

## Hartree-Fock Results for Some Excited States of $O^{+2}$ , $O^+$ , and $Ne^{\dagger}$

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Hartree-Fock results are reported for some excited states of  $O^{+2}$ ,  $O^+$ , and  $Ne^+$ , all of which involve two incomplete groups. The off-diagonal energy parameters included in the calculation turn out to be large in some cases. A procedure is suggested for dealing with nondiagonal terms in the Hamiltonian.

### I. INTRODUCTION

MOST of the Hartree-Fock calculations which have been reported are for atoms and ions in their ground-state configurations, with at most one incomplete group.<sup>1</sup> A few have been reported in connection with transition probabilities for excited configurations with either one incomplete group or an incomplete group plus an unpaired  $s$  electron.<sup>2</sup> The present calculations deal entirely with excited configurations each containing two incomplete groups.

The presence of incomplete groups in a configuration results in several terms being associated with it. The dependence on the term of various atomic parameters such as the spin-orbit parameter, the  $F^k$  and  $G^k$  integrals, or the transition integral, has not been fully investigated. In a study of forbidden transitions in P, S, Cl, and Ar, Czyzak<sup>1</sup> attributes at least part of the improved agreement with observations to the fact that Hartree-Fock wave functions were computed for each term.

For some incomplete groups, and particularly when a configuration consists of several incomplete groups besides  $s$  electrons, an additional complication is introduced in that there may be several terms of the same type with nondiagonal matrix elements in the Hamiltonian connecting them. A procedure is suggested for including them in the Hartree-Fock calculations.

The present calculations also show that when two incomplete groups with the same angular quantum

number  $l$  are present, the off-diagonal energy parameters introduced in order to satisfy orthogonality conditions, may be large for some terms. For example, for  $2p^4(^3P)3p^2P$  in  $Ne^+$ ,  $\epsilon_{3p,3p} = 0.69745$ , whereas  $\epsilon_{3p,2p} = -0.42515$ . This is quite different from the usual case of a single incomplete group outside closed shells where the off-diagonal energy parameters are small and can be treated as a final minor perturbation on wave functions which are nearly self-consistent. As a result, a general Hartree-Fock procedure must take the off-diagonal energy parameters into account right from the start of a self-consistent field iteration.

Numerical Hartree-Fock calculations are reported for a series of terms in  $O^{+2}$ ,  $O^+$ , and  $Ne^+$  which illustrate the points mentioned earlier. These wave functions were required for a study of model atmospheres in  $B$ -type stars.<sup>3</sup> In the remainder of the paper, the general numerical procedure is first discussed, then each atom in turn. The wave functions themselves are not included<sup>4</sup>; instead certain atomic parameters are tabulated including transition integrals.

### II. NUMERICAL PROCEDURE

A procedure for solving the Hartree-Fock equations was described in a previous paper,<sup>5</sup> but it ignored the off-diagonal energy parameters which must be introduced in order to satisfy the orthogonality conditions. In ground states the orthogonality corrections are usually quite small, but this is not true in general, and therefore a general Hartree-Fock procedure must take the off-diagonal energy parameters into account.

The Hartree-Fock wave function  $P_i(r)$  for the  $i$ th group of electrons with quantum numbers  $n_i l_i$ , is a solution of an equation of the form

$$P_i''(r) + \left\{ (2/r)[Z - Y_i(r)] - \epsilon_{ii} - [l_i(l_i+1)/r^2] \right\} P_i(r) + (2/r)X_i(r) = \sum_{j \neq i} \delta_{l_i l_j} \epsilon_{ij} P_j(r). \quad (1)$$

The off-diagonal energy parameters  $\epsilon_{ij}$  and  $\epsilon_{ji}$  are related by the fact that  $\epsilon_{ij} = \lambda_{ij}/q_i$ , where  $q_i$  is the number of electrons in the  $i$ th group:  $\lambda_{ij}$  is a Lagrange multiplier, and therefore  $\lambda_{ij} = \lambda_{ji}$ .<sup>6</sup> If  $P_i(r)$  and  $P_j(r)$

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<sup>1</sup> A complete bibliography of calculations done prior to 1948 was published by D. R. Hartree in Rept. Progr. Phys. **11**, 113 (1948) and updated in *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York 1957). The following are some more recent references: B. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958); C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960); R. E. Watson, Phys. Rev. **118**, 1036 (1960); **119**, 1934 (1960); R. E. Watson and A. J. Freeman, *ibid.* **123**, 521 (1961); **124**, 1117 (1961); A. J. Freeman and R. E. Watson, *ibid.* **127**, 2058 (1962); L. C. Allen, J. Chem. Phys. **34**, 1156 (1961); S. J. Czyzak, Astrophys. J. Suppl. Ser. **65**, 53 (1962); E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962); E. Clementi, J. Chem. Phys. **38**, 996 (1963); **38**, 1001 (1963).

<sup>2</sup> L. Biermann and E. Treffitz, Z. Astrophys. **26**, 213 (1949); E. Treffitz, *ibid.* **26**, 240 (1949); **29**, 287 (1951); E. Treffitz and L. Biermann, *ibid.* **30**, 275 (1951); C. Froese, Monthly Notices Roy. Astron. Soc. **117**, 615 (1957); A. S. Douglas and R. H. Garstang, Proc. Cambridge Phil. Soc. **58**, 377 (1962); A. W. Weiss, Astrophys. J. **138**, 1262 (1963); C. Froese, *ibid.* **140**, 361 (1964).

<sup>3</sup> A. B. Underhill (to be published).

<sup>4</sup> These are available upon request.

<sup>5</sup> C. Froese, Can. J. Phys. **41**, 1895 (1963).

<sup>6</sup> Note that the matrix  $(\epsilon_{ij})$  is symmetric only for configurations in which groups of electrons with the same angular quantum number  $l$ , all have the same number of electrons. An example is a configuration consisting entirely of complete groups. The diagonalization of the  $\epsilon$  matrix as suggested by W. W. Piper, General

are two different wave functions with  $l_i=l_j$ , and therefore assumed to be orthogonal, then the fact that each is a solution of a differential equation of the form of Eq. (1) yields the expression

$$\lambda_{ij} = \frac{q_i q_j}{q_j - q_i} \int_0^\infty \frac{2}{r} \{ (Y_j - Y_i) P_i P_j + X_i P_j - X_j P_i \} dr, \quad (2)$$

provided  $q_i \neq q_j$ . When  $q_i = q_j$ , and the integrand in Eq. (2) is identically zero, then the wave functions will be orthogonal with  $\lambda_{ij} = 0$ . Consequently, the off-diagonal energy parameters between complete groups can always be set equal to zero. When  $q_i = q_j$ , and the integrand is not zero, the Hartree-Fock equations are inconsistent,<sup>7</sup> and the wave functions should be determined by applying the variational procedure to an expression for the energy which does not assume orthogonality.<sup>8</sup>

Equation (2) was used to compute the off-diagonal energy parameters for the results reported here. Because it assumes  $P_i$  is already orthogonal to  $P_j$ , the outermost wave function was first made orthogonal to the inner one by the Gram-Schmidt process before  $\lambda_{ij}$  was computed during a self-consistent field iteration.

Roothaan and Bagus<sup>9</sup> have extended the analytic self-consistent field calculations to configurations with incomplete groups, but restrict their derivation to configurations with at most one incomplete group with a given quantum number  $l$ . Huzinaga<sup>10</sup> has suggested a scheme with somewhat wider range of applicability.

In the previous paper,<sup>5</sup> the differential equation, together with its boundary conditions and the normalization condition, was solved by first selecting an initial slope and adjusting the energy to satisfy the boundary conditions, then adjusting the initial slope, and repeating the process until a normalized solution was obtained. This procedure converges well for inner wave functions and for most ground-state configurations, but not for excited states. On the other hand, the method described by Dettmar and Schlüter<sup>11</sup> is not nearly as efficient for inner wave functions, but will compute outer wave functions even for states above the ionization potential. The two methods complement each other very nicely.

Briefly, the solution of the differential equation

$$y'' + [f(r) - \lambda]y = g(r), \quad y(0) = y(\infty) = 0$$

is a function of  $\lambda$ , namely,  $y(r, \lambda)$ , and can be expanded

Electric Rept. No. 59-RL-2242 G7 (published by Research Information Section, The Knolls, Schenectady, New York, 1959) is therefore not valid in general.

<sup>7</sup> C. Froese, *Astrophys. J.* (to be published).

<sup>8</sup> H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Academic Press Inc., New York, p. 141, 1957).

<sup>9</sup> C. C. J. Roothaan and P. S. Bagus, in *Methods in Computational Physics* edited by B. Adler, S. Fernback, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 47.

<sup>10</sup> S. Huzinaga, *Phys. Rev.* **122**, 131 (1961).

<sup>11</sup> H. K. Dettmar and A. Schlüter, *Z. Angew. Math. Mech.* **38**, 220 (1958).

in a Taylor's series about a point  $\lambda = \bar{\lambda}$ , provided  $\bar{\lambda}$  is not an eigenvalue of the homogeneous equation. Then

$$y(r, \lambda) = y_1(r, \bar{\lambda}) + (\lambda - \bar{\lambda})y_2(r, \bar{\lambda}) + \dots,$$

where

$$y_i'' + [f(r) - \bar{\lambda}]y_i = y_{i-1}, \\ y_i(0) = y_i(\infty) = 0, \quad y_0(r, \bar{\lambda}) = g(r).$$

These equations can be solved without iteration by computing a particular solution along with a solution of the homogeneous equation for both outward and inward integration and then forming a general solution in each region such that the solutions and their derivatives match at the common boundary point. By relating the functions  $y_i(r, \bar{\lambda})$  with the coefficients in a Laurent expansion which has a wider radius of convergence, Dettmar and Schlüter derive formulas of various orders for estimating that solution  $y(r, \bar{\lambda})$  which is normalized.<sup>12</sup> The first-order process was found to be adequate, namely,

$$\beta = (-a_3 \pm [a_3^2 + a_4(1 - a_2)]^{1/2}) / a_4, \\ \bar{\lambda} = \bar{\lambda} + a_3\beta / (a_4\beta + a_3), \\ \tilde{y}(r, \bar{\lambda}) = y_1(r, \bar{\lambda}) + \beta y_2(r, \bar{\lambda}),$$

where

$$a_2 = \int_0^\infty y_1^2 dr, \quad a_3 = \int_0^\infty y_1 y_2 dr, \quad a_4 = \int_0^\infty y_2^2 dr.$$

Of the two values of  $\beta$ , the one which resulted in the smallest change in the eigenvalue was selected provided both resulted in a function with positive values near the origin; otherwise the one associated with positive values was selected. The  $k$ th estimate of the wave function was then taken to be

$$P^k(r) = (P^{k-1}(r) + \tilde{y}(r, \bar{\lambda})) / 2$$

normalized to unity. In other words, an exact solution to Eq. (1) for a given  $Y_i(r)$  and  $X_i(r)$  was not obtained during the intermediate stages of a self-consistent field iteration, but only as the over-all process converges.

The results of the Hartree-Fock calculations are reported in the form of tables of atomic parameters. These include the following:

- (i) diagonal energy parameters  $\epsilon_{nl, nl}$  for outer electrons,
- (ii) the Hartree screening parameters defined as  $\sigma_{nl} = Z - (\bar{r}_{nl}^H / \bar{r})$ ,
- (iii)  $F^k(nl, n'l')$  and  $G^k(nl, n'l')$  integrals for outer electrons,
- (iv) the total Hartree-Fock energy, and
- (v) the spin-orbit parameter  $\zeta_{nl}$ .

Some remarks are in order with regard to the calculation of the spin-orbit parameter. When the configuration includes only one incomplete group, the value of

<sup>12</sup> The formulas for the second-order process contain several errors.

TABLE I. Hartree-Fock results for terms in  $O^{+2}$ ,  $O^+$ , and  $Ne^+$ .

$$E_{total}(O) = -70 - E \text{ (au)}$$

$$E_{total}(Ne) = -120 - E \text{ (au)}$$

	$2p3p O^{+2}$			$2p^23p O^+$		$2p3d O^{+2}$	
	$^1P$	$^3S$	$^3D$	$^4D$	$^4P$		$^3P$
$\epsilon_{2p, 2p}$	5.03504	5.00024	5.02033	3.52585	3.52717	$\epsilon_{2p, 2p}$	5.01113
$\epsilon_{3p, 3p}$	1.35694	1.30309	1.33492	0.68151	0.66746	$\epsilon_{3d, 3d}$	1.02120
$\sigma_{2p}$	2.490	2.465	2.480	2.938	2.932	$\sigma_{2p}$	2.521
$\sigma_{3p}$	3.954	4.076	4.004	4.907	4.958	$\sigma_{3d}$	4.849
$F^2(2p, 2p)$				0.43107	0.43166		
$F^2(2p, 3p)$	0.07562	0.06978	0.07325	0.04636	0.04426	$F^2(2p, 3d)$	0.06536
$G^0(2p, 3p)$	0.02757	0.02511	0.02658	0.01663	0.01564	$G^1(2p, 3d)$	0.04264
$G^2(2p, 3p)$	0.02906	0.02623	0.02791	0.01664	0.01561	$G^3(2p, 3d)$	0.02429
$E$	1.7731	1.7461	1.7621	3.4410	3.4340	$E$	1.6053
$\zeta_{2p}(\text{cm}^{-1})$	263.64	266.90	264.98	220.80	221.33	$\zeta_{2p}(\text{cm}^{-1})$	261.75
$\zeta_{3p}(\text{cm}^{-1})$	30.66	27.38	29.33	14.74	13.78	$\zeta_{3d}(\text{cm}^{-1})$	1.66

  

	$2p3s O^{+2}$		$2p^23s O^{+2}$	$2p^43s Ne^+$			$^3S$
	$^3P$	$^1P$	$^4P$	$^4P$	$^2P$	$^2D$	
$\epsilon_{2p, 2p}$	4.94790	4.92549	3.44866	4.30182	4.31577	4.19673	4.03517
$\epsilon_{3s, 3s}$	1.57253	1.53292	0.87340	0.99228	0.95061	0.97615	0.97846
$\sigma_{2p}$	2.547	2.527	2.962	3.821	3.807	3.855	3.913
$\sigma_{3s}$	3.375	3.525	4.165	5.646	5.848	5.717	5.707
$F^2(2p, 2p)$			0.42885	0.52108	0.52226	0.51756	0.51171
$G^1(2p, 3s)$	0.03435	0.02572	0.02539	0.02520	0.01690	0.02201	0.02249
$E$	1.8802	1.8604	3.5354	6.8672	6.8467	6.7347	6.5495
$\zeta_{2p}(\text{cm}^{-1})$	258.38	258.93	218.91	590.64	591.52	587.06	581.40

  

	$2p^43p Ne^+$								
	$(^3P)^4D$	$(^3P)^4P$	$(^6P)^4S, ^3S$	$(^1D)^2F$	$(^1D)^2D$	$(^3P)^2D$	$(^3P)^2P^a$	$(^1D)^2P^a$	$(^1S)^2P$
$\epsilon_{2p, 2p}$	4.41069	4.40064	4.42554	4.30068	4.31198	4.42103	4.43914	4.32652	4.14612
$\epsilon_{3p, 3p}$	0.72831	0.75101	0.69902	0.73216	0.70696	0.71353	0.70154	0.70954	0.71874
$\sigma_{2p}$	3.802	3.818	3.785	3.841	3.829	3.783	3.752	3.792	3.887
$\sigma_{3p}$	6.654	6.554	6.786	6.644	6.750	6.741	6.886	6.840	6.709
$F^2(2p, 2p)$	0.52278	0.52146	0.52432	0.51889	0.51994	0.52448	0.52756	0.52343	0.51402
$F^2(2p, 3p)$	0.04336	0.04810	0.03753	0.04426	0.03976	0.03848	0.02985	0.03232	
$G^0(2p, 3p)$	0.01581	0.01876	0.01239	0.01644	0.01387	0.01245	0.00612	0.00750	0.01508
$G^2(2p, 3p)$	0.01524	0.01798	0.01202	0.01581	0.01337	0.01220	0.00666	0.00799	0.01457
$E$	6.7364	6.7474	6.7215	6.6130	6.6004	6.7290	6.7163	6.6001	6.4200
$\zeta_{2p}(\text{cm}^{-1})$	593.03	591.57	594.74	589.03	590.03	594.56	597.06	592.84	584.15
$\zeta_{3p}(\text{cm}^{-1})$	28.26	33.79	21.87	29.21	24.41	22.15	10.39	12.62	26.26

<sup>a</sup> These represent mixed states.

$\zeta_{nl}$  is that of the parameter  $\zeta_{nl}'$  first introduced by Horie<sup>13</sup> for a group of equivalent electrons, and extended by Blume and Watson<sup>14</sup> to equivalent electrons outside closed shells. The spin-orbit interactions can be interpreted as arising from three sources:

- (i) the spin-orbit interaction of an electron in the Coulomb field of the nucleus,
- (ii) the spin-orbit interaction of an electron in the Coulomb field of another electron, and
- (iii) the magnetic interaction of the spin moment of one electron with the orbital moment of the other.

The interactions of type (ii) and (iii) between electrons in an unfilled shell and a closed shell of electrons behave like an effective one-particle spin-orbit potential. Similarly a large part of the interactions within an unfilled shell behaves in this manner. These interactions

are included in the definition of  $\zeta_{nl}$ . Blume and Watson have shown that for one unfilled shell outside closed shells, the contribution from the nuclear term and the direct matrix elements of the above two-body interactions is of the form  $\frac{1}{2}\alpha^2 \langle \partial V / r \partial r \rangle$ , where  $V$  is a Hartree potential. They also give a table for determining the contribution from exchange matrix elements in this case. These results were generalized to configurations of more than one incomplete group by ignoring the exchange-type interactions between electrons in different incomplete groups, and assuming that the form of the direct matrix element was unchanged.

The atomic parameters computed from the Hartree-Fock results are listed in Table I; Table II consists of a list of transition integrals.

### III. RESULTS FOR $O^{+2}$ AND $O^+$

The Hartree-Fock calculations for  $2p3s\ ^3,^1P$  and  $2p3d\ ^3P$  of  $O^{+2}$ , and those for  $2p^23s\ ^4P$  and  $2p^23p\ ^4D$ ,  $^4P$  of  $O^+$  are standard in that no special problems arise.

<sup>13</sup> H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

<sup>14</sup> M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A280**, 127 (1962).

TABLE II. Transition integrals  $\int P_i(nl; r)rP_f(n'l'; r)dr$ .

O <sup>2+</sup>	$2p3p^1P \rightarrow 2p3s^1P$	-3.0441
	$2p3p^3S \rightarrow 2p3s^3P$	-3.0162
	$2p3p^3D \rightarrow 2p3d^3P$	-3.1859
	$2p3p^3D \rightarrow 2p3s^3P$	-2.9987
	$2p3p^3D \rightarrow 2p3d^3P$	-3.1473
O <sup>+</sup>	$2p^23s^4P \rightarrow 2p^23p^4D$	-3.6905
	$2p^23s^4P \rightarrow 2p^23p^4P$	-3.7022
Ne <sup>+</sup>	$2p^4(^3P)3s^4P \rightarrow 2p^4(^3P)3p^4D$	-3.2795
	$2p^4(^3P)3s^4P \rightarrow 2p^4(^3P)3p^4P$	-3.2628
	$2p^4(^3P)3s^4P \rightarrow 2p^4(^3P)3p^4S$	-3.2937
	$2p^4(^3P)3s^2P \rightarrow 2p^4(^3P)3p^2D$	-3.4227
	$2p^4(^3P)3s^2P \rightarrow 2p^4(^3P)3p^2P$	-3.4485
	$2p^4(^3P)3s^2P \rightarrow 2p^4(^3P)3p^2S$	-3.4278
	$2p^4(^1D)3s^2D \rightarrow 2p^4(^1D)3p^2F$	-3.3207
	$2p^4(^1D)3s^2D \rightarrow 2p^4(^1D)3p^2D$	-3.3355
	$2p^4(^1D)3s^2D \rightarrow 2p^4(^1D)3p^2P$	-3.3460

The off-diagonal energy parameters must be introduced, but these remain small compared to the diagonal energy parameters. However, the  $2p3p$  configuration is an example of a case where  $q_i = q_j$  when Eq. (2) is used to determine  $\lambda_{2p3p}$ . The energies of the terms  $1,^3D$ ,  $1,^3P$ , and  $1,^3S$  are all of the form<sup>15</sup>

$$a[F^0(2p, 3p) \pm G^0(2p, 3p)] + b[F^2(2p, 3p) \pm G^2(2p, 3p)].$$

It is easy to show that the integrand of (2) is identically zero for those terms in which the minus sign applies, namely,  $^3S$ ,  $^1P$ , and  $^3D$ . In these cases the self-consistent Hartree-Fock wave functions should be orthogonal when the off-diagonal parameters are set equal to zero. The computed orthogonality integral serves as a check on the numerical calculation: it never exceeded 0.0000002.

#### IV. RESULTS FOR NE<sup>+</sup>

Hartree-Fock wave functions were computed for all the terms of  $2p^43s$  and  $2p^43p$ . The latter is an example of a configuration with two  $^2D$  and three  $^2P$  terms with non-diagonal elements in the Hamiltonian connecting them. The numerical procedure adopted for including these terms was similar to the method of superposition of configurations introduced by Hartree, Hartree, and Swirls.<sup>16</sup> Hartree-Fock calculations were first performed for states in a definite coupling scheme,  $2p^4(S_1L_1)3p^2P$  or  $^2D$ . From these results, the matrix elements of the Hamiltonian<sup>17</sup> were computed and the matrix diagonalized. The eigenvectors defining the mixing of configurations are given in Table III. The mixing of states is quite small. The largest amount occurs between the  $2p^4(^3P)3p^2P$  and  $2p^4(^1D)3p^2P$  states.

<sup>15</sup> E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 199 (2nd ed., 1951).

<sup>16</sup> D. R. Hartree, W. Hartree, and B. Swirls, *Phil. Trans. Roy. Soc. London A238*, 229 (1939).

<sup>17</sup> J. C. Slater, *Quantum Theory of Atomic Structures* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 290.

TABLE III. The mixing coefficients for  $^2D$  and  $^2P$  states of  $2p^43p$  Ne<sup>+</sup>.

Old \ New	( <sup>3</sup> P) <sup>2</sup> D	( <sup>1</sup> D) <sup>2</sup> D	$E_{total}$	
<sup>2</sup> D <sub>1</sub>	0.99989	0.01459	-126.7290	
<sup>2</sup> D <sub>2</sub>	-0.01459	0.99989	-126.6004	
Old \ New	( <sup>3</sup> P) <sup>2</sup> P	( <sup>1</sup> D) <sup>2</sup> P	( <sup>1</sup> S) <sup>2</sup> P	$E_{total}$
<sup>2</sup> P <sub>1</sub>	0.99117	-0.13054	-0.02346	-126.7169
<sup>2</sup> P <sub>2</sub>	0.13102	0.99117	0.02039	-126.6011
<sup>2</sup> P <sub>3</sub>	0.02059	-0.02328	0.99952	-126.4198

The wave functions for the corresponding two mixed states were recomputed assuming a superposition of vector coupling states. The resulting total energy differed from the eigenvalues determined earlier by at most 0.001.

The results for the different  $^2P$  vector coupling states show some interesting trends which can be related to the off-diagonal energy parameters. Some of these are listed in Table IV. The three parent states are  $2p^4^1S$ ,  $^1D$ , and  $^3P$  and the off-diagonal energy parameters increase in magnitude in going from one parent state to the next. The Lagrange multipliers in this case are of the form

$$aR^0(2p2p; 2p3p) + bR^2(2p2p; 2p3p) + cR^0(3p3p; 3p2p) + dR^2(3p3p; 3p2p).$$

The largest  $R$  integral is  $R^0(2p2p; 2p3p)$  and its coefficients are 1/3, 5/3, and 9/3, respectively, for the three states. This explains the differences of similar magnitude.

The effect of an off-diagonal energy parameter is predominantly in the region of the main maximum of the wave function appearing with the parameter in Eq. (1). Thus the changes in magnitude of the first maximum of the  $3p$  wave functions can be attributed to the changes in the off-diagonal energy parameters. Again, the differences are approximately equal. In the case of the  $2p$  wave function, the off-diagonal energy parameters affect the tail of the wave function, and in fact introduce an extra node. The extra maximum is too large to be attributed to numerical errors, and also is

TABLE IV. Trends related to the Lagrange multipliers.

	$\lambda_{2p3p}$	$\Delta\lambda$	First max. of $3p$	$\Delta\max.$	Second max. of $2p$	$\Delta\max.$
<sup>1</sup> S	-0.03396		0.2042		-0.00046	
<sup>1</sup> D	-0.26748	-0.23352	0.1632	0.0410	-0.00656	-0.00610
<sup>3</sup> P	-0.42515	-0.15767	0.1184	0.0448	-0.01169	-0.00513

roughly proportional to the magnitude of the off-diagonal parameters. When these are large, the Hartree-Fock equations can no longer be interpreted as representing an electron in a potential field.

The ionized neon configuration has already been investigated by Garstang.<sup>18</sup> He compared the one-electron energies of self-consistent Hartree wave functions with observed energies and found a considerable difference; in each case the observed energies were larger. He also compared the transition integrals with those derived from the Coulomb approximation of

<sup>18</sup> R. H. Garstang, *Monthly Notices Roy. Astron. Soc.* **110**, 612 (1950).

Bates and Damgaard.<sup>19</sup> Again a significant difference occurred when the Coulomb approximation was based on observed energies. It is interesting to note that the Hartree-Fock energies agree more closely with the observed than with the Hartree energies; in fact, a difference of about 10% between observed and Hartree energies is reduced to 2% with Hartree-Fock energies. Even so, the transition integrals are about half-way between those of the Coulomb approximation based on observed energies, and those from the Hartree wave functions.

<sup>19</sup> D. R. Bates and A. Damgaard, *Phil. Trans. Roy. Soc. London* **A242**, 101 (1949).

## Atomic Absorption Cross Section of Lithium Vapor Between 2300 and 1150 Å

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The continuous atomic absorption cross section of lithium vapor has been measured using photoelectric techniques from the  $2s^2S \rightarrow np^2P^0$  series limit at 2300 to 1150 Å. The bandwidth of the monochromator was 0.75 Å and values of the cross section were obtained at 2-Å intervals. The best value for the atomic absorption cross section at the series limit was  $1.54 \pm 0.23$  Mb. The shape of the curve near the series limit is in close agreement with some recent theoretical predictions. There is an apparent disagreement with recent experimental results.

### I. INTRODUCTION

CONSIDERABLE interest exists in experimentally obtained absorption cross sections of the alkali metals at energies greater than that at their ionization edge. Apart from the immediate quantitative need for these data, comparison with the theoretically predicted absorption curves can lead to an insight into the nature of the alkali metal wave functions themselves.<sup>1</sup> Lithium is of particular interest because of the relatively straightforward nature of its configuration and the singular absence of a predicted absorption zero minimum near its ionization edge.

Theoretical estimates have been made by Stewart,<sup>2</sup> and Burgess, and Seaton,<sup>3</sup> of the variation with wavelength of the atomic absorption cross section of lithium from the ionization edge at 2300 to 1800 Å. Within this wavelength range, both curves show a gradual increase of the cross section with energy, but differ in their absolute magnitude. Tait's recent theoretical results<sup>4</sup> in the dipole velocity formulation agree in magnitude with the former works, but his dipole

length formulation yields results approximately 50% higher. Both curves indicate a slight decrease in cross section with decreasing wavelength. The recent experimental results obtained by Marr<sup>5</sup> using photographic techniques agree in magnitude, within experimental error, with Tait's dipole length data. This agreement is considerably improved if Marr's results are adjusted for more recent vapor pressure data.

Marr's results show a maximum at 1900 Å which is not apparent in any of the theoretical curves. Thus, although the agreement between theoretical and experimental magnitudes is good, the shape of the curve of atomic absorption cross section versus wavelength remains in doubt.

This paper is an account of the determination of the atomic absorption cross section of lithium from 2300 to 1150 Å in which photoelectric techniques and the most recent vapor pressure data are employed.

### II. EXPERIMENTAL APPARATUS

The basic theory and experimental arrangement employed in this laboratory in the measurement of the cross sections of alkali metal vapors have been discussed previously by Hudson.<sup>6</sup> Certain modifications to the instrumentation were incorporated prior to the work on

<sup>1</sup> R. W. Ditchburn and V. Öpik, *Atomic and Molecular Processes* (Academic Press, Inc., New York, 1962).

<sup>2</sup> A. Stewart, *Proc. Phys. Soc. (London)* **67**, 917 (1954).

<sup>3</sup> A. Burgess and M. J. Seaton, *Monthly Notices Roy. Astron. Soc.* **120**, 121 (1960).

<sup>4</sup> J. H. Tait, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions* (North-Holland Publishing Company, Amsterdam, 1964), p. 586.

<sup>5</sup> G. V. Marr, *Proc. Phys. Soc. (London)* **81**, 9 (1963).

<sup>6</sup> R. D. Hudson, *Phys. Rev.* **135**, A1212 (1964).