Theor Chim Acta (1990) 78: 165–173

Theoretica Chimica Acta

Charge and radial correlations in helium and helium-like atoms

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Received March 9, 1990; received in revised form May 12, 1990/Accepted May 23, 1990

Summary. For two-electron atoms, the method of a variable exponent, which treats the orbital exponent (or effective nuclear charge) of an electron as an explicit function of the radial coordinate of the other electron, is studied. The method is shown to improve the energy and other electronic properties remarkably. An incorporation of the variable exponent into the Kellner approximation for He, for example, gives the energy −2.872 606 1 a.u., which is lower than the original Kellner energy by 0.024 949 8 a.u. and exceeds the Hartree–Fock limit energy by 0.010 926 1 a.u. The improvement due to the variable exponent originates from the inclusion of the charge and radial correlations. Applications of the method to the Eckart and Hylleraas approximations are also presented.

Key words: Variable exponent – Electron correlation – Helium and helium-like atoms

1. Introduction

In the fixed-nucleus approximation, helium and helium-like atoms can be treated as a two-body problem in the external Coulombic field due to the point nuclear charge $+Z$. Nevertheless, exact analytic solution of the Schrödinger equation is not possible due to the interelectronic repulsion term, $1/r_{12}$, in the Hamiltonian. Various approximate solutions have been hitherto studied, some of which attach importance to a clear physical picture of the system and some to a quantitative description of properties such as the electronic energy and other spectroscopic constants.

The simplest approximation is the pure independent-particle model which completely neglects the electron repulsion term in the Hamiltonian. The quantitative utility of this model is very limited. The Hartree–Fock method retains some of the simple features of the pure independent-particle model and yet introduces the electron interaction in a well-defined fashion. This method has the physical interpretation that each electron in the system moves in a potential field which is an average of that provided by the remaining electrons. Because of this simplicity, however, the Hartree–Fock method cannot describe the correlated motion of electrons (which is sometimes referred to as the Coulomb correlation

[1]): Due to their mutual repulsion, any pair of electrons tends to be somewhat further apart than the Hartree–Fock wave function indicates.

In the case of atoms, Pilar classified the electron correlation into three types [2]: (i) *charge correlation*, which refers to the screening effect of an inner electron upon outer electrons; (ii) *radial correlation*, which refers to the situation where one electron is close to the nucleus so the others tend to be farther away; and (iii) *angular correlation*, which refers to the tendency of two electrons to be on opposite sides of the nucleus. Pilar also discussed [2] how the charge correlation can be largely accounted for by scaling or self-consistent-field procedures. This may result in the adjustment of the effective nuclear charge or the average potential field.

In the present paper, we study the role of the effective nuclear charge (or orbital exponent) on the electron correlation in the two-electron atoms. We make the exponent of an electron an explicit function of the radial coordinate of the remaining electron. The procedure is referred to as the method of a variable exponent, and is applied to three well-known simple wave functions.

Kellner function [3]:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \exp[-\zeta(r_1 + r_2)], \tag{1a}$$

Eckart function [4–6]:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \exp(-\alpha r_1 - \beta r_2) + \exp(-\beta r_1 - \alpha r_2), \tag{1b}$$

Hylleraas function [7]:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1 + \kappa r_{12}) \exp[-\gamma(r_1 + r_2)], \tag{1c}$$

where $r_i = |\boldsymbol{r}_i|$ and $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. These three approximate wave functions are considered to include the charge, radial, and angular correlations, respectively, in the simplest manner. ζ, α, β, κ, and γ are variational parameters in the standard treatment, but, except for κ, they are assumed to be functions of the radius of an electron coordinate in this work. In the next section, the method of a variable exponent is presented for the Kellner function. The energy and other electronic properties are shown to be surprisingly improved; the energy of Eq. (1a) with a variable exponent exceeds the Hartree–Fock limit value and compares with the Eckart energy with constant exponents. The fact that the method of variable exponent accounts for both the charge and radial correlations is discussed. The same procedure is applied in Sect. 3 for the Eckart and Hylleraas functions. The energy lowering is found to be smaller than for the Kellner function, but the improvement is still meaningful. Atomic units are used throughout this paper.

2. The Kellner function with a variable exponent

The introduction of a variable exponent modifies the original Kellner function [Eq. (1a)] to

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \exp[-\zeta(r_2)r_1] \exp[-\zeta(r_1)r_2] \equiv F(r_1, r_2), \tag{2}$$

where the exponent (or effective nuclear charge) ζ for an electron is treated as an explicit function of the radial coordinate of the *other* electron. An analogous concept can be found in the distinguishable electron model [8] and in the perturbative treatment [9] of excited states. Our method is, however, essentially different from that of ten Hoor [10] who studied the effective nuclear charge of an electron as a function of *its own* radial coordinate.

The determination of an optimum functional form for $\zeta(r)$ is a variation problem. The energy expectation value E associated with the wave function (2) is given by

$$E[\zeta] = (T + U + W)/S, \tag{3a}$$

where

$$\begin{aligned} T &= -(1/2)\langle \Delta_1 + \Delta_2 \rangle \\ &= (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 [\zeta(r_2) + r_2\, d\zeta(r_1)/dr_1]^2 [F(r_1, r_2)]^2, \end{aligned} \tag{3b}$$

$$\begin{aligned} U &= -Z\langle 1/r_1 + 1/r_2 \rangle \\ &= -2Z(4\pi)^2 \int_0^\infty dr_1 r_1 \int_0^\infty dr_2 r_2^2 [F(r_1, r_2)]^2, \end{aligned} \tag{3c}$$

$$\begin{aligned} W &= -\langle 1/r_{12} \rangle \\ &= (4\pi)^2 \int_0^\infty dr_1 r_1 \int_0^{r_1} dr_2 r_2^2 [F(r_1, r_2)]^2 \\ &\quad + (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_{r_1}^\infty dr_2 r_2 [F(r_1, r_2)]^2, \end{aligned} \tag{3d}$$

$$\begin{aligned} S &= \langle 1 \rangle \\ &= (4\pi)^2 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 [F(r_1, r_2)]^2. \end{aligned} \tag{3e}$$

To optimize $\zeta(r)$ analytically from the energy functional $E[\zeta]$ does not seem easy. Therefore, we assume some function with adjustable parameters $a, b, c, \ldots$ for $\zeta(r)$. Then the problem reduces to the optimization of the parameters with respect to the energy $E[\zeta] = E(a, b, c, \ldots)$.

For a given $\zeta(r; a, b, c, \ldots)$, we have evaluated all the integrals appearing in Eq. (3) numerically using the Romberg method [11]. To facilitate convergence, an exponential transformation of the variable r, $r = \exp(x)$, has been introduced and the integral region $[0, \infty)$ has been approximated by $[e^{-16}, e^{+4}]$. This approximation has been shown to reproduce all the original results of the Kellner treatment. The Powell method of conjugate directions [12] has been employed in the search for optimum parameters.

We have examined various functions for $\zeta(r)$ based on a trial and error procedure where the number of parameters is limited to less than six for the computational reason. Several $\zeta(r)$ functions, which give a remarkable lowering in the energy, are summarized in Table 1. The best result in our present study is obtained by the function

$$\zeta(r) = a + \ln(b + cr + dr^2)\exp(-er). \tag{4}$$

For the helium atom, this function results the energy $-2.872\,606\,1$, which is lower than the Kellner energy $(-2.847\,656\,3)$ by $0.024\,949\,8$ and exceeds the Hartree–Fock limit energy [13, 14] $(-2.861\,680\,0)$ by $0.010\,926\,1$. This comparison clearly shows that a variable exponent method introduces an electron correlation effect. The energy improvement resulting from the variation of exponent is quite noticeable.

Table 1. Some $\zeta(r)$ functions for He which give significant improvement for the Kellner wave function

Functional form of $\zeta(r)$	Optimum parameters	Energy
a (=constant)	$a = 1.6875$	$-2.847\,656\,3^a$
$a + br^c \tanh(dr^e)$	$a = 1.3839$, $b = 0.3830$, $c = -0.6653$, $d = 0.6339$, $e = 1.5036$	$-2.872\,494\,6$
$a + br^c \ln(1 + dr^e)$	$a = 1.3856$, $b = 0.7681$, $c = -2.0482$, $d = 0.3195$, $e = 2.9136$	$-2.872\,539\,8$
$a + br^c \arctan(dr^e)$	$a = 1.3867$, $b = 0.1633$, $c = 0.9003$, $d = 3.5515$, $e = -1.9498$	$-2.872\,545\,7$
$(a + br^c)/(1 + dr^e)$	$a = 1.3944$, $b = 0.4777$, $c = 1.2070$, $d = 0.1720$, $e = 1.6590$	$-2.872\,598\,1$
$a + br^c \exp(-dr^e)$	$a = 1.3916$, $b = 0.2952$, $c = 1.0309$, $d = 0.3596$, $e = 1.4547$	$-2.872\,602\,4$
$(a + br + cr^2)/(1 + dr + er^2)$	$a = 1.3902$, $b = 0.2488$, $c = 0.1652$, $d = -0.0299$, $e = 0.1591$	$-2.872\,604\,3$
$a + (b + cr + dr^2) \exp(-er)$	$a = 1.3208$, $b = 0.0702$, $c = 0.3450$, $d = 0.2892$, $e = 0.9338$	$-2.872\,605\,2$
$a + \ln(b + cr + dr^2) \exp(-er)$	$a = 1.2572$, $b = 1.1432$, $c = 0.4056$, $d = 0.2691$, $e = 0.5628$	$-2.872\,606\,1$

[a] The original Kellner approximation

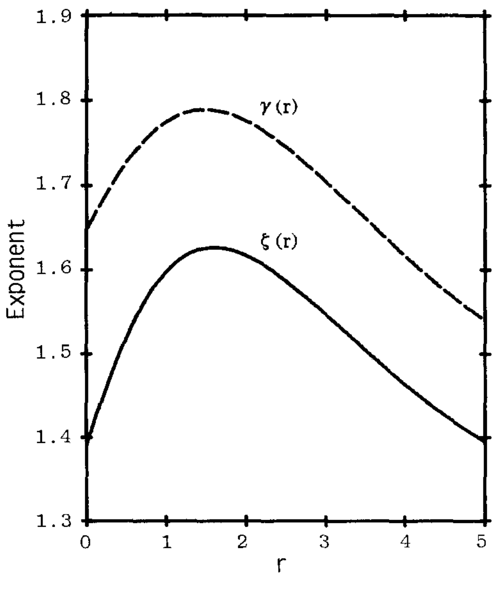

Fig. 1. Behaviors of the best exponent functions $\zeta(r)$ and $\gamma(r)$ for the Kellner and Hylleraas approximations of the helium atom. For the functional form, see Eqs. (4) and (9), and for the parameter values, see the last entry of Table 1 and Eq. (10)

The behavior of the $\zeta(r)$ function, Eq. (4), is shown in Fig. 1. When r increases, $\zeta(r)$ first increases, reaches a maximum value of 1.6265 at $r = 1.597$, and then decreases. The value of $\zeta(r)$ is considerably smaller than the original Kellner value 1.6875. To explain the nonmonotonic behavior of the $\zeta(r)$ function, we have to consider two effects. (a) The *Shielding effect* suggests that an inner electron feels a larger nuclear charge in an average sense than an outer electron.

For the wave function (2), we have $\zeta(r_2) > \zeta(r_1)$ if $r_1 < r_2$ and $\zeta(r_2) < \zeta(r_1)$ if $r_1 > r_2$. Using the notation $r_> = \max(r_1, r_2)$ and $r_< = \min(r_1, r_2)$, we can unify the above inequalities as $\zeta(r_>) > \zeta(r_<)$, which implies that $\zeta(r)$ is a monotonically increasing function of r. This behavior applies to the small r region of Fig. 1. (b) The *Interelectronic repulsion effect* means that the interelectronic repulsion is reduced if two electrons are separated. We can presume that the change in $\zeta(r)$ is smaller than that in r. Then for $r_1 \gg r_2$, Eq. (2) becomes $\Psi \simeq \exp[-\zeta(r_2)r_1]$. As r_2 increases, electron 1 favors a smaller exponent $\zeta(r_2)$ so that it can be away from electron 2. This effect is essentially equivalent to radial correlation and predicts a monotonically decreasing behavior for $\zeta(r)$, as is observed in the large r region of Fig. 1.

The actual behavior of the $\zeta(r)$ function (Fig. 1) can be considered as a compromise of these two opposite effects, and hence the method of a variable exponent may take both the charge and radial correlations into account. In fact, the energy of $-2.872\,606\,1$ for the Kellner function with variable exponent compares with the energy of $-2.875\,661\,3$ for the Eckart function [4–6], which includes the radial correlation. The present energy approximately corresponds to that of Srivastava and Bhaduri [15], who modified the Kellner function by assigning different exponents to $r_>$ and $r_<$.

The improvement due to the variable exponent is also found for properties other than the energy. In Table 2, the results of this work for He are summarized and compared with the original Kellner and with exact [16] values. The quantities C_{EN} and C_{EE} appearing in the table are, respectively, the electron-nuclear

Table 2. Various electronic properties for He resulting from the application of the variable exponent method to the Kellner wave function. Values in parentheses are errors in percent relative to the exact value

Property	Kellner	Kellner with variable exponent	Exact[a]
E	$-2.847\,656\,3$ $(+1.93)$	$-2.872\,606\,1$ $(+1.07)$	$-2.903\,724\,4$
V/T	$-2000\,000\,0$	$-1.999\,999\,6$	-2
$\langle r_1^{-2}\rangle$	5.695 31 (-5.35)	5.912 42 (-1.74)	6.017 41
$\langle r_1^{-1}\rangle$	1.687 50 (-0.05)	1.686 74 (-0.09)	1.688 32
$\langle r_1\rangle$	0.888 889 (-4.37)	0.920 933 (-0.92)	0.929 474
$\langle r_1^2\rangle$	1.053 50 (-11.73)	1.164 23 (-2.45)	1.193 48
$\langle r_1^3\rangle$	1.560 74 (-20.69)	1.881 62 (-4.39)	1.967 94
$\langle r_1^4\rangle$	2.774 64 (-30.17)	3.709 18 (-6.65)	3.973 53
$\langle\delta(\mathbf{r}_1)\rangle$	1.529 61 (-15.51)	1.711 67 (-5.45)	1.810 43
C_{EN}	1.687 50 (-15.63)	1.873 97 (-6.30)	2
$\langle r_{12}^{-2}\rangle$	1.898 44 $(+29.61)$	1.701 07 $(+16.13)$	1.464 77
$\langle r_{12}^{-1}\rangle$	1.054 69 $(+11.51)$	1.001 75 $(+5.91)$	0.945 818
$\langle r_{12}\rangle$	1.296 30 (-8.84)	1.361 71 (-4.24)	1.422 07
$\langle r_{12}^2$	2.107 00 (-16.27)	2.328 47 (-7.47)	2.516 44
$\langle r_{12}^3\rangle$	4.096 94 (-22.82)	4.785 06 (-9.85)	5.308 00
$\langle r_{12}^4\rangle$	9.248 82 (-28.75)	11.500 0 (-11.41)	12.981 2
$\langle\delta(\mathbf{r}_{12})\rangle$	0.191 202 $(+79.78)$	0.159 651 $(+50.12)$	0.106 352
C_{EE}	0	0	0.5

[a] [16]

cusp constant defined [16] by

$$C_{EN} = -(1/2) \lim_{r \to 0} [\varrho'(r)/\varrho(r)], \tag{5a}$$

where

$$\varrho(r) = (4\pi)^{-1} \int d\Omega \int d\boldsymbol{r}_2 \, |\Psi(\boldsymbol{r}, \boldsymbol{r}_2)|^2, \tag{5b}$$

$$\varrho'(r) = d\varrho(r)/dr, \tag{5c}$$

and the electron-electron cusp constant defined [16] by

$$C_{EE} = +(1/2) \lim_{r_{12} \to 0} [h'(r_{12})/h(r_{12})], \tag{6a}$$

where

$$h(r_{12}) = (4\pi)^{-1} \int d\Omega_{12} \int d\boldsymbol{R} \, |\Psi(\boldsymbol{R} + \boldsymbol{r}_{12}/2, \boldsymbol{R} - \boldsymbol{r}_{12}/2)|^2, \tag{6b}$$

$$h'(r_{12}) = dh(r_{12})/dr_{12}, \tag{6c}$$

with $\boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ and $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$. By the use of a variable exponent, the error for the one-electron moments $\langle r_1^n \rangle$ is reduced to approximately one fifth. The behavior of the wave function is also improved in the vicinity of the nucleus as can be seen from the values for $\langle \delta(\boldsymbol{r}_1) \rangle$ and C_{EN}. The improvement is also remarkable for the two-electron moments $\langle r_{12}^n \rangle$, the error being halved by the variable exponent. However, the values for $\langle \delta(\boldsymbol{r}_{12}) \rangle$ and C_{EE} suggest that the explicit inclusion of an r_{12} term is needed for an accurate description of the coalescent region of the two electrons.

The method of a variable exponent is also effective for other two-electron atoms. Table 3 summarizes the energetic results for several helium-like atoms. We find that the energy lowering is relatively constant when the nuclear charge Z is varied from 1 to 5. This is a reflection of the fact that the method of a variable exponent mainly reduces $\langle 1/r_{12} \rangle$ keeping $\langle 1/r_1 \rangle$ almost unchanged (see Table 2).

Table 3. Results of the variable exponent method applied to the Kellner approximation of several helium-like atoms

Atom	Optimum parameters[a]	Energy	Energy lowering[b]
H^-	$a = 0.3748$, $b = 1.0054$, $c = 0.0661$, $d = 0.0506$, $e = 0.2832$	−0.502 407 0	0.029 750 7
He	$a = 1.2572$, $b = 1.1432$, $c = 0.4056$, $d = 0.2691$, $e = 0.5628$	−2.872 606 1	0.024 949 8
Li^+	$a = 2.2107$, $b = 1.1985$, $c = 0.7662$, $d = 0.6329$, $e = 0.8266$	−7.246 702 4	0.024 046 1
Be^{2+}	$a = 3.1868$, $b = 1.2277$, $c = 1.1321$, $d = 1.1419$, $e = 1.0892$	−13.621 318 6	0.023 662 3
B^{3+}	$a = 4.1717$, $b = 1.2464$, $c = 1.5020$, $d = 1.7965$, $e = 1.3503$	−21.996 106 1	0.023 449 8

[a] See Eq. (4) for the $\zeta(r)$ function

[b] Energy lowering from the original Kellner approximation

3. Eckart and Hylleraas functions with variable exponent

We have also applied the variable exponent method to the Eckart wave function, Eq. (1b). Two modifications have been considered,

$$\Psi(r_1, r_2) = \exp[-\alpha(r_2)r_1 - \beta r_2] + \exp[-\beta r_1 - \alpha(r_1)r_2], \tag{7a}$$

$$\Psi(r_1, r_2) = \exp[-\alpha(r_2)r_1 - \beta(r_1)r_2] + \exp[-\beta(r_2)r_1 - \alpha(r_1)r_2], \tag{7b}$$

which respectively associate the energy functionals $E[\alpha]$ and $E[\alpha, \beta]$. The same functional form as Eq. (4) has been assumed for the exponents, but the parameters (six for Eq. (7a) and ten for Eq. (7b)) have been optimized independently. For the helium atom, the resultant energies are $-2.877\,003\,8$ for Eq. (7a) and $-2.877\,842\,9$ for Eq. (7b). The energy improvements relative to the Eckart energy ($-2.875\,661\,3$) are $0.001\,342\,5$ and $0.002\,181\,6$, respectively, which is less than 9% of the improvement found for the Kellner function. Since the Eckart function already involves the radial correlation, the method of a variable exponent appears to give little improvement to this function. This result may be better understood by comparison with the radial limit energy [17] which has the value $-2.879\,027\,8$. The Kellner and Eckart wave function cannot exceed this limit even when variable exponents are introduced. Since the original Eckart function is much closer to the radial limit than the Kellner function, the improvement by the variable exponent is very limited for the Eckart function.

For the Hylleraas function, Eq. (1c), however, the incorporation of variable exponent is again helpful. We modify Eq. (1c) as

$$\Psi(r_1, r_2) = (1 + \kappa r_{12}) \exp[-\gamma(r_2)r_1 - \gamma(r_1)r_2], \tag{8}$$

and optimize the exponent function $\gamma(r)$ and the constant parameter κ with respect to the energy $E[\gamma]$. After the examination of various functions with five parameters, we have found that for He the function of Eq. (4) gives the best result, that is,

$$\gamma(r) = a + \ln(b + cr + dr^2) \exp(-er), \tag{9}$$

with

$$a = 1.3466, \quad b = 1.3525, \quad c = 0.4274, \quad d = 0.2304, \quad e = 0.4893, \tag{10}$$

and $\kappa = 0.2944$. The associated energy is $-2.899\,641\,2$ which is lower than the original Hylleraas energy ($-2.891\,120\,7$) by $0.008\,520\,5$. This energy improvement is about 34% of that for the Kellner wave function, but is still significant compared to the result for the Eckart function. The exponent function $\gamma(r)$ is depicted in Fig. 1 for the helium atom. $\gamma(r)$ behaves similarly to $\zeta(r)$ with a peak of 1.7888 at $r = 1.477$. Therefore, the discussion given for $\zeta(r)$ applies to $\gamma(r)$ as well.

Table 4 presents the results of the variable exponent method for several one- and two-electron properties of the helium atom. We find that all the one-electron properties are improved by the method of a variable exponent, the error being reduced to approximately one third. A similar improvement is observed for the two-electron moments $\langle r_{12}^n \rangle$, especially for $n = 3$ and 4. However, the electron-electron cusp constant C_{EE} is worse than for the unmodified Hylleraas function. Since $C_{EE} = \kappa$ for the wave function (8), this corresponds to the reduction of the angular correlation effect upon the introduction of the variable exponent. The physical picture remains unclear for this result.

Table 4. Various electronic properties for He resulting from the application of the variable exponent method to the Hylleraas wave function. Values in parentheses are errors in percent relative to the exact value

Property	Hylleraas	Hylleraas with variable exponent	Exact[a]
E	−2.891 120 7 (+0.43)	−2.899 641 2 (+0.14)	−2.903 724 4
V/T	−2.000 000 0	−2.000 000 0	−2
$\langle r_1^{-2}\rangle$	5.813 63 (−3.39)	5.942 83 (−1.24)	6.017 41
$\langle r_1^{-1}\rangle$	1.689 13 (+0.05)	1.688 48 (+0.01)	1.688 32
$\langle r_1\rangle$	0.896 846 (−3.51)	0.918 104 (−1.22)	0.929 472
$\langle r_1^2\rangle$	1.076 79 (−9.78)	1.151 43 (−3.52)	1.193 48
$\langle r_1^3\rangle$	1.616 81 (−17.84)	1.835 31 (−6.74)	1.967 94
$\langle r_1^4\rangle$	2.908 55 (−26.80)	3.547 87 (−10.71)	3.973 53
$\langle \delta(\boldsymbol{r}_1)\rangle$	1.640 98 (−9.36)	1.744 62 (−3.64)	1.810 43
C_{EN}	1.849 68 (−7.52)	1.932 04 (−3.40)	2
$\langle r_{12}^{-2}\rangle$	1.552 70 (+6.00)	1.496 97 (+2.20)	1.464 77
$\langle r_{12}^{-1}\rangle$	0.974 297 (+3.0)	0.954 619 (+0.93)	0.945 818
$\langle r_{12}\rangle$	1.372 43 (−3.49)	1.406 70 (−1.08)	1.422 07
$\langle r_{12}^2\rangle$	2.327 30 (−7.52)	2.459 22 (−2.27)	2.516 44
$\langle r_{12}^3\rangle$	4.669 83 (−12.02)	5.126 01 (−3.43)	5.308 00
$\langle r_{12}^4\rangle$	10.784 4 (−16.92)	12.413 4 (−4.37)	12.981 2
$\langle \delta(\boldsymbol{r}_{12})\rangle$	0.119 912 (+12.75)	0.115 787 (+8.87)	0.106 352
C_{EE}	0.365 796 (−26.84)	0.294 440 (−41.11)	0.5

[a] [16]

Table 5. Results of the variable exponent method applied to the Hylleraas approximation of several helium-like atoms

Atom	Optimum parameters[a]	Energy	Energy lowering[b]
H^-	$a = 0.4634$, $b = 1.1290$, $c = 0.0971$, $d = 0.0461$, $e = 0.2661$; $\kappa = 0.3396$	−0.521 166 3	0.012 385 8
He	$a = 1.3466$, $b = 1.3525$, $c = 0.4274$, $d = 0.2304$, $e = 0.4893$; $\kappa = 0.2944$	−2.899 641 2	0.008 520 5
Li^+	$a = 2.3260$, $b = 1.3971$, $c = 0.7270$, $d = 0.5151$, $e = 0.7217$; $\kappa = 0.2780$	−7.275 906 1	0.007 748 9
Be^{2+}	$a = 3.3381$, $b = 1.3860$, $c = 0.9823$, $d = 0.8815$, $e = 0.9770$; $\kappa = 0.2697$	−13.651 496 8	0.007 444 7
B^{3+}	$a = 4.3553$, $b = 1.3650$, $c = 1.2131$, $d = 1.3286$, $e = 1.2464$; $\kappa = 0.2648$	−22.026 833 0	0.007 289 3

[a] See Eq. (9) for the $\gamma(r)$ function

[b] Energy lowering from the original Hylleraas approximation

The application of the method to several helium-like atoms is summarized in Table 5. The energy lowering is approximately independent of Z, since the variable exponent method is mainly concerned with the electron repulsion term not the nuclear attraction term in the energy expectation. The energies of this work may compare with those due to Lie et al. [18] and Wu [19]. These authors introduced radial correlation into the Hylleraas wave function by the adoption of different exponents for $r_>$ and $r_<$.

4. Conclusion

For two-electron atoms, we have studied the method of a variable exponent which treats the exponent of an electron as an explicit function of the radial coordinate of the other electron. Application of this method to simple wave functions has shown that the variable exponent gives a significant improvement when the radial correlation is absent in the original wave function. The variation of the orbital exponent has been found to improve both the one- and two-electron properties except for the electron-electron cusp constant, which seems to be connected with the angular correlation rather intimately.

Acknowledgments. The authors thank Miss H. Gotoh for her computational assistance. Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

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