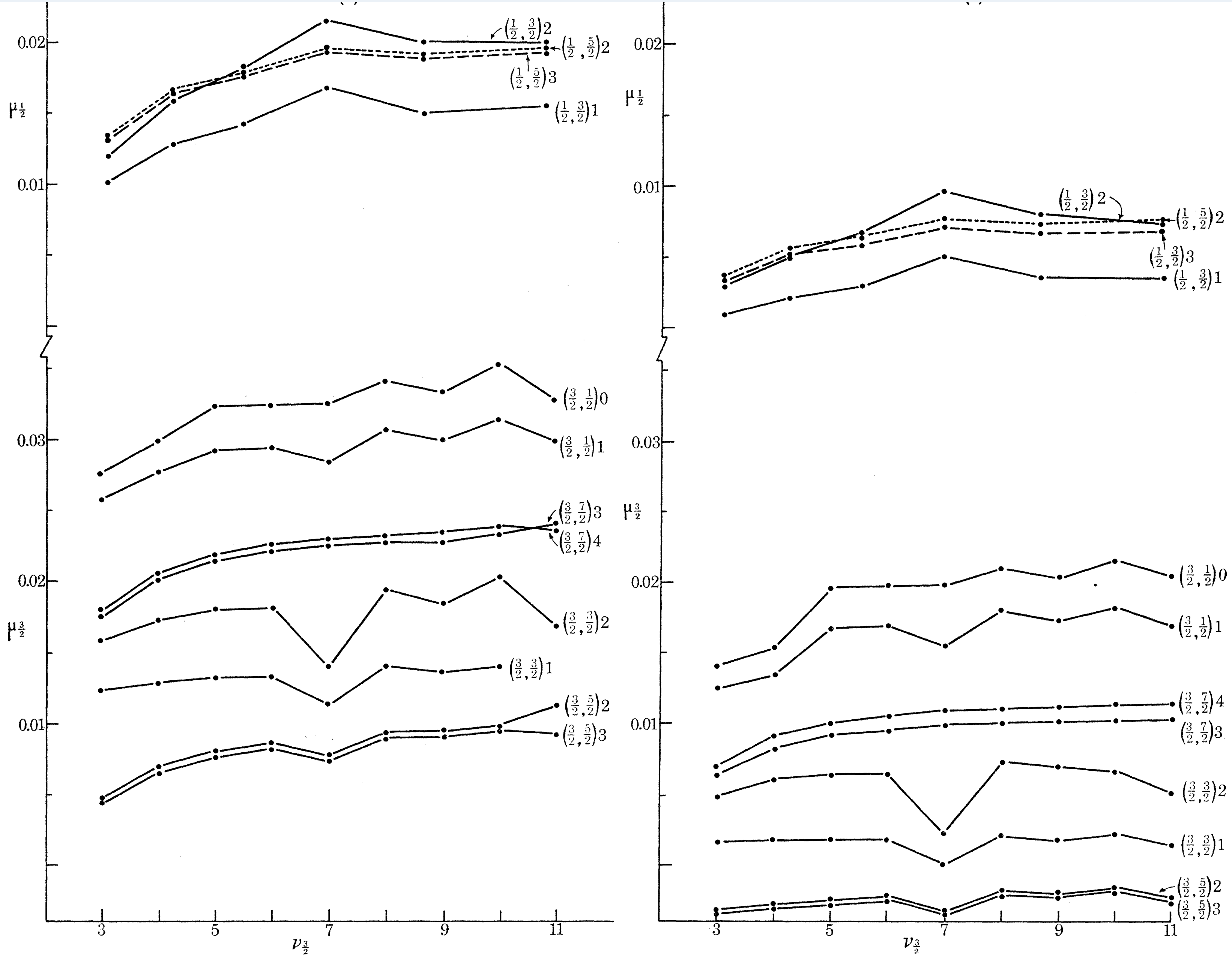

FIGURE 3. Quantum defects μ_{J_i} for Ne I $2p^5nd$ levels, against $\nu_{\frac{3}{2}}$. A pair coupling notation, $(J_i, K)\ J$, is used. (*a*) Experimental results. (*b*) Results calculated in the distorted wave approximation.

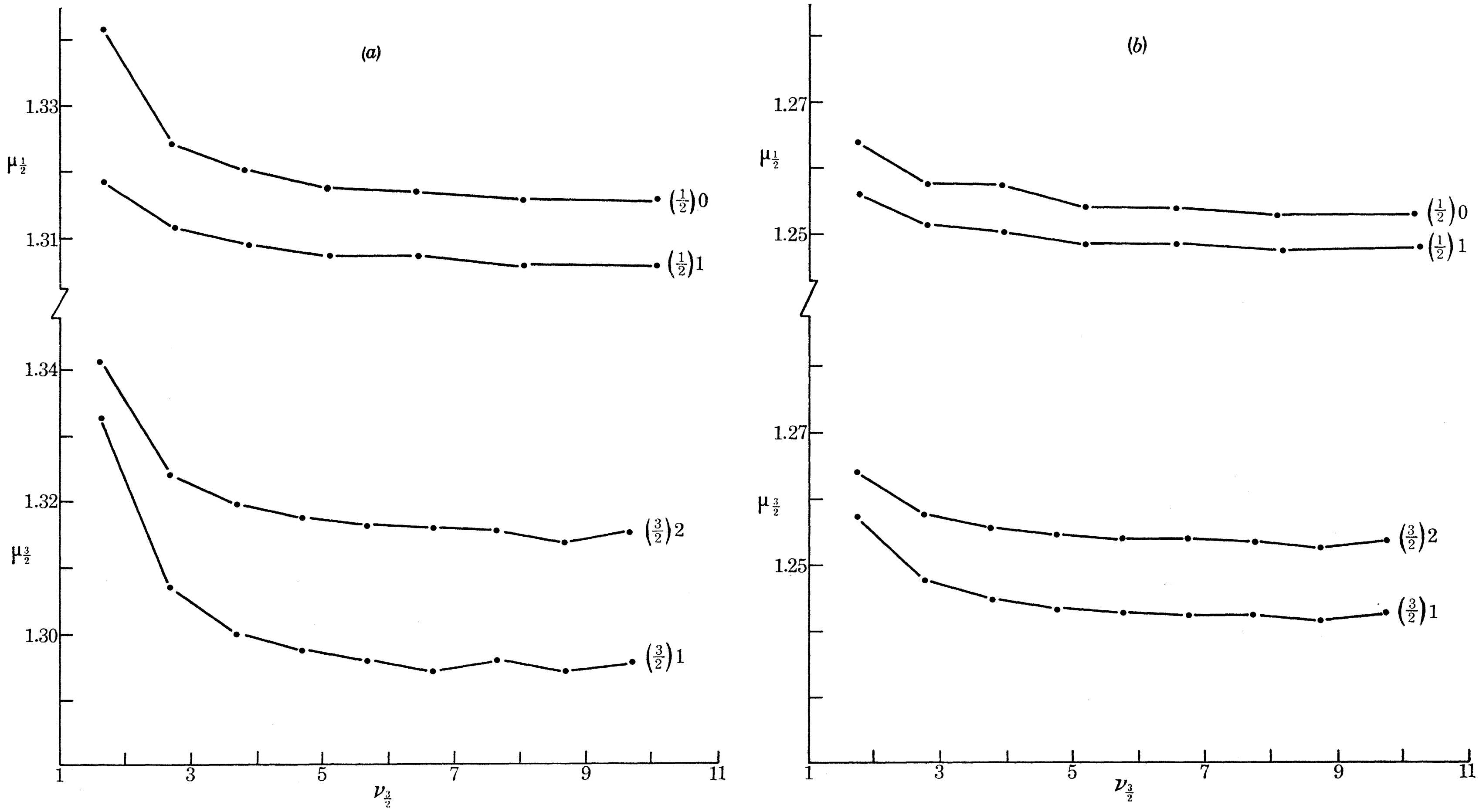

FIGURE 4. Quantum defects μ_{J_i} for Ne I 2p^5 *ns* levels, against $\nu_{\frac{3}{2}}$. Quantum numbers $(J_i)\,J$ are indicated. (*a*) Experimental results. (*b*) Calculations in the distorted wave approximation. Note the difference in the μ_{J_i} scales for (*a*) and (*b*).

5.4. *Isoelectronic sequences*

In comparing calculated and observed levels along isoelectronic sequences belonging to configurations of type (5.1) we must consider the effect of interactions with configurations of type (5.2).

(*a*) *Results for the* C I *sequence*

We consider calculated results for configurations $2s^2\,2p\,np$, of type (5.1). The observed levels are effected by interaction with configurations $2s2p^2\,ns$, of type (5.2).

The lowest term in $2s2p^2$ is $2s2p^2\,{}^4P$ and the lowest level of the type $2s2p^2\,n's$, which interacts with $2s^2\,2p\,np$, is $2s2p^2({}^4P)\,3s\,{}^3P$. Some energy levels for C I, N II and O III are shown in figure 5; we plot values of $\Delta E/z^2$ relative to the $2s^2 2p\,{}^2P$ limit. For each ion we show the positions of the levels $2s^2\,2p({}^2P)\,3p$ and $4p\,{}^3P$, and $2s2p^2({}^4P)\,3s\,{}^3P$; we also show the position of the $2s2p^2\,{}^4P$ limit.

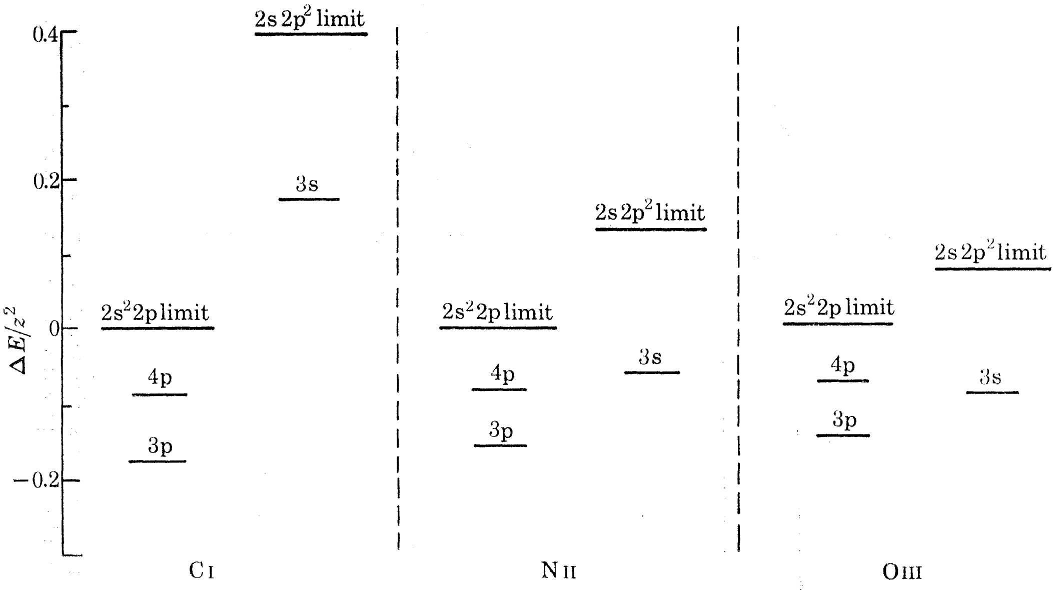

FIGURE 5. Energies $\Delta E/z^2$ for the C I sequence. For each ion the figure shows: (*a*) The position of the $2s^2\,2p({}^2P)$ limit and the 3p and 4p levels in the series $2s^2\,2p({}^2P)\,np\,{}^3P$. (*b*) The position of the $2s^2\,2p^2({}^4P)$ limit and the 3s level in the series $2s\,2p^2({}^4P)\,ns\,{}^3P$.

For the valence-electron states values of $\Delta E/z^2$, relative to the appropriate limit, vary slowly along the isoelectronic sequence; this variation is caused by the change in the quantum defects along the sequence. The separation $\Delta E/z^2$ of the two limits, $2s^2\,2p\,{}^2P$ and $2s2p^2\,{}^4P$, varies much more rapidly along the sequence.

For C I the level $2s2p^2({}^4P)\,3s\,{}^3P$ has been obtained from the extrapolation along the sequence. It is seen that this level lies well above the $2s^2\,2p\,{}^2P$ limit. For N II the level $({}^4P)\,3s\,{}^3P$ comes below the $2s^2\,2p\,{}^2P$ limit and will produce a perturbation in the $2s^2\,2p({}^2P)\,np\,{}^3P$ series between $n = 4$ and $n = 5$. For O III, $({}^4P)\,3s\,{}^3P$ comes still lower and produces a perturbation in the $({}^2P)np\,{}^3P$ series between $n = 3$ and 4. A number of other $2s2p^2\,n'l'$ levels will also produce perturbations in O III series of the type $2s^2\,2p\,nl$.

Results for C I $2s^2 2p\,np$ have been given in table 9 and similar results for N II and O III are given in table 22. For N II it is seen that the error in the calculated results $(\nu^{(c)}-\nu^{(e)})$ is largest for the series $(^2P)\,np\ ^3P$, particularly for $4p\ ^3P$. This is a consequence of perturbation of the ^3P series by $2s2p^2(^4P)\,3s\ ^3P$. It is also seen that adjustment of the matrices does not give much improvement for $4p\ ^3P$; the form assumed in making the adjustments does not take account of perturbations of the type which occur here. For O III, the level $(^4P)\,3s\ ^3P$ lies below $(^2P)\,4p\ ^3P$, and $4p\ ^3P$ is therefore perturbed upwards. In our calculations we neglect this perturbation and other perturbations which tend to produce downward shifts in the *n*p levels; in consequence, we obtain a fortuitously close agreement between $\nu^{(c)}$ and $\nu^{(e)}$ for $4p\ ^3P$.

Table 22. Effective quantum numbers for levels $2s^2 2p\,np$ in N II and O III, referred to the $2s^2 2p\ ^2P$ limit

		N II			O III		
SL	*n*	$\nu^{(c)}$	$(\nu^{(c)}-\nu^{(e)})$	$(\nu^{(a)}-\nu^{(e)})$	$\nu^{(c)}$	$(\nu^{(c)}-\nu^{(e)})$	$(\nu^{(a)}-\nu^{(e)})$
^1S	3	2.746	0.054	−0.003	2.799	0.035	+0.005
	4	3.754	0.048	−0.007	3.802	0.047	+0.017
^1P	3	2.471	0.040	+0.004	2.576	0.028	−0.006
	4	3.498	0.039	+0.008	3.601	0.027	−0.004
^1D	3	2.651	0.046	+0.003	2.724	0.035	+0.004
	4	3.667	0.049	+0.009	2.733	0.034	+0.005
^3S	3	2.541	0.037	+0.001	2.632	0.027	+0.008
	4	3.557	0.032	+0.000	3.647	0.021	+0.003
^3P	3	2.597	0.060	+0.030	2.677	0.046	+0.016
	4	3.614	0.106	+0.078	3.689	0.000	−0.028
^3D	3	2.498	0.033	−0.002	2.598	0.024	−0.004
	4	3.521	0.032	+0.001	3.619	0.023	−0.002

(*b*) *Results for the* N I *sequence*

Perturbations in the N I sequence have been discussed by Eissner *et al.* (1969) (see §§ 5.1 and 5.2). The lowest level of the type $2s2p^3 n'l'$ which interacts with $2s^2 2p^2 np$ is $2s\,2p^3(^5S)\,3s\ ^4S$. The $(^5S)\,3s\ ^4S$ level lies above the $2s^2\,2p^2\ ^3P$ limit for N I but below the ^3P limit for all other ions in the sequence.

Results for N I $2p^2 np$ are given in table 13 and results for O II have been given in § 5.2 (tables 5 to 7) in the course of a discussion of our methods of computation. In table 23 we give a summary of results for O II and F III. For each level we give effective quantum numbers ν_i, where $2p^2(S_i\,L_i)$ gives the dominant parentage contribution (the significance of parentage assignments, for the case of O II, may be judged from the results given in table 5). The experimental data used for O II is taken from Moore (1949) and that for F III is from the recent work of Palenius (1970). It should be noted that for F III we have experimental data for all $2p^2 3p$ levels, including those with ^1D and ^1S parentage.

In both O II and F III it is seen that the largest discrepancies, $\nu_i^{(c)}-\nu_i^{(e)}$, occur for $3p\ ^4S$; this is a consequence of perturbations by $(^5S)\,3s\ ^4S$. In general, our adjusted results for O II and F III are in rather close agreement with experiment, although it must be recognized that there are a number of perturbations not correctly allowed for in our calculations. Some predicted level positions for O II are given in table 24.

Table 23. Effective quantum numbers ν_i for $2p^2(S_iL_i)\ np\ SL$ in O II and F III

SL	n	S_iL_i	O II $\nu_i^{(c)}$	O II $\nu_i^{(c)}-\nu_i^{(e)}$	O II $\nu_i^{(a)}-\nu_i^{(e)}$	F III $\nu_i^{(c)}$	F III $\nu_i^{(c)}-\nu_i^{(e)}$	F III $\nu_i^{(a)}-\nu_i^{(e)}$
^2S	3	^3P	2.396	0.043	0.011	2.502	0.032	0.007
	4	^3P	—	—	—	3.529	0.033	0.011
^2P	3	^3P	2.550	0.032	−0.002	2.631	0.028	0.002
	4	^3P	3.578	0.036	0.001	3.676	0.028	−0.003
	3′	^1D	2.520	0.038	−0.002	2.624	0.032	0.003
	4′	^1D	3.518	—	—	3.613	−0.008†	−0.030
	3″	^1S	2.471	—	—	2.563	0.021	−0.006
	4″	^1S	—	—	—	3.571	0.013	−0.009
^2D	3	^3P	2.505	0.033	0.005	2.593	0.027	0.003
	4	^3P	3.562	0.036	0.007	3.635	0.030	−0.003
	5	^3P	4.535	0.033	0.004	4.655	0.038†	0.004
	3′	^1D	2.484	0.045	0.005	2.592	0.036	−0.004
	4′	^1D	3.490	—	—	3.576	0.020	−0.008
^2F	3′	^1D	2.444	0.025	−0.008	2.548	0.021	−0.001
	4′	^1D	3.470	—	—	3.562	0.019	0.000
^4S	3	^3P	2.546	0.065	0.030	2.631	0.056	0.004
^4P	3	^3P	2.446	0.028	−0.003	2.550	0.024	0.002
	4	^3P	3.467	—	—	3.569	0.024	0.004
	5	^3P	4.475	0.025	−0.003	4.575	0.027†	0.006
^4D	3	^3P	2.424	0.030	−0.003	2.531	0.024	0.000
	4	^3P	3.448	0.028	−0.002	3.553	0.026	0.006
	5	^3P	4.456	0.027	−0.001	4.569	0.043†	0.023

† These levels were not included in the calculation of the adjusted matrices, since the experimental level positions were not available at the time when the calculations were made.

Table 24. Predicted term values for $2p^2\ np$ levels in O II

level	T/cm^{-1}	x/cm^{-1}
$(^3P)4p\ ^4P_{\frac{1}{2}}$	$246\,244+x$	200 ± 50
$^4P_{\frac{3}{2}}$	$246\,286+x$	
$^4P_{\frac{5}{2}}$	$246\,379+x$	
$(^3P)5p\ ^4P_{\frac{1}{2}}$	$261\,184+x$	35 ± 5
$(^1S)3p\ ^2P_{\frac{1}{2}}$	$252\,789+x$	± 500
$^2P_{\frac{3}{2}}$	$252\,803+x$	

(c) *Results for the* O I *sequence*

There is little good experimental data available for the higher members of the O I sequence, but extensive data has been compiled by Palenius (1969) for F II. We therefore consider only the case of F II.

Table 25 gives results for 29 levels belonging to configurations $2p^3\,np$ in F II. It is seen that, by using adjusted matrices, the residuals $(\nu_i^{(a)}-\nu_i^{(e)})$ remain quite large for some of the levels.

The series $2p^3(S_iL_i)np\ ^3P$ calls for special comment. We have three possible values for S_iL_i, ^4S, ^2D and ^2P. Figure 6 shows $|V_1|$, $|V_2|$ and $|V_3|$ plotted against ν_1. There is no difficulty in making assignments for the levels labelled 3′p (for which $|V_2|$ is larger than $|V_1|$ and $|V_3|$) and 3″p (for which $|V_3|$ is larger than $|V_1|$ and $|V_2|$). It is seen that there is an additional perturbation occurring high in the ^3P series, at $\nu_1 \simeq 13$. In this region, $|V_2|$ passes through a maximum value, but remains small compared with $|V_1|$. Palenius gives a level labelled 4′p ^3P, obtained from observed lines

TABLE 25. EFFECTIVE QUANTUM NUMBERS ν_i FOR F II $2p^3(S_iL_i)\,np\,SL$

SL	n	S_iL_i	$\nu_i^{(c)}$	$(\nu_i^{(c)}-\nu_i^{(e)})$	$(\nu_i^{(a)}-\nu_i^{(e)})$
^1S	3″	^2P	2.583	0.030	0.006
^1P	3′	^2D	2.376	0.042	0.004
	4′	^2D	3.409	0.051	0.024
	3″	^2P	2.393	0.021	−0.007
	4″	^2P	3.417	0.017	−0.005
^1D	3′	^2D	2.537	0.031	−0.004
	4′	^2D	3.571	0.078	0.047
	3″	^2P	2.450	0.026	0.003
	4″	^2P	3.475	0.023	0.005
^1F	3′	^2D	2.409	0.035	0.003
	4′	^2D	3.430	0.031	0.002
^3S	3″	^2P	2.391	0.053	0.020
^3P	3	^4S	2.455	0.026	−0.014
	4	^4S	3.573	0.051	−0.003
	5	^4S	4.572	0.060	0.022
	6	^4S	5.508	0.008	−0.024
	3′	^2D	2.435	0.032	0.009
	3″	^2P	2.419	0.023	0.000
^3D	3′	^2D	2.375	0.032	−0.002
	4′	^2D	3.399	0.028	−0.001
	3″	^2P	2.381	0.022	−0.009
	4″	^2P	3.405	0.021	−0.006
^3F	3′	^2D	2.397	0.035	0.002
	4′	^2D	3.418	0.031	0.001
^5P	3	^4S	2.374	0.025	−0.007
	4	^4S	3.396	0.024	−0.006
	5	^4S	4.404	0.024	−0.005
	6	^4S	5.408	0.024	−0.004
	7	^4S	6.410	0.025	−0.003

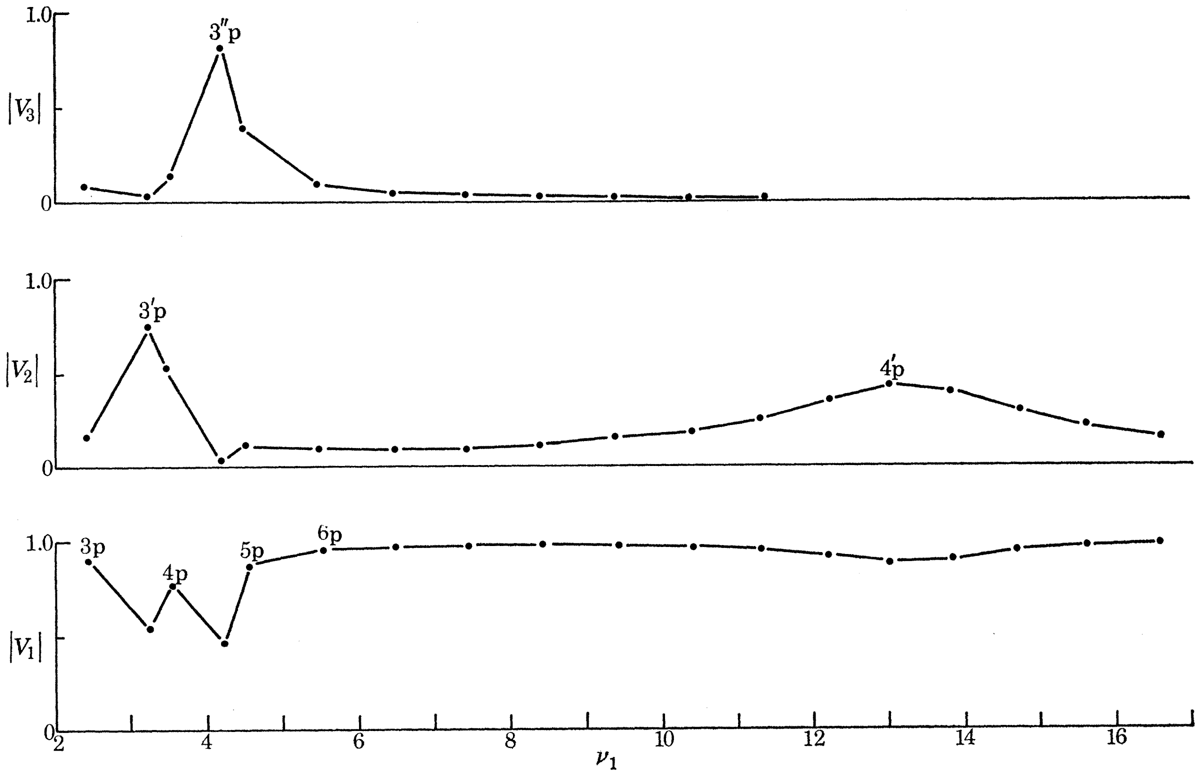

FIGURE 6. Values of $|V_i|$ for F II $2p^3(S_iL_i)\,np\,^3P$, calculated by using adjusted matrices.

assigned to transitions $2p^3(^2D)3'd\,^3D \rightarrow 2p^3(^2D)4'p\,^3P$ and $2p^3(^2D)4'p\,^3P \rightarrow 2p^3(^2D)3's\,^3D$. The intensities in such transitions will be sensitive to $|V_2|$. The observed level labelled $4'p\,^3P$ occurs at $\nu_2 = 3.408$, whereas the maximum in the calculated value of $|V_2|$ occurs at $\nu_2 = 3.486$. It is clear that there is no single level which can be correctly labelled $4'p\,^3P$, in the sense that a state of $2p^3(^2D)$ parentage gives the dominant contribution to the wavefunction. A more detailed comparison of calculated and observed results would have to be based on a study of calculated line intensities.

(*d*) *Results for the* F I *sequence*

Results for F I $2p^4\,np$ have been given in table 19 and similar results for Ne II are given in table 26, the experimental data being taken from Moore (1949). For Ne II all levels with configuration $2p^4\,3p$ have been observed. We do not consider higher members of the F I sequence, since there is little good experimental data.

TABLE 26. EFFECTIVE QUANTUM NUMBERS ν_i FOR Ne II $2p^4\,(S_iL_i)\,np\,SL$

SL	n	S_iL_i	$\nu_i^{(c)}$	$\nu_i^{(c)} - \nu_i^{(e)}$	$\nu_i^{(a)} - \nu_i^{(e)}$
^2S	3	^3P	2.389	0.030	0.002
^2P	3	^3P	2.429	0.047	−0.003
	3′	^1D	2.383	0.054	0.011
	3″	^1S	2.352	0.035	−0.003
^2D	3	^3P	2.369	0.033	0.000
	3′	^1D	2.377	0.033	0.000
^2F	3′	^1D	2.348	0.046	0.000
^4S	3	^3P	2.389	0.028	0.000
^4P	3	^3P	2.314	0.046	0.000
^4D	3	^3P	2.342	0.033	−0.006

For Ne II the agreement with experiment is particularly good when adjusted matrices are used. It is of interest to compare O II $2s^2\,2p^2\,np$ with Ne II $2s^2\,2p^4\,np$. All series $2s^2\,2p^2\,np\,SL$, with the exception of $SL = {}^2F$, are perturbed by $2s2p^3\,3s\,SL$. In § 5.4 (*b*) this perturbation was seen to be particularly important for $2s^2\,2p^2\,np\,^4S$. For $2s^2\,2p^4\,np\,SL$, on the other hand, perturbations by $2s2p^5 3s$ occur only for $SL = {}^2P$ and ^4P.

(*e*) *The* Ne I *sequence*

There is little spectroscopic data available for higher members of the Ne I sequence, and we therefore do not consider this sequence further.

6. THE CALCULATION OF COLLISION STRENGTHS

6.1. *Accuracy of the collision strength calculations*

We have used the extrapolated matrices of paper I to calculate energy levels for configurations $2s^2\,2p^q\,nl$, and we have attempted to make semi-empirical adjustments in the matrices so as to obtain an improved agreement between observed and calculated energy levels. In undertaking this work our original aims were to check the accuracy of the collision strengths of paper I, and to obtain more accurate collision strengths using the adjusted matrices. In achieving these aims we have been only partially successful. In many cases the differences between observed and calculated energy levels are largely due to perturbations, such as those between configurations

$2s^2\,2p^q\,nl$ and $2s2p^{q+1}\,n'l'$, which are not allowed for explicitly in our formulation. Unfortunately it is not possible to make a more explicit allowance for these perturbations, in a semi-empirical treatment, since the number of unknown parameters would be much too large.

The difficulties which arise may be appreciated by considering the system $e+O^{2+}$. The calculated energies for O^+ $2s^2\,2p^2\,np$ are always higher than the observed energies. It is probable that neglect of interactions between $2s^2\,2p^2\,np$ and $2s2p^3\,n'l'$ is one of the main sources of error in the calculations. We obtain some improvement in the energy levels using adjusted matrices, but in making these adjustments we do not allow explicitly for interactions with $2s2p^3\,n'l'$. The work of Eissner *et al.* (1969) shows that interactions with $2s2p^3 3s$ give rise to resonances in the near-threshold collision strengths for excitation of terms in the O^{2+} $2s^2\,2p^2$ ground-configuration. It is clear that one cannot make any significant improvement in the O^{2+} collision strength calculations of paper I without taking explicit account of these resonant interactions.

For the case of electron collisions with singly ionized ions in configurations $2s^2\,2p^q$, additional resonances of a type not allowed for in our formulation occur only at energies well above excitation thresholds. For these ions we may therefore attempt to obtain improved estimates of the near-threshold collision strengths using the adjusted reactance matrices.

In paper I reactance matrices $\boldsymbol{R}$ were calculated by using theory energy differences, $\Delta_i^{(c)}$. In the present paper we use $\Delta_i^{(c)}$ in calculating $\boldsymbol{Y} = A^{-\frac{1}{2}}\boldsymbol{R}A^{-\frac{1}{2}}$ as a function of ϵ_1, but experimental energy differences, $\Delta_i^{(e)}$, in all subsequent work. Let $\boldsymbol{Y}^{(c)}(\epsilon_1)$ and $\boldsymbol{Y}^{(a)}(\epsilon_1)$ be the calculated and adjusted $\boldsymbol{Y}$ matrices, and let

$$\boldsymbol{R}^{(c)}(\epsilon_1) = A^{\frac{1}{2}}\boldsymbol{Y}^{(c)}(\epsilon_1)\,A^{\frac{1}{2}}, \tag{6.1}$$

$$\boldsymbol{R}^{(a)}(\epsilon_1) = A^{\frac{1}{2}}\boldsymbol{Y}^{(a)}(\epsilon_1)\,A^{\frac{1}{2}}, \tag{6.2}$$

be the corresponding $\boldsymbol{R}$ matrices. It should be noted that $\boldsymbol{R}^{(c)}$ is slightly different from the $\boldsymbol{R}$ matrix of paper I, since we use $\Delta_i^{(e)}$ in calculating the factors A in (6.1); according to an argument given in § 4.1, $\boldsymbol{R}^{(c)}$ may be slightly more accurate than $\boldsymbol{R}$ of paper I.

We calculate collision strengths using the matrices $\boldsymbol{R}^{(c)}$ and $\boldsymbol{R}^{(a)}$. The adjusted matrices have been obtained only for the p-states, and we therefore consider only the p-wave contributions to the collision strengths, Ω^{pp}. These are the dominant contributions for transitions involving a change in the spin of the target ion.

Table 27. p-Wave contributions to collision strengths: calculated results (c); and adjusted results (a)

ion	$\Omega^{pp}(^2P_{\frac{1}{2}}, {}^2P_{\frac{3}{2}})$	
	(c)	(a)
C^+	1.03	0.89
Ne^+	0.184	0.295

	$\Omega^{pp}(^3P, {}^1D)$		$\Omega^{pp}(^3P, {}^1S)$		$\Omega^{pp}(^1D, {}^1S)$	
	(c)	(a)	(c)	(a)	(c)	(a)
N^+	2.66	3.06	0.288	0.450	0.028	0.056
F^+	1.23	1.27	0.140	0.142	0.019	0.020

	$\Omega^{pp}(^4S, {}^2D)$		$\Omega^{pp}(^4S, {}^2P)$		$\Omega^{pp}(^2D, {}^2P)$	
	(c)	(a)	(c)	(a)	(c)	(a)
O^+	1.30	1.48	0.381	0.451	0.599	0.722

Table 27 gives p-wave collision strengths for singly ionized ions, obtained using calculated matrices, (c), and adjusted matrices, (a). In general, comparison of the (c) and (a) results gives a useful indication of the accuracy of the calculations. We cannot, however, be sure that the (a) results are always more accurate than the (c) results. We select a few cases for special comment.

(*a*) $\Omega^{\mathrm{pp}}({}^2\mathrm{P}_{\frac{1}{2}}, {}^2\mathrm{P}_{\frac{3}{2}})$ *for* Ne^+

The adjusted collision strength is larger than the calculated collision strength by a factor of 1.6. For $\mathrm{e}+\mathrm{Ne}^+$ we have six one-channel $\boldsymbol{R}$-matrices in LS coupling. Using adjusted matrices we obtain a marked improvement in the agreement with experiment for a large number of energy levels (table 20). For this case the adjusted result for Ω^{pp} should be of quite high accuracy.

(*b*) $\Omega^{\mathrm{pp}}({}^3\mathrm{P}, {}^1\mathrm{S})$ *for* N^+

From table 4 it is seen that only the ${}^2\mathrm{P}$ total angular momentum state contributes to the p-wave ${}^3\mathrm{P}$–${}^1\mathrm{S}$ transition. For ${}^2\mathrm{P}$ we have a 3×3 symmetric matrix containing six linearly independent elements. But now from table 13 we see that only two members of the $2\mathrm{p}^2 n\mathrm{p}\ {}^2\mathrm{P}$ series in N I have been observed and that neither of the observed levels contain much admixture of the state with $2\mathrm{p}^2\,{}^1\mathrm{S}$ parentage. It follows that we have no direct empirical information on the matrix elements of importance for the calculation of $\Omega^{\mathrm{pp}}({}^3\mathrm{P}, {}^1\mathrm{S})$. In our adjustment procedure (see § 4.3) we assume a functional form involving four adjustable parameters, F_0, F_2, G_0 and G_2, and obtain values of these parameters by considering all 12 observed $2\mathrm{p}^2 n\mathrm{p}\, SL$ levels. This procedure may lead to the (a) result for $\Omega^{\mathrm{pp}}({}^3\mathrm{P}, {}^1\mathrm{S})$ being more accurate than the (c) result, but we cannot be sure that this will be the case.

(*c*) $\Omega^{\mathrm{pp}}({}^1\mathrm{D}, {}^1\mathrm{S})$ *for* N^+

This is a sensitive case involving a lot of cancellation. The p-wave collision strengths are small and there is a large difference between the (a) and (c) results. This is of little importance, since the main contributions to $\Omega({}^1\mathrm{D}, {}^1\mathrm{S})$ come from other partial waves.

For the other cases considered in table 27 the differences between the (c) and (a) results are fairly small (factors not exceeding 1.2). This gives a fair indication of the accuracy of the calculations.

6.2. *Resonances in collision strengths*

In the neighbourhood of a resonance the collision strength $\Omega(i, i')$ varies rapidly as a function of the energy. A detailed discussion of the theory for resonances in electron-ion collisions is given in the paper QDT VII (Seaton 1969*a*). We are particularly interested in the collision strengths at low energies for configurations $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^q$ with $q = 2$, 3 and 4. Denoting the three terms of the ion by $S_i L_i$, $i = 1, 2$ and 3, we obtain resonances in $\Omega(1, 2)$ at energies below the threshold for excitation of the term $i = 3$. Reactance matrices are calculated at energies above the $i = 3$ threshold, and extrapolated to lower energies using the techniques described in § 3.2. Some typical results for resonances in colllision strengths $\Omega(1, 2)$ have been given in a review paper (Seaton 1969*b*). For many applications one may use collision strengths $\bar{\Omega}(1, 2)$ averaged over resonances; results for $\bar{\Omega}(1, 2)$ are given in paper I.

For ions with $q = 3$ one must also consider the collision strengths $\Omega({}^2\mathrm{D}_{\frac{3}{2}}, {}^2\mathrm{D}_{\frac{5}{2}})$. When fine structure is taken into account, one obtains complicated profiles of over-lapping resonances. Detailed results for $\Omega({}^2\mathrm{D}_{\frac{3}{2}}, {}^2\mathrm{D}_{\frac{5}{2}})$ in O^+ have been given by Martins & Seaton (1969), and values of $\bar{\Omega}({}^2\mathrm{D}_{\frac{3}{2}}, {}^2\mathrm{D}_{\frac{5}{2}})$ for other ions have been given by Martins, Saraph & Seaton (1969).

Further calculations of collision strengths in O^{2+} have been made by Eissner *et al.* (1969), who make approximate allowance for resonance states of the type 1s^{2}2s2p^{3}3s. More accurate calculations for various ions, allowing for coupling between configurations 1s^{2}2s^{2}2p^q and 1s^{2}2s2p^{q+1} in the collision problem, are being made at University College London.

Note added in proof 5 *October* 1971

We are indebted to Professor Edlén for bringing the following points to our attention.

(i) New measurements for N I have been made by Eriksson & Pettersson (1971). They obtain term values for 4p ^{2}P and ^{2}D which agree reasonably well with the predicted values of table 15.

(ii) Isberg (1967) gives term values for O I 5p and 6p ^{5}P. This series is unperturbed and values of $(\nu^{(c)} - \nu^{(e)})$ for 5p and 6p are similar to those in table 17 for 3p and 4p.

(iii) Eriksson & Isberg (1968) obtain $T = 113\,204$ cm^{-1} for O I (^{2}D) 3p ^{1}P, which is not in such good agreement with our estimate of $113\,590 \pm 100$ cm^{-1}.

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