

## A PERTURBATION TREATMENT OF THE MANY-ELECTRON PROBLEM II. THIRD ORDER SOLUTIONS FOR THE GROUND STATE OF HELIUMLIKE SYSTEMS

By K. JANKOWSKI

Institute of Physics, Nicholas Copernicus University, Toruń\*

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A perturbation treatment of many-electron systems, proposed before [1], is applied to the ground state of heliumlike ions  $H^-$ , He,  $Li^+$ . For a formulation based on two simple correlation factors energy values up to third order as well as expectation values of some operators up to second order are presented. The influence of poles appearing in the perturbation operator upon the rate of convergence of the perturbation series is briefly discussed.

### 1. Introduction

In a previous publication [1] we proposed a perturbation treatment of many-electron systems which makes essential use of the pole-less eigenvalue equation of the form introduced by Hirschfelder [2] and further modified by Jankowski and Woźnicki [3]. For an  $N$ -electron system when the wavefunction  $\Psi$  is presented in the form

$$\Psi = \chi^{(\alpha)} \Phi^{(\alpha)} = \chi^{(\alpha)} \prod_{i < j} \varphi^{(\alpha)}(r_{ij}) \quad (1)$$

this equation may be written as

$$H^{(\alpha)} \chi^{(\alpha)} = E^{(\alpha)} \chi^{(\alpha)} \quad (2)$$

with

$$H^{(\alpha)} = \sum_{i=1}^N H_i + \sum_{i>j=1}^N \omega^{(\alpha)}(r_{ij}) - \sum_{i=1}^N \sum_{k>j>1}^N f^{(\alpha)}(r_{ij}) f^{(\alpha)}(r_{ik}) \frac{r_{ij}}{r_{ij}} \frac{r_{ik}}{r_{ik}} + \\ + \sum_{i>j=1}^N f^{(\alpha)}(r_{ij}) \frac{r_{ij}}{r_{ij}} (\vec{V}_i - \vec{V}_j), \quad (3)$$

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\* Address: Instytut Fizyki, Uniwersytet M. Kopernika, Toruń, Grudziądzka 5, Polska

where

$$f^{(\alpha)}(u) = \varphi^{(\alpha)-1} \frac{d\varphi^{(\alpha)}}{du}.$$

It is evident that the properties of  $H^{(\alpha)}$  are determined by the correlation factor  $\varphi^{(\alpha)}(r_{12})$ . For certain classes of correlation factors discussed in [3]  $H^{(\alpha)}$  is the demanded pole-less operator.

In [1] arguments for the use of Eq. (2) as a starting point of a perturbation procedure as well as some numerical first order results for the ground state of the helium atom were presented.

The aim of the present paper is to obtain information concerning the convergence properties of the method. Therefore second- and third-order corrections to the energy for heliumlike ions were calculated in the case when the very simple correlation factors

$$\varphi^{(1)} = \exp(r_{12}/2) \quad (4a)$$

$$\varphi^{(2)} = 1 + r_{12}/2 \quad (4b)$$

were employed for the construction of the operator  $H^{(\alpha)}$ .

In order to get a non-energetical measure of the accuracy of the first- and second-order wavefunctions matrix elements of some one- and two-electron operators are also presented. It should be mentioned that operator  $H^{(\alpha)}$  is non-Hermitian [2], but it may be separated to a Hermitian zero-order Hamiltonian and a non-Hermitian perturbation operator. Our results may also be treated as a numerical test of the applicability of the perturbation method in that case.

Our calculations may also be of some importance from another point of view. It seems that they allow to obtain further insight into the problem of the influence of the electron-electron poles on the convergence of the perturbation series. We have already drawn on the ground of another perturbation scheme [4] some conclusions concerning that subject which is the matter of several opinions.

## 2. Details of the method

In the present perturbation scheme operator  $H^{(\alpha)}$  may be written in the form

$$H^{(\alpha)} = H_0 + V^{(\alpha)} \quad (5)$$

where  $H_0$  is the sum of one-electron Hamiltonians  $H_i$ . The operator  $V^{(\alpha)}$  is in the case of two-electron atomic problems given by the expression

$$V^{(\alpha)} = \omega^{(\alpha)}(r_{12}) + f^{(\alpha)}(r_{12}) \frac{r_{12}}{r_{12}} (\vec{V}_1 - \vec{V}_2), \quad (6)$$

Taking the familiar set of  $r_1, r_2, r_{12}$  variables Eq. (6) may be rewritten in the form

$$V^{(\alpha)} = \omega^{(\alpha)}(r_{12}) + f^{(\alpha)}(r_{12}) \left[ \frac{r_2^2 - r_1^2 - r_{12}^2}{2r_1 r_{12}} \frac{\partial}{\partial r_1} - \frac{r_1^2 - r_2^2 - r_{12}^2}{2r_2 r_{12}} \frac{\partial}{\partial r_2} \right] - 2 \frac{\partial}{\partial r_{12}} \quad (7)$$

with

$$\omega^{(1)} = \frac{1}{4}, \quad f^{(1)} = \frac{1}{2},$$

and

$$\omega^{(2)} = \frac{1}{2+r_{12}}, \quad f^{(2)} = \frac{1}{2+r_{12}}$$

for the factors (4a) and (4b) respectively. The functions  $\chi^{(\alpha)}$  and the eigenvalues of Eq. (2) may be expanded in the following way

$$\chi^{(\alpha)} = \chi_0 + \chi_1^{(\alpha)} + \chi_2^{(\alpha)} + \dots \quad (8a)$$

$$E^{(\alpha)} = E_0 + \varepsilon_1^{(\alpha)} + \varepsilon + \varepsilon_2^{(\alpha)} \dots \quad (8b)$$

The zero-order solutions are of the form

$$\chi_0 = \exp[-Z(r_1+r_2)], \quad \text{and} \quad E_0 = -Z^2 = \varepsilon_0.$$

The sums

$$E_i^{(\alpha)} = \sum_{k=0}^i \varepsilon_k^{(\alpha)}, \quad \text{and} \quad \chi_i^{(\alpha)} = \sum_{k=0}^i \chi_k^{(\alpha)}$$

are called the  $i$ -th order energy and  $i$ -th order eigenfunction respectively. The functions  $\chi_1^{(\alpha)}$  and  $\chi_2^{(\alpha)}$  are solutions of the well known equations

$$(H_0 - \varepsilon_0)\chi_1^{(\alpha)} + (V^{(\alpha)} - \varepsilon_1^{(\alpha)})\chi_0 = 0 \quad (9a)$$

$$(H_0 - \varepsilon_0)\chi_2^{(\alpha)} + (V^{(\alpha)} - \varepsilon_1^{(\alpha)})\chi_1^{(\alpha)} = \varepsilon_2^{(\alpha)}\chi_0 \quad (9b)$$

of the perturbation theory.

We will seek the approximation to  $\chi_1^{(\alpha)}$  and  $\chi_2^{(\alpha)}$  as expansions of the form

$$\chi_i^{(\alpha)} = \sum_{m,n,l} C_{mnl}^{i,\alpha} (r_1+r_2)^m (r_1-r_2)^{2n} r_{12}^l \exp[-Z(r_1+r_2)] \quad (10)$$

*i.e.* in the familiar Hylleraas basis. The coefficients are obtained as solutions of sets of linear equations received after the transformation of (9a-9b) to algebraic form in the Hylleraas basis. All the integrals were calculated by means of analytical expressions. In the case of Eq. (9b) the  $\chi_1^{(\alpha)}$  function obtained from (9a) was used. It should be mentioned that the commonly used Hylleraas variation-perturbation procedure is not applicable in our case because  $V^{(\alpha)}$  is not Hermitian in the ordinary sense. To get an estimate of the convergence of the approximate solution of (9) in the basis just mentioned, expansions of different length were used in our calculations. The energy corrections and expectation values obtained indicate that the convergence is good and our results for the 35 function basis set represent the true value to, at least, five decimal places.

The second- and third-order energy corrections were calculated by means of the well known formulas.

$$\varepsilon_1^{(\alpha)} = \langle \chi_0 | V^{(\alpha)} | \chi_0 \rangle, \quad (11a)$$

$$\varepsilon_2^{(\alpha)} = \langle \chi_0 | V^{(\alpha)} - \varepsilon_1^{(\alpha)} | \chi_1^{(\alpha)} \rangle, \quad (11b)$$

$$\varepsilon_3^{(\alpha)} = \langle \chi_0 | V^{(\alpha)} - \varepsilon_1^{(\alpha)} | \chi_2^{(\alpha)} \rangle - \varepsilon_2^{(\alpha)} \langle \chi_0 | \chi_1^{(\alpha)} \rangle. \quad (11c)$$

Bearing in mind Eq. (1) the eigenfunctions of the Schrödinger equation may be written in the form

$$\Psi = \sum_i \chi_i^{(\alpha)} \Phi^{(\alpha)} = \sum_i \Psi_i^{(\alpha)} \quad (12a)$$

where

$$\Psi_i^{(\alpha)} = \chi_i^{(\alpha)} \Phi^{(\alpha)}.$$

The functions  $\chi_i^{(\alpha)}$  have been modified to satisfy the normalization conditions

$$\langle \Psi_0^{(\alpha)} | \Psi_1^{(\alpha)} \rangle = 0 \quad (13a)$$

$$\langle \Psi_1^{(\alpha)} | \Psi_1^{(\alpha)} \rangle + 2 \langle \Psi_0^{(\alpha)} | \Psi_2^{(\alpha)} \rangle = 0 \quad (13b)$$

necessary in order to obtain a normalized total wavefunction (5).

All our calculations were performed on the GIER computer. In order to avoid the loss of accuracy the integrals

$$\int_0^{\infty} \frac{u^n}{1+\alpha u^n} e^{-2Zu} du = \sum_{k=1}^n (-1)^{k+1} \frac{(n-1)!}{\alpha^k (2Z)^{n-k+1}} + (-1)^n \alpha^{-n-1} e^{\frac{2Z}{\alpha}} E_1 \left( \frac{2Z}{\alpha} \right)$$

appearing in the expressions containing integrals with the perturbation operator  $V^{(\alpha)}$ , were calculated with double precision.

### 3. Numerical results and discussion

Energy corrections up to the third order obtained by means of Eq. (11), as well as first-, second-, and third-order energies defined above are presented in Table I for the case of the first three members of the helium isoelectronic series. Our calculations were performed for factors of the form (4a-4b) when expansions of the form (10) with 35 terms were used. The results are compared with the ones obtained by means of the so called hydrogenic scheme in which the whole interelectronic interaction potential was taken as a perturbation [5]. Also the results of the scheme with correlated zero-order functions (CZOF) formulated in [4] are given. The CZOF-scheme is another possible formulation of a pole-less perturbation method.

The results obtained for both correlation factors in the case of all  $Z$ -values indicate that a perturbation procedure may be used with success to approximate the solutions of the pole-less equation (2) with a non-Hermitian operator  $H^{(\alpha)}$ . When second- and third-order energies are considered the results obtained for the simple exponential factor  $\varphi^{(1)}$  are identical with the ones of the hydrogenic formulation. One may therefore come to conclusion that  $Z$ -dependence of the perturbation operator is similar here to the hydrogenic scheme. For the linear correlation factor  $\varphi^{(2)}$  the convergence is inferior for all members of the isoelectronic series. The  $Z$ -dependence of the perturbation operator is also different, although the main character is similar *i.e.* the perturbation decreases when  $Z$  increases. This diminution of the second-order energy correction, which for the previous formulation had a constant value is especially rapid.

In Table II, zero-, first- and second-order expectation values obtained when the cor-

TABLE I  
 Comparison of the energy convergence up to the third order of the perturbation procedure defined by the correlation factors  $\varphi^{(1)}$  and  $\varphi^{(2)}$ , Eq. (4), with the results of the hydrogenic scheme and the CZOF method<sup>b</sup>

	$H^- (E_{\text{exact}} = -0.52759)^a$			$\text{He} (E_{\text{exact}} = -2.90372)^a$			$\text{Li}^+ (E_{\text{exact}} = -7.27991)^a$					
	This work $\varphi^{(1)}$	This work $\varphi^{(2)}$	Hydro- genic scheme [5]	CZOF scheme [4]	This work $\varphi^{(1)}$	This work $\varphi^{(2)}$	Hydro- genic scheme [5]	CZOF scheme [4]	This work $\varphi^{(1)}$	This work $\varphi^{(2)}$	Hydro- genic scheme [5]	CZOF scheme [4]
$\varepsilon_1$	0.375	0.55614	0.625	0.56733	1.0	1.13621	1.25	1.19106	1.625	1.73397	1.875	1.81666
$\varepsilon_2$	0.09235	-0.06136	-0.15767	-0.02430	0.09235	-0.02792	-0.15767	-0.02983	0.09235	-0.00636	-0.15767	-0.03265
$\varepsilon_3$	0.00865	-0.01566	0.00870	-0.00517	0.00432	-0.00989	0.00435	-0.00217	0.00288	-0.00645	0.00290	-0.00131
$E_0$	-1.0	-1.0	-1.0	-1.0625	-4.0	-4.0	-4.0	-4.0625	-9.0	-9.0	-9.0	-9.0625
$E_1$	-0.625	-0.44386	-0.375	-0.49517	-3.0	-2.86379	-2.75	-2.87144	-7.375	-7.26603	-7.125	-7.24584
$E_2$	-0.53265	-0.50522	-0.53267	-0.51947	-2.90765	-2.89171	-2.90767	-2.90127	-7.28265	-7.27239	-7.28267	-7.27849
$E_3$	-0.52400	-0.52088	-0.52397	-0.52463	-2.90332	-2.90160	-2.90332	-2.90344	-7.27977	-7.27884	-7.27977	-7.27981
Error	0.00359	0.00671	0.00362	0.00296	0.00040	0.00212	0.00040	0.00028	0.00014	0.00170	0.00014	0.00010

<sup>a</sup> "Exact" Pekeris results.

<sup>b</sup> See Ref. [4].

TABLE II  
Zero-, first- and second-order expectation values of some operators for the perturbation procedure defined by the correlation factor  $\varphi^{(2)}=1+0.5r_{12}$ . Results of the hydrogenic scheme (in parentheses) are given for comparison

Operator	H <sup>-</sup>			He			Li <sup>+</sup>			
	$\langle \Omega \rangle_0$	$\langle \Omega \rangle_1$	$\langle \Omega \rangle_2$	$\langle \Omega \rangle_0$	$\langle \Omega \rangle_1$	$\langle \Omega \rangle_2$	$\langle \Omega \rangle_0$	$\langle \Omega \rangle_1$	$\langle \Omega \rangle_2$	"Exact"
$r_{12}^{-1}$	0.46333 (0.625)	0.39284 (0.30967)	0.37156 (0.33576)	1.02215 (1.25)	0.97567 (0.93467)	0.96312 (0.94772)	1.61264 (1.875)	1.58302 (1.55967)	1.57481 (1.56837)	1.56722 <sup>a</sup>
$r_{12}$	2.79667 (2.18775)	3.24865 (3.21719)	3.45863 (3.64153)	1.29984 (1.09375)	1.36794 (1.35117)	1.33934 (1.40421)	0.83242 (0.72917)	0.85158 (0.84358)	0.85692 (0.85929)	0.86231 <sup>a</sup>
$r_1^{-1}$	0.85333 (1.0)	0.75525 (0.6875)	0.73290 (0.6875)	1.79747 (2.0)	1.72191 (1.6875)	1.70779 (1.6875)	2.76923 (3.0)	2.70779 (2.6875)	2.69784 (2.6875)	2.68792 <sup>a</sup>
$r_1$	1.77667 (1.5)	2.05981 (2.0625)	2.18130 (2.29529)	0.84335 (0.75)	0.89509 (0.89062)	0.90834 (0.91972)	0.54670 (0.5)	0.56504 (0.5625)	0.56854 (0.57112)	0.57277 <sup>a</sup>
$\delta(r_{12})$	0.00849 (0.03979)	0.00473 (-0.03754)	0.00406 (0.02101)	0.12894 (0.31831)	0.11544 (0.00900)	0.11148 (0.12609)	0.56666 (1.07430)	0.54768 (0.37832)	0.54055 (0.55399)	0.53378 <sup>b</sup>
$\delta(r_1)$	0.22069 (0.31831)	0.17621 (0.10580)	0.17040 (0.16371)	1.99850 (2.54648)	1.85662 (1.6962)	1.83183 (1.80883)	7.17771 (6.59437)	6.91713 (6.68178)	6.87098 (6.85070)	6.85197 <sup>b</sup>

<sup>a</sup> Scherr-Knight sixth-order results [6].

<sup>b</sup> Results of Pekeris [7-8].

relation factor  $\varphi^{(2)}$  has been used are presented and compared with their counterparts of the hydrogenic scheme. Although zero-order results of our method are for all  $Z$  values better than in the hydrogenic scheme, beginning with the first-order expectation values, nearly all results of the later scheme are closer to the "exact" ones than in our procedure. The only exception is for the case of the  $\delta(r_{12})$  operator for which the results of the standard method are rather bad. A common feature of all results in the Table is the decrease of the relative error when  $Z$  increases.

#### 4. Conclusions

All the calculations in the case of ground state of the members of the isoelectronic series presented here confirm the ability of the perturbation method to approximate with success the eigenvalues and eigenfunctions of the non-Hermitian equation (2). The convergence of our treatment is comparable to that of the standard hydrogenic scheme. It should be mentioned that the factors considered here have been chosen only for the reason of their simplicity. Keeping in mind, that the convergence of our method depends on the choice of the correlation factor it seems to be tempting to look for other factors which accelerate the convergence and thus to obtain an effective method for treating many-electron systems. Our results confirm the conclusions of our previous paper [4] as to what concerns the influence of the Coulomb poles of the perturbation operator on the rate of convergence of the perturbation series. Comparison of the present results obtained with a pole-less perturbation operator  $V^{(a)}$  with those of the hydrogenic scheme, for which electron-electron poles are present in the perturbation, indicate that the presence of poles is not the reason for the relatively slow convergence of the perturbation method.

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