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Variational Atomic Wave Functions

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The energy tables constructed by Morse, Young, and Haurwitz to facilitate the variational computation of wave functions for atoms containing $1s$, $2s$, and $2p$ electrons have been extended to include $3p$ and $3d$ electrons. The best parameters, total energies, and term values are given for the states $(1s3d)\ ^1D$, ^3D; $(2p^2)\ ^3P$, ^1D, ^1S; and $(1s^23d)\ ^2D$ of the atoms He, Li, Be, B, C, N, O, F and Ne, and for $(1s3p)\ ^1P$, ^3P of He I. It is shown that the observed energies of the $1snd$ states of He I are very accurately reproduced with the use of hydrogenic radial wave functions for both the $1s$ and nd electrons.

IN an earlier paper, Morse, Young and Haurwitz[1] described the construction of a set of tables that were employed to calculate simple, variational wave functions for atomic states involving $1s$, $2s$, and $2p$ electrons. The tables have now been extended[2] to include $3p$ and $3d$ electrons, and the present note gives the results of variational calculations on the states $1s3p$, $1s3d$, $2p^2$, and $1s^23d$. The following wave functions were utilized in the computations:

$$\begin{aligned}
&1s \quad u_1(r)=(\mu^3a^3/\pi)^{\frac{1}{2}}e^{-\mu ar},\\
&2p \quad u_3(r)=(\mu^5c^5/\pi)^{\frac{1}{2}}r\cos\theta e^{-\mu cr},\\
&3p \quad u_6(r)=(2\mu^7/15\pi N^2)^{\frac{1}{2}}r\cos\theta \\
&\qquad\qquad \times[(5/\mu)Ae^{-\mu dr}-re^{-\mu r}],\\
&3d \quad u_9(r)=(\mu^7f^7/18\pi)^{\frac{1}{2}}r^2(3\cos^2\theta-1)e^{-\mu fr}.
\end{aligned} \tag{1}$$

The constant A, which makes u_6 orthogonal to u_3, is given by:

$$A=(d+c)^5/(1+c)^6. \tag{2}$$

In order to avoid the use of more than three parameters in the calculations for the $1s3p$ configuration, we have made the following simplification to eliminate the parameter c. An inspection of the results obtained by Morse, Young and Haurwitz[1] for the $1s2s$ and $1s2p$ configurations shows that the screening of the inner electron by the outer one is negligible for those states. We have accordingly assumed in the $1s3p$ calculations for He I that $a\mu=2.00$. The value of $c\mu$ in the $1s3p$ calculations must be equivalent to that obtained for $1s2p$. Therefore, the ratio $c/a=\beta$ is taken as constant for $1s2p$ and $1s3p$. Eq. (2) then becomes

$$A=(d+\beta a)^5/(1+\beta a)^6, \tag{3}$$

where $\beta(^3P^0)=0.275$, and $\beta(^1P^0)=0.245$.

The procedure followed in obtaining the best values of the energies and the parameters is precisely that outlined in the earlier paper. We define the following integrals:

$$\mu^2T_n=-\int\bar{u}_n\nabla^2u_ndv, \quad \mu V_n=2\int(u_n^2/r)dv,$$

$$\mu V_{nm}=2\int[u_n^2(r_1)u_m^2(r_2)/r_{12}]dv_1dv_2, \tag{4}$$

$$\mu X_{nm}=2\int[\bar{u}_n(r_1)\bar{u}_n(r_2)u_m(r_1)u_m(r_2)/r_{12}]dv_1dv_2.$$

The energy W of any atomic state is then

$$W=\mu^2T+\mu V, \tag{5}$$

where T is a linear combination of the T's, and V a linear combination of the V's and X's. Both T and V are independent of μ, and hence the energy is minimized analytically with respect to this parameter. We obtain

$$\mu=-V/2T, \tag{6}$$

and

$$W=-V^2/4T. \tag{7}$$

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[1] Morse, Young and Haurwitz, Phys. Rev. **48**, 948 (1935).

[2] The extensions to the tables are being mimeographed; those interested in obtaining copies should write to the Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts.

TABLE I. *Wave function parameters and energies.*

ATOM	He	Li	Be	B	C	N	O	F	Ne
				TWO-ELECTRON STATES					
				$(2p^2)\ ^3P$ *State*					
$2c\mu$	1.672	2.672	3.672	4.672	5.672	6.672	7.672	8.672	9.672
W_{cal}	1.398	3.570	6.741	10.913	16.085	22.257	29.429	37.601	46.772
$\mathrm{Term}_{\mathrm{cal}}\times 10^{-6}$	−0.2856	−0.5959	−1.016	−1.546	−2.185	−2.935	−3.794	−4.762	−5.841
				$(2p^2)\ ^1D$ *State*					
$2c\mu$	1.630	2.630	3.630	4.630	5.630	6.630	7.630	8.630	9.630
W_{cal}	1.328	3.458	6.587	10.717	15.847	21.976	29.106	37.236	46.365
$\mathrm{Term}_{\mathrm{cal}}\times 10^{-6}$	−0.2932	−0.6082	−1.033	−1.567	−2.212	−2.966	−3.829	−4.802	−5.886
				$(2p^2)\ ^1S$ *State*					
$2c\mu$	1.566	2.566	3.566	4.566	5.566	6.566	7.566	8.566	9.566
W_{cal}	1.227	3.293	6.360	10.426	15.492	21.559	28.625	36.692	45.758
$\mathrm{Term}_{\mathrm{cal}}\times 10^{-6}$	−0.3043	−0.6262	−1.058	−1.599	−2.250	−3.011	−3.882	−4.862	−5.952
				$(1s3d)\ ^3D$ *State*					
a	6.00	4.50	4.00	3.75	3.60	3.50	3.43	3.38	3.33
$a\mu$	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
$3\mu f$	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00
W_{cal}	4.1111	9.4447	17.0006	26.7789	38.7790	53.0022	69.4465	88.113	109.005
W_{exp}	4.1113	9.4450							
$\mathrm{Term}_{\mathrm{cal}}$	12190	48800	109800	195210	304960	439190	597680	780600	988200
$\mathrm{Term}_{\mathrm{exp}}$	12209	48834							
				$(1s3d)\ ^1D$ *State*					
a	6.00	4.50	4.00	3.75	3.60	3.50	3.43	3.38	3.33
$a\mu$	2.00	3.00	4.00	5.006	6.00	7.00	8.00	9.00	10.00
$3\mu f$	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00
W_{cal}	4.1111	9.4443	16.9997	26.7772	38.7768	52.9989	69.4428	88.108	108.999
W_{exp}	4.1112	9.4447							
$\mathrm{Term}_{\mathrm{cal}}$	12190	48760	109700	195030	304720	438830	597280	780000	987500
$\mathrm{Term}_{\mathrm{exp}}$	12206	48804							

	He$(1s3p)\ ^3P^0$ *State*	*He*$(1s3p)\ ^1P^0$ *State*
a	6.29	6.15
$a\mu$	2.00	2.00
d	1.54	1.00
$d\mu$	0.490	0.325
3μ	0.954	0.975
W_{cal}	4.115	4.109
W_{exp}	4.116	4.110
$\mathrm{Term}_{\mathrm{cal}}$	12600	12000
$\mathrm{Term}_{\mathrm{exp}}$	12730	12080

ATOM	Li	Be	B	C	N	O	F	Ne
			THREE-ELECTRON STATES					
			$(1s^23d)\ ^2D$ *State*					
a	8.06	5.54	4.69	4.27	4.01	3.84	3.72	3.63
$a\mu$	2.69	3.69	4.69	5.69	6.69	7.69	8.69	9.69
$3f\mu$	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
W_{cal}	14.5556	27.6399	44.9458	66.4740	92.2244	122.1970	156.3919	194.8106
W_{exp}	14.6710	27.7520	45.0603	66.5721				
$\mathrm{Term}_{\mathrm{cal}}$	12200	48800	109900	195200	305000	439200	597700	780900
$\mathrm{Term}_{\mathrm{exp}}$	12203	48828	109861	195292	305210	439506	598004	
$^2D_{3/2}{}^2-D_{5/2\ \mathrm{cal}}$	0.036	0.58	2.91	9.26	22.4	46.7	86.2	147
$^2D_{3/2}-{}^2D_{5/2\ \mathrm{exp}}$				11.3			108	

The results of the present calculation are shown in Table I. No difficulty was encountered in obtaining energy minima for any but the $3\ ^1P^0$ level. For this state the energy was first computed over the range from $d=2.00$ to $d=1.00$. It appeared from the run of the energies that the minimum lay close to the value $d=1.00$. This value of d corresponds to the same average screening in both the inner and the outer parts of the electron orbit. In order that the minimization might be carried out accurately, the energies were computed for values of d less than unity. These computations indicated a point of inflection at $d=1.00$. The failure of the energy to minimize properly is probably due to the fact that the $3\,{}^1P^0$ function was made orthogonal to an approximate $2\,{}^1P^0$ function rather than to the true one. It is difficult to visualize a value of d less than unity, which would mean a more effective screening for r small than for r large. We have consequently adopted the value $d=1.00$ as close to the correct one. The resulting energy, obtained from the minimization with respect to a, is in satisfactory agreement with the observed term value. Furthermore, the average effective charge, 3μ, is 0.975, as compared with the value 0.97 obtained for the $2\,{}^1P^0$ level.

The quantity $3\mu f$ may be regarded as the average effective charge on the $3d$ electron. Table I shows that $3\mu f=Z$ for the $1s3d$ and $1s^23d$ configurations throughout the He I and Li I isoelectronic sequences. This result means that the screening by the inner electrons is probably negligible for the entire array of $1snd$ and $1s^2nd$ configurations. We may consequently seek to derive general expressions for the energy integrals by adopting hydrogenic $1s$ and nd wave functions. We write the hydrogenic functions in the following form:

$$u_{1s}=(\mu^3/\pi)^{\frac{1}{2}}e^{-\mu r}, \tag{8}$$

$$u_{nd}=\left[\frac{5\mu^7(n+2)\,!}{2^3n^84\pi(n-3)\,!(5\,!)^2}\right]^{\frac{1}{2}}(3\cos^2\theta-1)r^2 \times e^{-\mu r/2n}F(-n+3,\,6,\,\mu r/n), \tag{9}$$

where F is the confluent hypergeometric function:

$$F(\alpha,\gamma,x)=1+\frac{\alpha}{1!\gamma}x+\frac{\alpha(\alpha+1)}{2!\gamma(\gamma+1)}x^2+\cdots. \tag{10}$$

The parameter μ is retained as a scale constant, which may be evaluated from (6). The functions (9) will be exactly hydrogenic, provided that $\mu=Z$. The extent to which μ deviates from Z measures the degree by which the functions deviate from orthogonality.

To calculate the energies, we need to evaluate the following integrals:

$$T_{nd}=\frac{N^2}{\mu^2}\int_0^\infty r^6e^{-\mu r/n}(\mu/r-\mu^2/4n^2) \times F^2(-n+3,\,6,\,\mu r/n)dr, \tag{11}$$

$$V_{nd}=\frac{2N^2}{\mu}\int_0^\infty r^5e^{-\mu r/n}F^2(-n+3,6,\mu r/n)dr, \tag{12}$$

$$V_{1snd}=\frac{2N^2}{\mu}\int_0^\infty r^5e^{-\mu r/n}(1-\mu re^{-2\mu r}-e^{-2\mu r}) \times F^2(-n+3,\,6,\,\mu r/n)dr, \tag{13}$$

$$X_{1snd}=\frac{16}{5}\mu^2N^2\int_0^\infty r_2{}^6\exp\left[-\mu\left(\frac{2n+1}{2n}\right)r_2\right] \times F(-n+3,\,6,\,\mu r_2/n) \times\left[\int_{r_0}^\infty r_1\exp\left[-\mu\left(\frac{2n+1}{2n}\right)r_1\right] \times F(-n+3,\,6,\,\mu r_1/n)dr_1\right]dr_2, \tag{14}$$

where

$$N^2=\mu^7(n+2)\,!/(n-3)\,!(5\,!)^2. \tag{15}$$

The quantities T_{nd} and V_{nd} are made up of integrals of the form

$$\int_0^\infty r^{-k}R^2(nd)dr, \tag{16}$$

where $R(nd)$ is the radial part of the hydrogenic nd wave function. Values of this integral for different values of k have been tabulated by Condon and Shortley.[3] With the aid of their Table II,[5] we find

$$T_{nd}=1/4n^2,\quad V_{nd}=1/n^2. \tag{17}$$

The quantity V_{1snd} may be evaluated by the process of integrating (13) term by term and applying the well-known[4] transformations among the hypergeometric functions. We obtain

$$V_{1snd}=\frac{1}{n^2}\left\{1-\frac{n(n^2-1)(n^2-4)(2n)^{2n-6}}{5\,!(2n+1)^{2n}} \times\left[\frac{7n+4}{2n+1}F\left(-n+3,\,-n+2,\,6,\,\frac{1}{4n^2}\right) +\frac{4n^2-23n+33}{24n^2(2n+1)}F\left(-n+2,\,-n+2,\,7,\,\frac{1}{4n^2}\right)\right]\right\}, \tag{18}$$

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[3] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, p. 117.

[4] *Cf.* Forsyth, *Differential Equations*, p. 192.

where F is the ordinary hypergeometric function of four variables. Although the exchange integral (14) is easily evaluated for a particular value of n, we have been unable to obtain a simple, closed expression for n generally. Table II contains the results of energy calculations for the $1s3d$ and $1s4d$ configurations of He I, obtained with the use of the hydrogenic energy integrals. The agreement with experiment is excellent. Indeed, the calculated $1s4d$ energies are slightly below the experimental values, which is due to the departure of the hydrogenic functions from exact orthogonality. It may be noted that the parameter $\mu(4d)$, which would possess the value 2 if the functions were exactly orthogonal, departs from that figure only in the fifth decimal.

TABLE II. *Results for* He I *1s3d and 1s4d.*

	$1s3d$	$1s4d$		$1s3d$	$1s4d$
$\mu(3\,^3D)$	2.00000	2.00003	$\mu(3\,^1D)$	2.00000	2.00002
$W(3\,^3D)_{\text{cal}}$	4.11114	4.06261	$W(3\,^1D)_{\text{cal}}$	4.11109	4.06257
$W(3\,^3D)_{\text{exp}}$	4.11126	4.06257	$W(3\,^1D)_{\text{exp}}$	4.11123	4.06255

The wave functions derived in this investigation have been utilized by one of us[5] to calculate transition probabilities for a number of lines of He I.

It is a pleasure to record our thanks to Dr. P. M. Morse for his interest and guidance in this problem, and to Dr. D. H. Menzel for many valuable discussions of the properties of hypergeometric functions.

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[5] Goldberg, Astrophys. J., in press.

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Numerical Calculations of the Reflection of Electrons by Metals

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The specular reflection of electrons by metallic surfaces is considered. It is assumed that the potential energy of an electron is constant ($=-V_0$) in the interior of the metal, and account is taken of the image force acting on an electron outside the metal (Nordheim's problem). The reflection coefficient R is computed for the range of values of V_0 which is of interest in connection with real metals, and for the range of values of energy of the electrons in which R has appreciable values. In the Appendix there are given some values of the function $\Gamma'(iy)/\Gamma(iy)$, for real values of y, which were computed incidentally.

1. Introduction

THE chief purpose of this article is to give the results of some numerical calculations of the reflection coefficient for a beam of electrons impinging on the plane face of a thick metallic body. We make use of the crude and simple assumption that the potential energy of an electron is constant in the interior of the metal, and we take account of the electrostatic image force acting on an electron outside the metal. Most of the analytical features of the problem have been discussed in an article by Nordheim;[1] but his work was not carried to the point of obtaining numerical results, such as are given here.

2. General Formula for the Reflection Coefficient

We employ a rectangular coordinate system, and assume that the metallic body occupies the space to the left of the plane $x=0$. The potential energy of an electron at the point (x, y, z) is assumed to be given by the equations:

$$\begin{aligned} V(x, y, z) &= -V_0, \qquad x \leqq x_0, \\ &= -\epsilon^2/4x, \quad x \geqq x_0. \end{aligned}$$

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[1] L. Nordheim, Proc. Roy. Soc. London **A121**, 626–639 (1928). Unfortunately, Nordheim's article contains a number of typographical errors, which render the formulae unreliable. All formulae used in the present work have been derived independently.