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AN APPROXIMATE CALCULATION OF THE LOWER ENERGY LEVELS OF THE CARBON ATOM

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Abstract

Slater's theory of the complex atom as modified and extended by Zener and Eckart is applied to the $2p^2$ and $2p^3$ configurations of the carbon atom. The energy levels resulting from these configurations are computed. Some of the computed energy differences agree roughly with the experimental values, others indicate either that the method is not applicable or that the experimental data are not reliable. The $2p^3$, ^5S level is found to lie nearest to the normal $2p^2$, ^3P level. Of the levels for which experimental data are lacking or doubtful, the $2p^3$, ^1D is computed to lie 12.9 volts above the normal, the $2p^3$, ^3S, 13.7 volts and the $2p^3$, ^1P, 14.7 volts above the normal.

SINCE the completely rigorous solution of the complete wave equation for the more complex atoms seems to be impossible, many attempts at approximate solutions have been made. This paper is an application of certain of these approximate methods to the calculation of the lower energy levels of the carbon atom. Two principles must be considered in any such method. First, only those levels exist which are characteristic numbers of Schrödinger's equation for the atom. Second, only those levels exist which are associated with characteristic functions that are antisymmetric in the electrons. The electron spin is introduced from the beginning in connection with the second of these principles but is neglected with respect to the first. In determining approximate functions, it is assumed that each electron moves in a Coulomb field of force but that electrons with different total or different azimuthal quantum numbers move in fields of slightly different strengths. The best values for these fields, that is the best effective nuclear charges, are determined.

Following Slater,[1] the wave function for a single electron, that is, a solution of Schrödinger's equation for a single particle in a central field, may be written as $u(n_i/x_i)$ where n_i stands for the four quantum numbers: n_i, l_i, m_{s_i}, m_{l_i} and x_i stands for the four coordinates, three of position and one of spin. It is known that a product of N of these functions approximately satisfies the wave equation governing N electrons but is not antisymmetric. A linear combination of these solutions is also an approximate solution and that one which is antisymmetric may be written as a determinant:

$$\psi = \begin{vmatrix} u(n_1/x_1) & u(n_1/x_2) & \cdots & u(n_1/x_N) \\ \cdot & \cdot & \cdots & \cdot \\ u(n_N/x_1) & u(n_N/x_2) & \cdots & u(n_N/x_N) \end{vmatrix}. \tag{1}$$

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[1] J. C. Slater, Phys. Rev. **34,** 1293 (1929).

This form is frequently shortened to $|u(n_1/x_1) \cdots u(n_N/x_N)|$ by writing only the elements on the principal diagonal. When the subscripts are omitted, it is understood that they are in the normal order of cardinal numbers.

From this wave function, the diagonal terms of the energy matrix are then computed:

$$W_n = \int \psi_n H \psi_n^* d\tau / \int \psi_n \psi_n^* d\tau. \tag{2}$$

Here H is the energy operator neglecting spin:

$$H = \sum_i (\nabla_i^2 + 2Z/r_i) - \sum_{ij} (2/r_{ij}). \tag{3}$$

Distances are measured in units of $a_H = 0.528$A and energies in units of Rh cm$^{-1} = 13.529$ volts $= 109678$ wave numbers. Z is the true nuclear charge in units of e.

In the development of these integrals, theorems and methods given by Slater[1] and also by Zener[2] were used. Slater shows that except where energy levels lie very close together or are degenerate the non-diagonal terms of the energy matrix are negligible. As a spherically symmetrical energy operator without spin has been assumed, the non-diagonal terms involving transitions between states with the same n and l values but different m_l and m_s values can not be neglected since these states will have the samee nergy. However, use of the principle of the constancy of diagonal sums as discussed by Slater,[1] enables one to get the correct sums of energy values without actual use of pertubation calculations. This principle is: Given an orthogonal set of wave functions: $\psi_1 \cdots \psi_N$, make an orthogonal set of linear combinations of them: $\psi_1' \cdots \psi_N'$. Let the diagonal terms of the energy matrix, referred to the original set of wave functions, be $W_1 \cdots W_N$, and the diagonal terms of the energy matrix, referred to the new wave functions be $W_1' \cdots W_N'$. Then $W_1 + \cdots + W_N = W_1' + \cdots + W_N'$, that is, to the zeroth approximation, the sum of a number of energy values is not changed by applying a pertubation even if the individual values are. If, in such a sum, each of the energy values except one is known, that one can be determined by subtracting the known values from the sum. This "method of sums" is frequently used in this paper.

If the determinants of Eq. (1) were substituted directly into the integrals of Eq. (2), $(N!)^2$ terms would appear in each integral. However, Zener[2] shows that if but one term in the expansion of the first determinant is substituted into each of the integrals, there will be no change in W. This leaves only $N!$ terms. In developing the remaining determinant, terms containing all possible transpositions of the N electrons would be found. Any of these terms which contains the electron function of a particular electron with a spin opposite to the spin of that electron in the single term of the first determinant which was retained, will also vanish. Lastly, since all the electron functions except those for 1s and 2s electrons are orthogonal and since H acts on at

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[2] C. Zener, Phys. Rev. **36**, 51 (1930).

most two electron functions at a time, those terms containing three or more transpositions (except for 1*s* and 2*s*) from the order of the single term will vanish. These conditions greatly reduce the number of terms involved in computing W.

Eckart[3] has shown that if arbitrary screening constants, or as has been used in this paper, arbitrary effective nuclear charges are introduced into the electron functions and then these charges varied to give maximum negative values to W, the resulting value of W is a good approximation to the corresponding term value. From what has gone before, it is evident that this is true even when W has been calculated by the method of sums. Actually it was found in the cases tried that the numerical result was essentially the same whether the maximizing process was applied before or after the method of sums was used, though this is not theoretically necessary.

APPLICATION TO THE CARBON ATOM

It was found convenient in the actual calculations to replace the general notation $u(n_i/x_i)$ by a shorter non-systematic notation as given in Table I.

TABLE I.

$1s$	$u(100/x_i)$	$u=2(\alpha^3)^{1/2}e^{-\alpha r}Y_{0,0}$	$=u^*$
$2s$	$u(200/x_i)$	$v=(\beta^3/2)^{1/2-\beta r}(1-\beta r/2)Y_{0,0}$	$=v^*$
$2p(m_l=0)$	$u(210/x_i)$	$x=(\gamma^3/6)^{1/2}(\gamma r/2)e^{-\gamma r/2}Y_{1,0}$	$=x^*$
$2p(m_l=-1)$	$u(21-1/x_i)$	$w=(\gamma^3/6)^{1/2}(\gamma r/2)e^{-\gamma r/2}Y_{1,-1}$	$=y^*$
$2p(m_l=+1)$	$u(211/x_i)$	$y=(\gamma^3/6)^{1/2}(\gamma r/2)e^{-\gamma r/2}Y_{1,+1}$	$=w^*$
	$Y_{l,m_l}=\left(\frac{(2l+1)\,(l-m_l)!}{4\pi(l+m_l)!}\right)^{1/2}e^{im_l\phi}P_{lm_l}(\cos\theta)$		
	$Y_{0,0}=(1/4\pi)^{1/2}$		
	$Y_{1,0}=(3/4\pi)^{1/2}\cos\theta$		
	$Y_{1,-1}=(3/8\pi)^{1/2}\sin\theta\, e^{-i\phi}$		
	$Y_{1,+1}=(3/8\pi)^{1/2}\sin\theta\, e^{+i\phi}$		
	$Y_{2,0}=(5/4\pi)^{1/2}(1/2)\,(3\cos^2\theta-1)$		
	$Y_{2,\pm 1}=(15/8\pi)^{1/2}e^{\pm i\phi}\sin\theta\cos\theta$		
	$Y_{2,\pm 2}=(15/32\pi)^{1/2}e^{\pm 2i\phi}\sin^2\theta$		

In this new notation the spin quantum number is not directly included but is represented by a (+) or (−) sign written as a superscript. The undetermined nuclear charges which are to be determined by the maximizing process described above are represented by α for 1*s* electrons, β for 2*s* and γ for 2*p* electrons. It was found desirable in making the numerical calculations to transform these quantities by $\beta=\alpha/x$ and $\gamma=\alpha/(x+y)$.

The lowest states of the carbon atom arise from the configurations $1s^22s^2$ $2p^2$ and $1s^22s2p^3$. The possible wave functions for the first of these configurations are given in Table II and for the second in Table III. The fourth columns in these tables give the allowed states assuming Russell-Saunders coupling and noting that in the first configuration there are two "equivalent" *p*-electrons outside of the closed shells while in the second configuration there are three "equivalent" *p*-electrons and an *s*-electron outside of the closed shell. These allowed states are discussed in "Structure of Line Spectra" by

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[3] C. Eckart, Phys. Rev. **36**, 878 (1930).

TABLE II.

	Σm_l	Σm_s			
$\psi_a = \lvert u^+u^-v^+v^-y^+y^- \rvert$	2	0	^1D		
$\psi_b = \lvert u^+u^-v^+v^-y^+x^+ \rvert$	1	1	^3P		
$\psi_c = \lvert u^+u^-v^+v^-w^+y^+ \rvert$	0	1	^3P		
$\psi_d = \lvert u^+u^-v^+v^-y^+x^- \rvert$	1	0	^1D	^3P	
$\psi_e = \lvert u^+u^-v^+v^-x^+y^- \rvert$	1	0	^1D	^3P	
$\psi_f = \lvert u^+u^-v^+v^-y^+w^- \rvert$	0	0	^1D	^3P	^1S
$\psi_g = \lvert u^+u^-v^+v^-x^+x^- \rvert$	0	0	^1D	^3P	^1S
$\psi_h = \lvert u^+u^-v^+v^-w^+y^- \rvert$	0	0	^1D	^3P	^1S

TABLE III.

	Σm_l	Σm_s				
$\psi_1 = \lvert u^+u^-v^+w^+x^+y^+ \rvert$	0	2	^5S			
$\psi_2 = \lvert u^+u^-v^+y^+x^+y^- \rvert$	2	1	^3D			
$\psi_3 = \lvert u^+u^-v^+y^+x^+x^- \rvert$	1	1	^3D	^3P		
$\psi_4 = \lvert u^+u^-v^+y^+w^+y^- \rvert$	1	1	^3D	^3P		
$\psi_5 = \lvert u^+u^-v^+y^+x^+w^- \rvert$	0	1	^3D	^3P	^5S	^3S
$\psi_6 = \lvert u^+u^-v^+y^+w^+x^- \rvert$	0	1	^3D	^3P	^5S	^3S
$\psi_7 = \lvert u^+u^-v^+x^+w^+y^- \rvert$	0	1	^3D	^3P	^5S	^3S
$\psi_8 = \lvert u^+u^-v^-y^+x^+w^+ \rvert$	0	1	^3D	^3P	^5S	^3S
$\psi_9 = \lvert u^+u^-v^+y^+y^-x^- \rvert$	2	0	^3D	^1D		
$\psi_{10} = \lvert u^+u^-v^-y^+y^-x^+ \rvert$	2	0	^3D	^1D		
$\psi_{11} = \lvert u^+u^-v^+y^+y^-w^- \rvert$	1	0	^3D	^1D	^3P	^1P
$\psi_{12} = \lvert u^+u^-v^+x^+y^-x^- \rvert$	1	0	^3D	^1D	^3P	^1P
$\psi_{13} = \lvert u^+u^-v^-y^-y^+w^+ \rvert$	1	0	^3D	^1D	^3P	^1P
$\psi_{14} = \lvert u^+u^-v^-x^-y^+x^+ \rvert$	1	0	^3D	^1D	^3P	^1P
and six others						

Pauling and Goudsmit, Chapter IX and in many other places. The wave function of a state having a given value of $M = \Sigma m_l$ and a given Russell-Saunders symbol is a linear combination of the ψ's appearing opposite these entries in Tables II and III. Thus for example:

$$\psi(^3P,\ M = 1) = a\psi_d + b\psi_e$$

$$\psi(^1D,\ M = 1) = c\psi_d + d\psi_e.$$

These linear transformations are always orthogonal and it is thus possible to apply the method of sums.

In expanding the integrals of Eq. (2), the methods of Zener[2] as discussed above were followed. For example:

$$W_1 = \int \psi_1 H \psi_1{}^* d\tau \Big/ \int \psi_1 \psi_1{}^* d\tau$$

$$\begin{aligned} \int \psi_1 H \psi_1{}^* d\tau = \int uuvwxy\, H\, [&uuvyxw - vuuyxw - yuvuxw - xuvyuw \\ &- wuvyxu - uuyvxw - uuxyvw - uuwyxv - uuvwxy - uuvxyw \\ &- uuvywx + vuuwxy + vuuxyw + vuuywx + yuuvxw + xuuyvw \\ &+ wuuyxv + vuyuxw + vuxyuw + vuwyxu] d\tau \end{aligned}$$

$$\int \psi_1 \psi_1{}^* d\tau = \int uuvwxy[uuvyxw - vuuyxw] d\tau.$$

Here the conjugate complex functions have been replaced by their equivalents as given in Table I. Hence from here on, orthogonalities are computed without using the conjugate of one of the functions.

Because of orthogonalities between functions of *s*- and *p*-electrons and between those of two *p*-electrons, the sum of whose m_l values is not zero, $[\int(u \text{ or } v)(w \text{ or } x \text{ or } y)d\tau = \int wx\, d\tau = \int xy\, d\tau = \int ww\, d\tau = \int yy\, d\tau = 0]$ these integrals fall into two groups. In the first two integrals of the above example, there are no such orthogonalities and an integral takes the form:

$$\int uuvwxy \left[\sum_i (\nabla_i^2 + 2Z/r_i) - \sum_{ij} (2/r_{ij}) \right] uuvyxwd\tau .$$

In the others, the presence of two orthogonalities causes all terms coming from the first summation to vanish and only integrals of the form:

$$\int uuvwxy \sum_{ij} (2/r_{ij}) uuvyxwd\tau$$

remain. In expanding the summations, two distinct types of integrals result, those coming from the first summation and those from the second. The first of these types involves the product of two normalized spherical surface harmonics. Eckart[3] gives the following formulas (here corrected for certain typographical errors which appear in his paper) for reducing these to integrals of more familiar algebraic functions and for evaluation of the new integrals.

$$\begin{aligned}
&\iint \{f(r_1)[Y_1(\theta, \phi)]^2 g(r_2)/r_{1,2}\} d\tau_1 d\tau_2 \\
&\quad = 4\pi \int_{r_1=0}^{\infty} f(r_1) r_1 \int_{r_2=0}^{r_1} g(r_2) r_2^2 dr_2 dr_1 \\
&\qquad + 4\pi \int_{r_1=0}^{\infty} f(r_1) r_1^2 \int_{r_2=r_1}^{\infty} g(r_2) r_2 dr_2 dr_1 \\
&\iint \{f(r_1) Y_1(\theta_1, \phi_1) g(r_2) Y_1(\theta_2, \phi_2)/r_{1,2}\} d\tau_1 d\tau_2 \\
&\quad = \left\{ 4\pi \int_{r_1=0}^{\infty} f(r_1) r_1^{1-l} \int_{r_2=0}^{r_1} g(r_2) r_2^{l+2} dr_2 dr_1 \right. \\
&\qquad \left. + 4\pi \int_{r_1=0}^{\infty} f(r_1) r_1^{2+l} \int_{r_2=r_1}^{\infty} g(r_2) r_2^{1-l} dr_2 dr_1 \right\} \frac{1}{(2l+1)} \\
&\int_r^{\infty} r^n e^{-ar} dr = (n!/a^{n+1}) e^{-ar} \sum_{k=0}^{n} (ar)^k / k!
\end{aligned}$$

and of course

$$\int_0^r r^n e^{-ar} dr = \frac{n!}{a^{n+1}} - \int_r^{\infty} r^n e^{-ar} dr$$

since only integral values of *n* are involved. The second type involves the product of four harmonics. These can be reduced to products of two only by the following relations which are easily shown to be true by substituting the actual values of the harmonics.

$$Y_{1,0}{}^2 = \frac{1}{(4\pi)^{1/2}} Y_{0,0} + \frac{1}{(5\pi)^{1/2}} Y_{2,0} \qquad Y_{1,\pm1}Y_{10} = \left(\frac{3}{20\pi}\right)^{1/2} Y_{2,\pm1}$$

$$Y_{1,-1}Y_{1,+1} = \frac{1}{(4\pi)^{1/2}} Y_{0,0} - \frac{1}{(20\pi)^{1/2}} Y_{2,0} \qquad Y_{1,\pm1}{}^2 = \left(\frac{3}{10\pi}\right)^{1/2} Y_{2,\pm2}$$

Table IV gives all the resulting integrals.

TABLE IV.

$$b=\int uv d\tau=(2x)^{3/2}(x-1)/(x+\tfrac{1}{2})^4$$

$$h_u{}^u=\int u[\nabla^2 u+2Zu/r]d\tau=(2Z-\alpha)\alpha$$

$$h_v{}^v=\int v[\nabla^2 v+2Zv/r]d\tau=(2Z-\alpha/x)\alpha/4x$$

$$h_x{}^x=\int x[\Delta^2 x+2Zx/r]d\tau=\int w[\nabla^2 y+2Zy/r]d\tau=\frac{\alpha}{4(x+y)}[2Z-\frac{\alpha}{x+y}]$$

$$h_u{}^v=\int[u\nabla^2 v+v\nabla^2 u+4uvZ/r]d\tau=\{2\alpha bx/(x-1)\}[Z-\alpha/4-(Z-\alpha)/4x^2]$$

$$\alpha A=\int u_1{}^2u_2{}^2 2d\tau/r_{12}=1.25\alpha$$

$$\alpha B=\int u_1v_1u_2{}^2 2d\tau/r_{12}=\alpha 8(2x)^{1/2}[\frac{2x-1}{(2x+1)^3}-\frac{60x^2-8x-1}{(6x+1)^4}]$$

$$\alpha C=\int u_1{}^2v_2{}^2\ 2d\tau/r_{12}=\frac{\alpha}{2x}[1-\frac{2(4x+1)}{(2x+1)^3}-\frac{4(5x+1)}{(2x+1)^4}+\frac{3(6x+1)}{(2x+1)^5}]$$

$$\alpha D=\int u_1{}^2x_2{}^2 2d\tau/r_{12}=\int u_1{}^2w_2y_2 2d\tau/r_{12}=\frac{\alpha}{2(x+y)}[1-\frac{6(x+y)+1}{(2x+2y+1)^5}]$$

$$\alpha E=\int u_1v_1u_2v_2 2d\tau/r_{12}=\alpha 32x^2[\frac{20x^2-30x+13}{(2x+1)^7}]$$

$$\alpha G=\int u_1v_1x_2{}^2 2d\tau/r_{12}=\int u_1v_1w_2y_2 2d\tau/r_{12}=\alpha 8(2x)^{1/2}\left\{\frac{2x-1}{(2x+1)^3}-\right.$$
$$\frac{(x+y)^2}{(2x^2+2xy+3x+y)^3}\left[2x^2+2xy+x-y+\frac{6x(x^2+xy-y)}{2x^2+2xy+3x+y}+\right.$$
$$\left.\left.\frac{6x^2(2x^2+2xy-x-3y)}{(2x^2+2xy+3x+y)^2}.+\frac{16x^3(x^2+xy-x-2y)}{(2x^2+2xy+3x+y)^3}\right]\right\}$$

$$\alpha H=\int u_1w_1u_2y_2 2d\tau/r_{12}=\int u_1x_1u_2x_2 2d\tau/r_{12}=\frac{224\alpha(x+y)^2}{3[2x+2y+1]^7}$$

$$\alpha I=\int u_1y_1v_2w_2 2d\tau/r_{12}=\int u_1x_1v_2x_2 2d\tau/r_{12}=(-)(256/3)\alpha(2x)^{1/2}(x+y)^2$$
$$\left[\frac{y}{(2x+2y+1)^5\,(2x+y)^3}+\frac{2x^2+2xy+x-y}{(2x+2y+1)^5\,(2x^2+2xy+3x+y)^3}+\right.$$
$$\frac{4x(x^2+xy-y)}{(2x+2y+1)^4\,(2x^2+2xy+3x+y)^4}+\frac{3x^2(2x^2+2xy-x-3y)}{(2x+2y+1)^3\,(2x^2+2xy+3x+y)^5}+$$
$$\left.\frac{6x^3(x^2+xy-x-2y)}{(2x+2y+1)^2\,(2x^2+2xy+3x+y)^6}\right]$$

$$\alpha K=\int v_1{}^2x_2{}^2 2d\tau/r_{12}=\frac{\alpha}{2(x+y)}\left[1-\frac{x^4(45x^3+106x^2y+86xy^2+24y^3)}{(2x+y)^7}\right]$$

$$\alpha L=\int v_1x_1v_2x_2 2d\tau/r_{12}=\frac{2\alpha x^4(x+y)^2}{3(2x+y)^9}[45x^2+132xy+101y^2]$$

$$\alpha O=\int w_1y_1x_2{}^2 2d\tau/r_{12}=894\alpha/2560(x+y)$$

$$\alpha P=\int w_1x_1y_2x_2 2d\tau/r_{12}=54\alpha/2560(x+y)$$

$$(O+2P)\alpha=\int x_1{}^2x_2{}^2 2d\tau/r_{12}$$

$$(O+P)\alpha=\int w_1y_1w_2y_2 2d\tau/r_{12}$$

$$2\alpha P=\int w_1{}^2y_2{}^2 2d\tau/r_{12}$$

$$\alpha Q=\int v_1{}^2v_2{}^2 2d\tau/r_{12}=77\alpha/256x$$

$$\alpha T=\int v_1^2 v_2 u_2 2d\tau/r_{12}=\alpha 8(2x)^{1/2}\frac{1}{(2x+3)^5\,(2x+1)^2}\{32+80(2x+1)+24(2x+1)^2+10(2x+1)^3+(2x+1)^4-\frac{1}{(2x+1)\,(2x+3)}[128+384(2x+1)+490(2x+1)^2+100(2x+1)^3+36(2x+1)^4+3(2x+1)^5]\}$$

Certain useful contractions in notation.

$R_1=2h_u^u+h_v^v+3h_x^x-\alpha[A+2C+6D+3K]$	
$R_2=b^2h_u^u+2bh_u^v+3b^2h_x^x-\alpha[2bB+2b^2D+E+6G]$	
$R_a=2h_u^u+2h_v^v+2h_x^x-\alpha[A+4C+4K+Q]$	
$R_b=b^2h_u^u+b^2h_v^v+bh_u^v+2b^2h_x^x-\alpha[2bB+b^2C+2b^2D+E+4bG+2b^2K+2bT]$	
$R_c=2b^3h_u^v+2b^4h_x^x-\alpha[6b^2E+8bG]$	
$S_1=-\alpha[-3H+6bI-3L]$	$0.8369\ (1-b^2)$
$S_2=-\alpha[-(3-b^2)H+4bI-2L]$	$0.5841\ (1-b^2)$
$S_3=-\alpha[-3(1-b^2)H]$	$0.0785\ (1-b^2)$
$S_4=-\alpha[-(3-2b^2)H+2bI-L]$	$0.3313\ (1-b^2)$
$S_a=-\alpha[-2(1-b^2)H+4b(1-b^2)I-2(1-b^2)L]$	$0.5580\ (1-b^2)^2$
$F_1=[S_1+R_1-R_2]/(1-b^2)$	77.8358
$F_2=[S_2+R_1-R_2]/(1-b^2)$	77.5830
$F_3=[S_3+R_1-R_2]/(1-b^2)$	77.0774
$F_4=[S_4+R_1-R_2]/(1-b^2)$	77.3303
$F_a=[S_a+R_a-2R_b+R_c]/(1-b^2)^2$	75.8699
$(R_1-R_2)/(1-b^2)$	76.9989
$(R_a-2R_b+R_c)/(1-b^2)^2$	75.3119

NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

In evaluating the W's for different assumed values of α, x, and y, it was found that $\alpha=5.7$, $x=1.3$, $y=0.6$ or $\alpha=5.7$, $\beta=4.37$ and $\gamma=3.0$ gave maximum numerical values to all the W's of both configurations. The numerical values given in the different tables are all computed for these values of the effective nuclear charges. In varying α, x and y to get these values, the maximum was very flat, i.e., considerable changes in these parameters changed the value of the maximum but little. Hence this method is not at all critical for the determination of the best effective nuclear charges. However, this very flatness makes it unnecessary to vary α, x and y by excessively small steps.

The numerical values for the different W's are given in Table V.

TABLE V.

For the $1s^22s^22p^2$ configuration	Maximum numerical value
$W(^1D)=W_a=W_f=W_h=F_a-\alpha O-\alpha P$	74.7589
$W(^3P)=W_b=W_c=F_a-\alpha O+\alpha P$	74.8855
$W_d=W_\epsilon=F_a-\alpha O$	74.8222
$W_g=F_a-\alpha O-2\alpha P$	74.6956
and by the method of sums,	
$W(^1S)=W_f+W_g+W_h-W(^1D)-W(^3P)$	74.5691
For the $1s^22s2p^3$ configuration	
$W(^5S)=W_1=F_1-3\alpha O+3\alpha P$	74.8826
$W(^3D)=W_2=W_5=W_7=F_2-3\alpha O$	74.4401
$W_3=W_4=F_2-3\alpha O-\alpha P$	74.3769
$W_6=F_2-3\alpha O+\alpha P$	74.5034
$W_8=F_3-3\alpha O+3\alpha P$	74.1243
$W_9=W_{10}=F_4-3\alpha O$	74.1837
$W_{11}=W_{12}=W_{13}=W_{14}=F_4-3\alpha O-\alpha P$	74.1241
and by the method of sums,	
$W(^3P)=W_4+W_3-W(^3D)$	74.3135
$W(^3S)=W_5+W_6+W_7+W_8-W(^3D)-W(^3P)-W(^5S)$	73.8717
$W(^1D)=W_9+W_{10}-W(^3D)$	73.9345
$W(^1P)=4W_{11}-W(^3D)-W_7(^1D)-W(^3P)$	73.8083

A comparison of the results of these computations with experimental[4] data is given in Table VI. In the fourth column of this table are given some experimentally[5] determined intervals for the N^+ ion. Except for the effect of the increased nuclear charge, this ion should have the same possible levels as the carbon atom. The rather high value for the $2p^3$, ${}^3S$ level of carbon is suggested by the corresponding high value for this level in N^+.

TABLE VI.

$1s^22s^22p^2$ configuration	Computed	Experimental	N^+ Experimental
$2p^2, {}^3P-2p^2, {}^1D$	0.1266	0.0925	0.14
$2p^2, {}^3P-2p^2, {}^1S$	0.3164	0.1970	0.298
$1s^22s2p^3$ configuration			
$2p^3, {}^3D-2p^3, {}^5S$	−0.4425		
$2p^3, {}^3D-2p^3, {}^3P$	0.1266	0.1018	
$2p^3, {}^3D-2p^3, {}^1D$	0.5056	0.1288	
$2p^3, {}^3D-2p^3, {}^3S$	0.5684		
$2p^3, {}^3D-2p^3, {}^1P$	0.6318	0.1296	
$2p^2, {}^3P-2p^3, {}^5S$	0.0029	(0.12)	
$2p^2, {}^3P-2p^3, {}^3D$	0.4454	0.5839	0.84
$2p^2, {}^3P-2p^3, {}^3P$	0.5720	0.6857	1.0
$2p^2, {}^3P-2p^3, {}^1D$	0.9510	0.7127	
$2p^2, {}^3P-2p^3, {}^3S$	1.0138		1.42
$2p^2, {}^3P-2p^3, {}^1P$	1.0772	0.7135	

It has been suggested from band spectra data, but the evidence is of doubtful value, that the $2p^3$, ${}^5S$ level might lie about 1.6 volts above the normal and that is the only basis for the 0.12 value given in the table.

CONCLUSIONS

One of the reasons for undertaking this set of caluclations was to determine the position or the $2p^3$, ${}^5S$ level. According to certain theories of valence as applied to the carbon atom, this level should lie near the normal.[6] While these calculations are not able to fix its exact value, they do suggest that it is the level lying nearest to the normal $2p^2$, ${}^3P$ level.

It is to be noted that except for the $2p^3$, ${}^1D$ and ${}^1P$ levels, the computed intervals between different levels, of the same configuration are all larger (24, 37 and 55 percent) than the observed intervals. On the other hand, computed intervals between levels of different configurations are smaller (17 and 23 percent) than the observed intervals. In the case of the $2p^3$, ${}^1D$ and ${}^1P$ levels, it seems uncertain whether this form of calculation gives less satisfactory results for these levels or if, as is more probable, the published data which is admitted to be questionable, is wrong.

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[4] Experimental data for carbon from Paschen and Kruger, Ann. d. Pkysik **7**, 1 (1930).

[5] I. S. Bowen, Phys. Rev. **29**, 231 (1927).

[6] Molecular Binding and Low ${}^5S$ Terms of N^+ and C. L. A. Turner, Nat. Acad. Sci. Proc. **15**, 526 (1929).

The value of Slater's $F^2(1n:1n)$ comes out as $25\alpha P/3 = 0.5273$.

This set of calculations seems to show that while something can be learned of the location of energy levels by such approximations, still the accuracy of the results is rather worse than might have been expected from similar work on the still more simple atoms.

In conclusion I wish to express my sincere thanks to Professor Carl Eckart who suggested this problem and under whose general direction this work was done, and also my thanks to Professor R. S. Mulliken for his active interest in the work.