

## Atomic Energy States for Excited Helium

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By means of Slater's method the total atomic energies for the excited states,  $1s^2$ ,  $1s2s$ ,  $1s2p$ ,  $2s^2$ ,  $2s2p$  and  $2p^2$  of helium have been calculated with the use of Hartree functions previously published.

### INTRODUCTION

SLATER'S method<sup>1</sup> of calculating total atomic energies has been applied to several atoms.<sup>2</sup> The success of these calculations suggested the desirability of determining theoretically the more important term values of the unobserved states of doubly excited helium, by using the results of self-consistent field calculations previously published.<sup>3</sup> The results are compared with experimental data as far as possible.

### METHOD OF CALCULATIONS

The method used in the present calculations was to consider the two-electron problem as a special case of the  $n$ -electron problem described by Slater, the procedure being similar to that used by Hartree and Black. Since no essentially new features were developed for this work, any description of the method will be omitted because the method is amply described in the two references given. However, there is one point to be noted; that is, if we omit the Hartree energy parameter from the definition of  $I(\alpha)$  as given by Hartree and Black, we can at once write the equality:

$$I(\alpha) = I(\beta) = F_0(\alpha\beta) = F_0(\beta\alpha)$$

for those states of two electron atoms or ions for which the Hartree functions are already orthogonal. In the present work this equality was used to check the numerical work by calculating a given quantity in two essentially different ways. Should the Hartree functions be changed by orthogonalization, it is necessary to use the method of treatment given by Hartree and Black. This was here necessary only for the  $(1s)(2s)^3S$  level.

In the actual calculations the full five place figures used in the Hartree calculations as well

as the values at the intervals omitted in the tabulation of references were used. These extra intervals enabled all integrals to be evaluated conveniently by direct quadratures rather than with the more elaborate method described by Macdougall for large  $k$ . The energy values were obtained from the integrals by using Eq. (8) of Hartree and Black in the manner outlined by Slater in the latter part of his article.

### RESULTS AND DISCUSSION

The results of these calculations are presented in Tables I and II. Table I gives the mean values of the various Slater integrals, Table II the energy values obtained from these, together with experimental values and the results of other computations where such are available. The fourth column of this table gives the values obtained if the smaller Hartree energy parameter is assumed to be equal to the first ionization potential of that state. The agreement of the calculated energy values with the experimental ones where such are available is satisfactory, there being a maximum deviation of 1.5 percent for  $(1s)^2^1S$  and a much smaller deviation for other levels. The agreement with calculations is very good, save for  $^1S$  states. An exception to this last statement is the discrepancy of the  $(2p)^2^3P$  level when com-

TABLE I. *The Slater functions for the several excited states (in units Rhc where  $R=109,737$ ).*

CONFIGURATION	ELECTRON	$\epsilon$	$I(n,l) = I(n'l') = F_0(nl, n'l')$	$G(nl, n'l')$
$(1s)^2$	1s	1.836	2.051	
$(2s)^2$	2s	0.4606	0.5189	
$(1s)(2s)^1S$	1s 2s	3.469 0.3068	0.5317	$G_0 = 0.0740$
$(1s)(2s)^3S$	1s 2s	3.469 0.3068	$I(1s) = 0.5317$ $I(2s) = 0.4911$ $F_0(1s2s) = 0.4764$	$G_0 = .0123$
$(1s)(2p)$	1s 2p	3.496 0.2522	0.5070	$G_1 = .0261$
$(2s)(2p)$	2s 2p	0.4195 0.4443	0.5403	$G_1 = .2942$
$(2p)^2$	2p	0.3861	0.5761 $F_2(2p, 2p) = 0.2675$	Same as $F_i(2p, 2p)$
$Be^{++}(1s)^2$	1s	11.344	4.558	

<sup>1</sup> J. C. Slater, Phys. Rev. **34**, 1293 (1929).

<sup>2</sup> See, for example, D. R. Hartree and M. M. Black, Proc. Roy. Soc. **A139**, 311 (1933); J. Macdougall, *ibid.* **A138**, 550 (1932).

<sup>3</sup> W. S. Wilson and R. B. Lindsay, Phys. Rev. **47**, 681 (1935).

TABLE II. *The atomic energies (units Rhc).*

CONFIGURATION	MULTIPLY	ENERGY	HARTREE	EXPERIMENTAL <sup>1</sup>	OTHER METHODS
(1s) <sup>2</sup>	<sup>1</sup> S	-5.723	-5.836	-5.807	-5.809 <sup>2</sup>
(2s) <sup>2</sup>	<sup>1</sup> S	-1.4400	-1.4605		-1.49 <sup>4</sup>
(1s)(2s)	<sup>1</sup> S	-4.232	-4.3062	-4.2919	-4.290 <sup>2</sup> -4.289 <sup>3</sup>
	<sup>3</sup> S	-4.334		-4.3499	-4.334 <sup>5</sup>
(1s)(2p)	<sup>1</sup> P	-4.246 <sup>+</sup>	-4.2517	-4.2473	-4.245 <sup>5</sup>
	<sup>3</sup> P	-4.264		-4.2660	-4.262 <sup>5</sup>
(2s)(2p)	<sup>1</sup> P	-1.3060	-1.4194		-1.301 <sup>4</sup> -1.308 <sup>6</sup>
	<sup>3</sup> P	-1.5022			-1.498 <sup>4</sup> -1.504 <sup>6</sup>
(2p) <sup>2</sup>	<sup>3</sup> P	-1.4018	-1.3860		-1.662 <sup>6</sup>
	<sup>1</sup> D	-1.3376			-1.320 <sup>6</sup>
	<sup>1</sup> S	-1.2323			
Be <sup>++</sup> (1s) <sup>2</sup>	<sup>1</sup> S	-27.246	-27.344	-27.312	-27.308 <sup>7</sup>

<sup>1</sup> Bacher and Goudsmit, *Atomic Energy States*.<sup>2</sup> E. A. Hylleraas, *Zeits. f. Physik* **65**, 209 (1930).<sup>3</sup> J. P. Vinti, *Phys. Rev.* **37**, 448 (1931).<sup>4</sup> F. G. Fender and J. P. Vinti, *Phys. Rev.* **46**, 78 (1934).<sup>5</sup> C. Eckart, *Phys. Rev.* **36**, 878 (1930).<sup>6</sup> Ta-You Wu, *Phys. Rev.* **46**, 239 (1934).<sup>7</sup> E. A. Hylleraas, *Zeits. f. Physik* **83**, 739 (1933).

pared with Wu's value. The value listed by him gives too large a multiplet separation.<sup>4</sup> Further as we will see later the present value is in line with some experimental predictions. The simple Hartree values in most cases gave very closely the center of gravity of the multiplet system as calculated by the Slater method for states having but two levels. The values for Be<sup>++</sup>(1s)<sup>2</sup><sup>1</sup>S<sup>5</sup> are included to show the trend for the more closely bound beryllium charge. The fractional error is smaller than for normal helium. Whether this is generally true for other levels of Be<sup>++</sup> cannot be stated at present.

The assignment of the newly calculated levels to experimental results is restricted because of the lack of data. If we calculate transitions from singly to doubly excited states using the known experimental values for the singly excited states, we may note the following results. Wilson and Lindsay's assignment of the transition (1s)<sup>2</sup><sup>1</sup>S - (2s)<sup>2</sup><sup>1</sup>S to the energy lost observed by Whiddington and Priestley seems to be further verified. It might be that the line is due to transitions from 1s<sup>2</sup><sup>1</sup>S to both (2s)<sup>2</sup><sup>1</sup>S and

<sup>4</sup> If we apply the rule that the <sup>3</sup>P-<sup>1</sup>D separation is three halves the <sup>1</sup>D-<sup>1</sup>S separation we find, using Wu's value for this separation, the <sup>1</sup>S level to lie at -0.777 Rhc, which indeed is unlikely since this is greater than the ionization potential of the ion He<sup>+(2p)</sup>.

<sup>5</sup> Based on the wave function recently published by D. R. Hartree, *Proc. Roy. Soc.* **A149**, 210 (1935).

TABLE III. *Observed lines from the helium spectrum.*

LINE	PREVIOUS ASSIGNMENT	PRESENT PAPER
357.507 <sup>1</sup> A	(1s)(2s) <sup>1</sup> S - (2s) <sup>2</sup> <sup>1</sup> S <sup>1</sup>	none
322.517 <sup>1</sup>	(1s)(2p) <sup>1</sup> P - (2p) <sup>2</sup> <sup>1</sup> D <sup>1</sup>	none
321.186 <sup>1</sup>	(1s)(2p) <sup>1</sup> P - (2p) <sup>2</sup> <sup>1</sup> S <sup>1</sup>	none
320.392 <sup>1</sup>	(1s)(2s) <sup>3</sup> S - (2p) <sup>2</sup> <sup>3</sup> P <sup>1</sup> (1s)(2s) <sup>3</sup> S - (2s)(2p) <sup>3</sup> P <sup>3</sup>	(1s)(2s) <sup>3</sup> S - (2s)(2p) <sup>3</sup> P
309.04 <sup>2</sup>	(1s)(2p) <sup>1</sup> P - (2s)(2p) <sup>1</sup> P <sup>3</sup>	(1s)(2s) <sup>3</sup> S - (2p) <sup>2</sup> <sup>3</sup> P

<sup>1</sup> P. G. Kruger, *Phys. Rev.* **36**, 855 (1930).<sup>2</sup> K. T. Compton and J. C. Boyce, *J. Frank. Inst.* **205**, 497 (1928).<sup>3</sup> F. G. Fender and J. P. Vinti, *Phys. Rev.* **46**, 78 (1934).

(2p)<sup>2</sup><sup>3</sup>P which lie very close together. This would also explain the indications of structure observed.

The results of a study of the observed lines in the helium spectrum and their previous assignments are given in Table III. In this respect the results of these calculations verify those given by Fender and Vinti with the one exception noted. Calculation of transitions between the doubly excited levels fail to fit any of the corona lines discussed by Rosenthal.<sup>6</sup> The values thus calculated might, however, be in error by an amount which would mask any agreement and too definite conclusions cannot be drawn from these transitions between doubly excited states.

It is believed that the error in the doubly excited states is much less than that in some of the singly excited states. This belief is founded on the excellent agreement of calculations for higher atoms by other workers with observed values which involve 2s and 2p electrons, as well as the agreement with other calculations noted in Table II. Further, should it prove that the absolute errors in these levels remain essentially the same for all levels of higher two electron ions as it does for Be<sup>++</sup>(1s)<sup>2</sup><sup>1</sup>S, this would introduce a great simplification in the calculation of the relative positions of many closely lying transitions for the helium atom. For in that case one need only compute the larger and more easily obtainable similar separations for higher ions and contract them suitably, thus rendering the error small. The Hartree-Slater method, though having the great drawback of involving considerable work seems on the whole to give quite tenable results for two electron atoms and ions.

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<sup>6</sup> A. H. Rosenthal, *Zeits. f. Astrophysik* **1**, 115 (1930).