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Effect on the Energy of Increased Flexibility in the Separable Factor of Hylleraas-Type Atomic Wave Functions from H^- to OVII*†

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A number of wave functions of the form $f(r_1)f(r_2)g(r_1,r_2,r_{12})$ are applied to the two-electron systems from H^- to OVII. Various analytic expressions for f and g are employed. The values of the various parameters in f and g are chosen to yield the minimum energy. The wave functions, the values of the parameters, and the minimum energies are tabulated. Twenty of the twenty-six functions tabulated are presented here for the first time. For five of the remaining six functions the values of the parameters and the energies have been recomputed. The energies obtained with these wave functions as well as with functions investigated by others are examined to ascertain what improvement in the energy results from considering other functional forms for $f(r)$ than the customary negative exponential. In the case of H^-, it is clear that certain types of flexibility in $f(r)$ can substantially improve the energies obtained with the simpler functions. For larger nuclear charge the improvement is definite but smaller.

The functions obtained are of interest in themselves. Several of them give the lowest energies for H^- so far found for various specific numbers of parameters. Beyond LiII, no simple wave functions involving the interelectron distance were previously available.

INTRODUCTION

IN recent years it has become apparent that if the accuracy of atomic wave functions is to be increased beyond the level represented by the self-consistent field with exchange and the superposition of a modest number of configurations, it will be necessary to examine the possibilities offered by generalizing the concept of superposition of configurations and by including the interelectron distances explicitly in the wave function.[1] In connection with the second of these two lines, it is desirable to examine the advantages offered by various forms for the trial wave functions in the case of two-electron systems. It seems best to undertake this examination before attempting to include the interelectron distances in the treatment of more complex systems.

The purpose of the present investigation is to ascertain what improvement can be obtained in the energies, and therefore by implication in the wave functions, of the ground states of the two-electron systems by the use of increased flexibility in the separable factor of Hylleraas-type wave functions, that is, in $f(r)$ in functions of the type

$$\psi=f(r_1)f(r_2)g(r_1,r_2,r_{12}). \qquad (1)$$

A by-product of this work has been a number of ground-state wave functions of various forms and for various atoms. Twenty new wave functions together with several which have been investigated by other workers, but are recomputed here, are presented in Table I.

TRIAL WAVE FUNCTIONS

Four forms have been employed for the f functions in Eq. (1) and two for the g function,

$$f=\begin{cases} e^{-Zr} & \text{(2a)}\\ e^{-Zr}(1+br^2) & \text{(2b)}\\ e^{-Zr}+ce^{-kZr} & \text{(2c)}\\ \dfrac{1}{r}\{e^{-Z(1-h/2Z)r}-e^{-Z(1+h/2Z)r}\} & \text{(2d)}\\ \dfrac{1}{r}\{e^{-(1-h/2)r}-e^{-(1+h/2)r}\}, & \text{(2d}'\text{)} \end{cases}$$

and

$$g=\begin{cases} 1+\alpha r_{12} & \text{(3A)}\\ 1+\alpha r_{12}+\beta(r_1-r_2)^2. & \text{(3B)} \end{cases}$$

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[1] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley and Sons, Inc., New York, 1957), Chap. 10; G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U. S. **38**, 154 (1952); L. Biermann and E. Trefftz, in the *Proceeding of the Rydberg Centennial Conference on Atomic Spectroscopy*, Kgl. Fysiograf. Sällskap. Handl. **65**, No. 21, 1 (1955); Trefftz, Schluter, Dettmar, and Jorgens, Z. Astrophys. **44**, 1 (1957); P. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); S. F. Boys, Phil. Trans. (London) **A246**, 463 (1954) and references therein; R. K. Nesbet and R. E. Watson, Phys. Rev. **110**, 1073 (1958); L. C. Green, in *Proceedings of the National Science Foundation Conference on Stellar Atmospheres*, Indiana University, 1954, M. H. Wrubel, editor; Green, Chandler, and Rush, Phys. Rev. **104**, 1593 (1956); Visbaraite, Shironas, Kavetskis, and Yutsis, Optika i Spektrosk. **1**, 277 (1956); Vizbaraite, Kavetskis, and Yutsis, Optika i Spektrosk. **1**, 282 (1956) and earlier papers in Optika i Spektrosk. and Zhur. eksptl. i teoret. Fiz. U. S. S. R. by A. P. Yutsis and his collaborators.

Hereinafter a particular trial wave function of the form given in Eq. (1) will be said, for example, to be of type *aB* if ψ has the form,

$$\psi=e^{-Zr_1}e^{-Zr_2}\{1+\alpha r_{12}+\beta(r_1-r_2)^2\}.$$

Trial wave functions of the types *aA* and *aB* were employed quite early in the history of quantum mechanics for H^-, HeI, and Li^+.[2,3] In the case of HeI, a polynomial with six terms was also employed by Hylleraas for g.[2] Later more complicated functions, including a g of ten terms, were used for H^-.[4–6]

More recently ground-state wave functions of very high accuracy have been obtained for a number of two-electron systems.[7–12] These functions have been of the type given in Eq. (1) where f is defined by Eq. (2a) and g contains from 9 to 39 terms. The particular interest of this last group of functions arises from the possibility which a comparison of the resulting energies with experimental values offers for testing the form assigned to the quantum electrodynamic correction terms.

In the present work, the objective is different. The purpose is rather to find out how much the energy is improved by using for $f(r)$ functions of greater flexibility than the simple exponential. To be able to measure the improvement, a number of functions of type *aA* and *aB* were computed.

The next problem is to decide what analytic forms, other than the single exponential, to try for $f(r)$. The forms given by Eqs. (2b) and (2c) were included because, when they have been employed in simple separable product-type wave functions, they have yielded functions and energies which are very similar to those obtained by the Hartree-Fock procedure.[13] For example, one may compute the integral of the square of the difference between the normalized Hartree-Fock numerical 1*s* functions and the functions given by Eqs. (2b) and (2c) where the parameters in these expressions have been chosen to yield the minimum energy when the wave function is of the simple product type. When the function defined by Eq. (2b) is employed, one finds for this integral 4×10^{-5} as the average value for four atoms. If Eq. (2c) is used, one obtains 3×10^{-6} as the average for the same four atoms. It therefore appears that $f(r)$ as defined by either Eq. (2b) or Eq. (2c), and particularly the latter, has the flexibility to represent 1*s* wave functions effectively. It is interesting to note that work, which has been pursued concurrently with the present undertaking, has shown that for the case of HeI, the $f(r)$ of Eqs. (2b) and (2c) can be even closer in form to the arbitrary numerical functions, $f(r)$, which minimize the energy when the wave function is written in the form given by Eq. (1) with $g(r_1,r_2,r_{12})$ set equal to $1+\alpha r_{12}$.[14] The function defined by Eq. (2c) has been employed by Löwdin.[15]

The form given by Eq. (2d) for the function, $f(r)$, is the solution of the radial part of the Schrödinger equation for a single particle moving in the short-range force field which yields the potential energy term, $2Zhe^{-hr}/(1-e^{-hr})$.[16] The Schrödinger equation with this potential energy term can be solved in closed form. This expression for the potential energy has the physically correct behavior as a function of r for both large and small r. Furthermore the potential energy of an electron at a distance r from a neutral and unperturbed hydrogen atom in its ground state is $2e^{-2r}(r+1)/r$. Since the expression first given and this latter expression are very similar in behavior, it appears that wave functions derived from the Schrödinger equation containing the first expression for the potential energy should be particularly suitable for the discussion of H^-. This expression approaches zero as $2Z/r$, and since for H^- the approach should be as $2/r$, it is reasonable to try the effectiveness of $f(r)$ defined by Eq. (2d) with Z set equal to one. This simpler one parameter form of $f(r)$ is listed separately in Eqs. (2) as Eq. (2d′).

RESULTS

Table I gives the values found for the energy when the various parameters in the trial wave functions are chosen by the minimum principle. Twenty of the twenty-six functions are presented here for the first time. For five of the remaining six functions the values of the parameters and energies have been recomputed. The first column of Table I gives a reference number for the particular atom and wave function. The second column contains the atom or ion to which the wave function is applied. The third and fourth columns give the functional forms for f and g, respectively. The next seven columns contain the values for the various parameters which give the lowest energy which was obtained. Some of these parameters may be given to more figures than are significant in view of the number of figures given in the energy. Since the value of the energy is at or near, the minimum, it is relatively insensitive to the precise values of the parameters. It seemed wiser to give the parameters to a number of figures which was clearly adequate than to spend the time necessary to establish in every case a range of variation in the energy for a range of variation in each

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[2] E. A. Hylleraas, Z. Physik **54**, 347 (1929).

[3] H. Bethe, Z. Physik **57**, 815 (1929).

[4] R. E. Williamson, Astrophys. J. **96**, 438 (1942).

[5] L. R. Henrich, Astrophys. J. **99**, 59 (1943).

[6] S. Chandrasekhar, Revs. Modern Phys. **16**, 301 (1944).

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[8] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[9] H. M. Schwartz, Phys. Rev. **103**, 110 (1956).

[10] E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).

[11] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[12] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).

[13] Green, Mulder, Lewis, and Woll, Phys. Rev. **93**, 757 (1954).

[14] To be published.

[15] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

[16] L. Rosenfeld, *Nuclear Forces* (North-Holland Publishing Company, Amsterdam, 1948), Chap. 5.

TABLE I. Values of the minimum energy and of the parameters yielding that energy for wave functions of the form $\psi=f(r_1)f(r_2)g(r_1,r_2,r_{12})$ for the two-electron systems from H^- to OVII. Energies are given in units of Rhc where R is the Rydberg constant for the atom or ion concerned.

				Parameters in f					Parameters in g		
No.		f	g	Z	b	c	k	h	α	β	E
1	H^-	$\frac{1}{r}\{e^{-(1-h/2)r}-e^{-(1+h/2)r}\}$	1					1.425			−0.97570
2	H^-	$\frac{1}{r}\{e^{-Z(1-h/2Z)r}-e^{-Z(1+h/2Z)r}\}$	1	0.9781				1.3693			−0.97577
3	H^-	e^{-Zr}	$1+\alpha r_{12}$	0.8257					0.4933		−1.01756[a]
4	H^-	$\frac{1}{r}\{e^{-(1-h/2)r}-e^{-(1+h/2)r}\}$	$1+\alpha r_{12}$					1.083	0.4926		−1.03924
5	H^-	$\frac{1}{r}\{e^{-Z(1-h/2Z)r}-e^{-Z(1+h/2Z)r}\}$	$1+\alpha r_{12}$	1.0713				1.2642	0.5401		−1.04051
6	H^-	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}$	1.1295		0.2309	0.4444		0.5526		−1.04097
7	H^-	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	0.768					0.31	0.12	−1.0506[b]
8	H^-	$\frac{1}{r}\{e^{-(1-h/2)r}-e^{-(1+h/2)r}\}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$					0.54	0.40	0.075	−1.0526
9	H^-	$\frac{1}{r}\{e^{-Z(1-h/2Z)r}-e^{-Z(1+h/2Z)r}\}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	0.8696				0.7183	0.3569	0.0968	−1.05376
10	H^-	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	0.8660		0.0775	0.5000		0.3746	0.1043	−1.05464
									Lowest computed value		−1.05545[c]
11	HeI	e^{-Zr}	$1+\alpha r_{12}$	1.8497					0.3658		−5.78224[d]
12	HeI	$e^{-Zr}(1+br^2)$	$1+\alpha r_{12}$	2.0302	0.12				0.3477		−5.79595
13	HeI	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}$	1.571		0.91	1.60		0.3507		−5.79613
14	HeI	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	1.816					0.3287	0.1368	−5.80486[d]
15	HeI	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	1.720		0.37	1.30		0.2971	0.1122	−5.80523
									Experimental value		−5.80756[e]
16	LiII	e^{-Zr}	$1+\alpha r_{12}$	2.857					0.3359		−14.53631[a]
17	LiII	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}$	2.605		0.44	1.52		0.3135		−14.54769
18	LiII	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	2.827					0.3379	0.2084	−14.55606[a]
19	LiII	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	2.796		0.046	1.55		0.2784	0.1456	−14.55626
									Experimental value		−14.5608 ±0.0002[e]
20	BeIII	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	3.832					0.3209	0.2449	−27.30652
21	BeIII	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	3.747		0.043	1.45		0.3111	0.1932	−27.30666
									Experimental value		−27.3144 ±0.0009[e]
22	BIV	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	4.834					0.3114	0.2845	−44.05669
23	BIV	$e^{-Zr}+ce^{-kZr}$	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	4.727		0.032	1.45		0.3116	0.2904	−44.05682
									Experimental value		−44.071 ±0.002[e]
24	CV	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	5.835					0.3052	0.3273	−64.80687
									Experimental value		−64.834 ±0.003[e]
25	NVI	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	6.836					0.3009	0.3693	−89.55691
									Experimental value		−89.605 ±0.005[e]
26	OVII	e^{-Zr}	$1+\alpha r_{12}+\beta(r_1-r_2)^2$	7.837					0.2977	0.4133	−118.3070
									Experimental value		−118.387 ±0.005[e]

[a] A function of this type was first computed by H. Bethe, Z. Physik **57**, 815 (1929).
[b] The quantities in this line have been computed from those given by H. Bethe, Z. Physik **57**, 815 (1929).
[c] E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956).
[d] A function of this type was first computed by E. A. Hylleraas, Z. Physik **54**, 347 (1929).
[e] Except for HeI, the experimental values of the ionization potentials are all taken from C. E. Moore, reference 17. The values of the various Rydberg constants are taken from the same source. The ionization potential for HeI was taken to be the unpublished value of Herzberg and Zbinden (quoted in reference 18).

parameter. The last column of Table I contains the value of the energy expressed in units of Rhc, where R is the Rydberg constant for the particular atom. Experimental values of the energies have been included in this column for comparison. In the case of H^-, it seemed wise to give the lowest calculated value of the energy rather than the experimental value since no experimental value of high accuracy is available. The lowest calculated value is that due to Hylleraas and Midtdal.[10] Except for HeI, the experimental values of the ionization potentials as well as their uncertainties are all taken from Moore.[17] The values of the various Rydberg constants are taken from the same source.

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[17] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

The ionization potential for HeI was taken as the unpublished value of Herzberg and Zbinden.[18]

Most of the calculations on which Table I is based were carried out on the IBM-650 Magnetic Drum Calculator of the Watson Scientific Computing Laboratory of the International Business Machines Corporation, Columbia University, New York, New York.

DISCUSSION

The first two wave functions in Table I have g set equal to one, that is, they are simple product type functions and do not contain any expression involving r_{12}. They are included here to show how effectively the calculated energies for H^- are lowered when $f(r)$ is defined by Eqs. (2d) or (2d′). The energies obtained with these one and two parameter functions are the lowest which have been found for H^- with any simple product of radial functions, so far as the present authors are aware. These energies may be compared with the values $-0.94531R_Hhc$, $-0.96534R_Hhc$, and $-0.97565R_Hhc$ obtained when the $f(r)$ in the simple product type wave function is defined by Eqs. (2a), (2b), and (2c), respectively.[13]

If one adds the three wave functions mentioned at the end of the preceding paragraph to the ten functions for H^- listed in Table I, and considers simultaneously Williamson's function, Henrich's function, Chandrasekhar's two functions, the function of Hart and Herzberg, and the function of Hylleraas and Midtdal, one has in all nineteen functions for H^- with which to deal. One may divide these functions into four groups depending on whether g has zero, one, two, or more parameters. If attention is directed to the first three groups, it is found that $f(r)$ defined by Eq. (2d′) is always more effective in lowering the energy than $f(r)$ defined by Eq. (2a). Thus, as mentioned above, function 1 gives a lower energy than $f(r)$ defined by Eq. (2a) when these expressions are used in a simple product-type wave function. Functions 3 and 4 both contain two parameters, one in f and one in g, but function 4, with $f(r)$ defined by Eq. (2d′) picks up 57% of the difference in energy between function 3 and the lowest calculated energy, the value of Hylleraas and Midtdal. Similarly functions 7 and 8 both are three-parameter functions, with two of these parameters in g, but function 8 accounts for 41% of the difference in energy between function 7 and the lowest calculated value.

As long as g has a fixed number of parameters, $f(r)$ defined by Eq. (2d) must yield energies which are lower than, or equal to, the energies obtained from $f(r)$ defined by Eq. (2d′) since the former function contains the latter as a special case.

Turning to $f(r)$ defined by Eq. (2c), one finds that as the number of parameters in g is zero, one, or two, the energies obtained lie, respectively, $0.00012R_Hhc$ above, $0.00046R_Hhc$ below, and $0.00088R_Hhc$ below the energies yielded by $f(r)$ defined by Eq. (2d).

Next one may consider the H^- wave functions according to the total number of parameters which they contain. As mentioned above, function 1 is the best one parameter function known for H^-. Function 4 is the best two-parameter function. Function 8 is the best three-parameter function. It gives an energy lower by $0.0006R_Hhc$ than Chandrasekhar's three-parameter function which consists of a symmetrized exponential and a linear factor in r_{12},[19] and Chandrasekhar's function in turn gives an energy lower by $0.0012R_Hhc$ than Bethe's function, function 7 in Table I. Function 9, a four parameter form with $f(r)$ defined by Eq. (2d), picks up 88% of the difference between the lowest calculated value of the energy and the value obtained from function 6, which is the only other four-parameter function in the group of nineteen considered. Indeed function 9 gives an energy $0.00084R_Hhc$ below Williamson's six-parameter function[4] and only $0.00005R_Hhc$ above Chandrasekhar's seven-parameter one.[6] Function 10 with five parameters gives a lower value of the energy than Chandrasekhar's seven-parameter function[6] and picks up 63% of the difference between this function and Henrich's eleven-parameter function.[5] The latter function yields $-1.05512R_Hhc$. Hart and Herzberg with twenty parameters have obtained an energy lower than Henrich's by $0.00017R_Hhc$.[12] Finally, lowest of all, is the value of Hylleraas and Midtdal obtained with twenty-four parameters.

If attention is now turned to H^-, HeI, and LiII, it appears that with only two exceptions among the functions which are considered here, the energy is lowered more by the addition to g of αr_{12} and then $\beta(r_1-r_2)^2$ than by increasing the number of different parameters in the purely radial factor which multiplies g. The two exceptions to this rule occur in the case of H^- for Chandrasekhar's symmetrized exponential, which lies somewhat outside the domain of the other radial factors considered here since it cannot be written in the form $f(r_1)f(r_2)$. Even for the symmetrized exponential, the rule breaks down only when this function is compared with the radial factor in which $f(r)$ is defined by Eq. (2a) and even then only for H^- and not for HeI or LiII.[20]

In the case of H^-, once g contains the two parameters mentioned above, further improvement in the energy is obtained most rapidly by adding to $f(r)$ first a second and then a third parameter such as to give it suitable flexibility. For the other atoms in Table I, flexibility in f is less important. As would be expected, with increasing dominance of the nuclear charge, the wave functions become more hydrogenic, and flexibility in $f(r)$ becomes increasingly less important as the nuclear

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[18] This value is quoted by S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[19] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[20] Green, Lewis, Mulder, Wyeth, and Woll, Phys. Rev. **93**, 273 (1954).

charge increases. Indeed the improvement in the energy for BeIII and BIV is roughly only $0.0001Rhc$ when $f(r)$ is defined by Eq. (2c) instead of Eq. (2a). The computations with the more complicated function have therefore been omitted for the last three elements in Table I. The difference in response of H^- and the heavier elements to increased flexibility in $f(r)$ is illustrated in the case of H^- and HeI by the comparison of functions 10 and 15 with the corresponding six-parameter functions in which $f(r)$ is defined by Eq. (2a). For H^-, function 10 gives an energy $0.00172R_{\mathrm{H}}hc$ lower than the six-parameter function; but for HeI, function 15 yields an energy $0.00125R_{\mathrm{He}}hc$ above the value obtained with six parameters.

The more general case than that discussed in the present paper in which $f(r)$ is taken to be the arbitrary function giving the lowest energy has been investigated in the case of H^- by Conwell[21] and in the case of HeI by Baber and Hassé.[22] The energy obtained by Conwell is not as low as that given by function 4 in Table I. The reason for this high result would appear to be that only one iteration was performed. The case of HeI has been recomputed by several of the present authors for $f(r)$ arbitrary and for $g(r_{12})$ arbitrary.[14] The accuracy of the early calculations of Baber and Hassé would appear to be somewhat less than they supposed.

Finally it is interesting to note also that in the case of function 13, $f(r)$ defined by Eq. (2c) is known to have the flexibility to represent the best arbitrary function with a root-mean-square difference of only 4 parts in 10^5.[14]

SUMMARY

Table I contains a number of wave functions of the form given by Eqs. (1), (2), and (3) which have been applied to the two-electron systems from H^- to OVII. Included in the table are the values of the parameters which minimize the energy obtained from these functions. The minimum energy itself is also given. Twenty of the functions in Table I are new, and for five others the values of the parameters and energies have been recomputed. Functions 1, 4, 8, 9, and 10 for H^-, all of which are presented here for the first time, are of special interest since they yield the lowest energies so far obtained for one-, two-, three-, four-, and five-parameter wave functions, respectively.

In the case of H^-, it is clear that the type of flexibility represented by Eqs. (2d′), (2d) and (2c) can substantially improve the energies obtained with the simpler functions. For larger nuclear charge, increases in the flexibility of $f(r)$ beyond the simple exponential, which has been customarily employed, yields definite improvements in the energy but smaller than for H^-.

In the case of H^-, HeI, and LiII, it appears that, with the partial exception of Chandrasekhar's symmetrized exponential in the case of H^-, the energy is lowered more by the addition to g of the terms αr_{12} and $\beta(r_1-r_2)^2$ than by increasing the number of different parameters in $f(r)$.

For the ions from BeIII to OVII, where until now no simple wave functions involving the interelectron distance were available, Table I gives the values of the parameters for seven functions.

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[21] E. Conwell, Phys. Rev. **74**, 277 (1948).

[22] T. D. H. Baber and H. R. Hassé, Proc. Cambridge Phil. Soc. **33**, 253 (1937).