

# A Perturbation Treatment for Two-Electron Atomic Systems with Correlation in Zero Order

K. JANKOWSKI

Department of Experimental Physics, The Nicholas Copernicus University, Toruń, Poland

Received December 27, 1968

A modification of Pluinage's method which allows for the use of a great class of Coulomb-poles-eliminating correlation factors is proposed. This factors are better suited for the description of electron-correlation effects by means of perturbation procedures than the ones used hitherto.

## Introduction

One of the main difficulties for describing many-electronic systems is to find a suitable method to account for electron correlation effects. So far the best results were obtained on the ground of straight variational methods based on the minimization of the energy functional in various, often very elaborated, classes of trial functions. But there are also many workers that make attempts to describe electron correlation on the ground of the perturbation method. Some of them try to do this choosing such a partitioning of the Hamiltonian for which the perturbation is expected to be small by a formulation, which already in the zero-order problem accounts, to some extent, for correlation effects. This direction of attack represents, first of all, the methods that may be regarded as the extensions of the method proposed by Pluinage [1]. A review of papers representative for this direction has been given by Lebeda and Schrader [2] in their recent paper. A substantial different type of perturbation treatment with correlation in zero-order was formulated by the present author in 1967 [3] and further work in that direction is now in progress.

In the present paper we should like to propose a modification of Pluinage's method which allows for the use of a great class of Coulomb-poles eliminating correlation factors, which are better suited for the description of correlation effects by means of perturbation procedures than the ones used hitherto. The method presented here may be considered as a generalization of the very recently published method of Lebeda and Schrader [2]. It seems that if appropriate correlation factors were used it would be possible to obtain a fast converging perturbation formulation of the many-electron problem. Some preliminary numerical results indicate that progress may be really obtained. Further numerical work is in progress, and the results will be published in the nearest future [4].

The method proposed here may also be of some importance from another point of view. It seems that it allows to obtain some insight into the problem of the influence of the electron-electron poles on the convergence of the perturbation series which is the matter of several, as yet unproved, opinions.

### A. Formulation of the Method

Although a more general formulation is possible we will in the present note confine ourselves to two-electron atomic systems for which the formulation of the method is especially simple.

The Hamiltonian of the system may be written as

$$\begin{aligned}
 H = & -\frac{1}{2} \left( \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) - \frac{Z}{r_1} - \frac{1}{2} \left( \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right) \\
 & - \frac{Z}{r_2} - \left( \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) + \frac{1}{r_{12}} \\
 & - \frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}}.
 \end{aligned} \tag{1}$$

Let us take as the zero-order Hamiltonian  $H_0$  that Hermitian operator for which the function

$$\Psi_0^{(\alpha)} = \exp[-Z(r_1 + r_2)] \varphi^{(\alpha)}(r_{12}) \tag{2}$$

(where  $r_1, r_2$  and  $r_{12}$  are the well known variables), is the eigenfunction. Its construction may be performed *e.g.* by means of the so-called Sternheimer potential method [5]. After some simple mathematical operations one obtains

$$H_0^{(\alpha)} = H - \omega^{(\alpha)} - W^{(\alpha)}, \tag{3}$$

where

$$\omega^{(\alpha)} = \frac{1}{r_{12}} - \frac{2}{r_{12}} \frac{1}{\varphi^{(\alpha)}} \frac{d}{dr_{12}} \varphi^{(\alpha)} - \frac{1}{\varphi^{(\alpha)}} \frac{d^2}{dr_{12}^2} \varphi^{(\alpha)}, \tag{4}$$

$$W^{(\alpha)} = Z \frac{1}{\varphi^{(\alpha)}} \left[ \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \right] \frac{d}{dr_{12}} \varphi^{(\alpha)}. \tag{5}$$

It is now possible to formulate a perturbation procedure using the partitioning

$$H = H_0^{(\alpha)} + V^{(\alpha)}, \tag{6}$$

where

$$V^{(\alpha)} = \omega^{(\alpha)} + W^{(\alpha)}. \tag{7}$$

It is obvious that in that formulation both the zero-order Hamiltonian as well as the perturbation  $V^{(\alpha)}$  are Hermitian operators. We may hence use the well known Hylleraas's variational-perturbation theory and seek the corrections to the wavefunction in a class of trial functions by the minimization procedure described elsewhere [6], *e.g.* the first-order correction  $\Psi_1^{(\alpha)}$  we may obtain minimizing the functional

$$E_2[\Psi_1^{(\alpha)}] = \langle \Psi_1^{(\alpha)} | H_0^{(\alpha)} - E_0^{(\alpha)} | \Psi_1^{(\alpha)} \rangle + 2 \langle \Psi_1^{(\alpha)} | V^{(\alpha)} - E_1^{(\alpha)} | \Psi_0^{(\alpha)} \rangle, \tag{8}$$

where  $E_0^{(\alpha)}$  and  $E_1^{(\alpha)}$  are the zero- and first-order energies *i.e.*

$$E_1^{(\alpha)} = \langle \Psi_0^{(\alpha)} | V^{(\alpha)} | \Psi_0^{(\alpha)} \rangle / \langle \Psi_0^{(\alpha)} | \Psi_0^{(\alpha)} \rangle.$$

If we seek the first-order function in the form

$$\Psi_1^{(\alpha)} = F_1^{(\alpha)}(r_1, r_2, r_{12}) \Psi_0^{(\alpha)} \tag{9}$$

the integrals appearing in (8) become very simple, because the functions appearing in (4) and (5) in the denominator will be reduced with the correlation factor in (2).

It is obvious that by different choices of  $\varphi^{(\alpha)}$  it is possible to reduce the size of the perturbation and try in this way to improve the perturbation calculation. But we are now interested in a special class of correlation factors. Some years ago the present author together with Woźnicki [7] showed that when  $\omega^{(\alpha)}(r_{12})$  is a pole-less function it is possible to remove the singularities from the Schrödinger equation with the aid of correlation factors obtained as the solutions of (4) in a way being a generalization of the Hirschfelder method [8]. In [7] we presented some simple correlation factors useful in atomic and molecular calculations. Our results may also be applied to the present perturbation calculation. When  $\omega^{(\alpha)}$  is a pole-less function the whole perturbation  $V^{(\alpha)}$  contains no poles and therefore one may use the formalism to the numerical analysis of the influence of electron-electron poles on the convergence of the perturbation series. Taking into consideration that the solutions of (4) with  $\omega^{(\alpha)}(r_{12})$  under the interest allow the function (2) to fulfill the well known cusp conditions, and because in most cases (2) is considerable better than the Hartree-Fock function (from the point of view of the energy criterion), it is obvious that our  $\Psi_0^{(\alpha)}$  is a well adopted function to describe correlation effects.

In [7] we have shown that extraordinary simple functions may be found for which (4) is soluble. The most simple are, of course, the constants

$$\omega^{(n)} = \frac{-1}{4(n+1)^2}, \quad n = 0, 1, 2, \dots \tag{10}$$

for which the correlation factors get the form

$$\varphi^{(0)}(u) = \exp(u/2), \tag{11a}$$

$$\varphi^{(1)}(u) = (1 + \frac{1}{4}u) \exp(u/4), \tag{11b}$$

$$\varphi^{(2)}(u) = (1 + \frac{1}{3}u + \frac{1}{34}u^2) \exp(u/6) \tag{11c}$$

$$\dots\dots\dots$$

$$\varphi^{(\infty)}(u) = \sum_{m=0}^{\infty} \frac{u^m}{m!(m+1)!}. \tag{11d}$$

The last function is the often used factor of Walsh and Borowitz [9]. A simple form of  $\omega^{(\alpha)}$  may also be obtained when the important factor  $\varphi^H(r_{12}) = 1 + 0.5 r_{12}$  is used. We get then  $\omega^H(r_{12}) = 1/(2 + r_{12})$ .

When  $\omega^{(\alpha)}$  is of the form (10) it may be separated from the perturbation and included in the zero-order energy. Then

$$E_0^{(\alpha)} \Rightarrow E_0^{(\alpha)} + \omega^{(\alpha)}, \tag{12}$$

and the perturbation simplifies to the form

$$V^{(\alpha)} = W^{(\alpha)}. \tag{13}$$

When the factor (11 a) is used  $W^{(\alpha)}$  gets the form

$$W^{(0)} = \frac{Z}{2} \left[ \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \right], \tag{14}$$

which leads to the zero-order Hamiltonian obtained by Lebeda and Schrader [2].

### B. Preliminary Numerical Results and Discussion

In order to see how the method outlined in A) works we calculated the first-order correction to the wavefunction as well as the energy to third order in the case of the ground state of the helium atom basing on the factor (11b) which in the series (11) in the next neighbour of the factor used by Lebeda and Schrader. The choice is determined only by the fact that the function (2) obtained with the help of this factor is better than the Hartree-Fock one, when the energy criterion

Table 1. *Perturbation energies to the third order obtained for the helium ground state (in a.u.)*

	This work	Lebeda-Schrader [2]	Conventional HSKM-method <sup>a</sup>
$E_0$	-4.0625	-4.25	-4
$E_1$	1.19106	1.39450	1.25
$E_0 + E_1$	-2.87144	-2.85550	-2.75
$E_2$	-0.02980	-0.04644	-0.15767
$E_0 + E_1 + E_2$	-2.90123	-2.90194	-2.90767
$E_3$	-0.00217	-0.00137	0.00435
$E_0 + E_1 + E_2 + E_3$	-2.90341	-2.90331	-2.90332
error <sup>b</sup>	(0.00031)	(0.00041)	(0.00040)

<sup>a</sup> The results of the conventional Hylleraas-Scherr-Knight-Midtal method.

<sup>b</sup> Compared with the "exact" Pekeris [13] result.

is concerned, while the function with (11a) is not. We hope that there exist the pole-eliminating correlation factors which are from the point of view of convergence properties still better suited for the construction of the zero-order problem than the one just employed. An analysis in that direction is now in progress.

When (11b) is used we obtain

$$\Psi_0^{(1)} = \{\exp[-2Z(r_1 + r_2)]\}(1 + \frac{1}{4}r_{12}) \exp(r_{12}/4) \quad (15)$$

and

$$E_0^{(1)} = -4.0625 \text{ a.u.} \quad (16)$$

The  $F$  function from (9) has get the form

$$F^{(1)}(s, t, u) = \sum_{k,l,m} c_{klm} s^k t^{2l} u^m, \quad (17)$$

where  $s, t, u$  are the well known Hylleraas coordinates. In the minimization procedure we used 20 and 25 termes in (17) but the results, with the accuracy indicated in the Tables, were the same.

In Table 1 we present the perturbation energies to the third order. From the Table 1 it is evident that with our choice of  $\varphi^{(2)}$  it is possible to obtain the third order energies,  $E_0 + E_1 + E_2 + E_3$ , not only better than the one calculated by Lebeda and Schrader but also given by the conventional Hylleraas-Scherr-Knight-Midtal (HSKM) method. This is worth noticing because, to the knowledge of the author, all existing perturbation calculations for the He ground state disclose the same property that, even when the first- and second-order energies were better than in the conventional case, the third-order ones were worse see *e.g.* the results given in [10]–[12].

In Table 2 the first-order expectation values of some one- and two-electron operators  $\Omega$  are presented. The elements  $\langle \Omega \rangle_a$  are calculated by means of the well known first-order formula

$$\langle \Omega \rangle_a = \langle \Psi_0^{(a)} | \Omega | \Psi_0^{(a)} \rangle + 2 \langle \Psi_0^{(a)} | \Omega | \Psi_1^{(a)} \rangle. \tag{18}$$

To achieve the possibility of comparison with the results of Lebeda and Schrader we used also the formula

$$\langle \Omega \rangle_1 = \langle \Psi | \Omega | \Psi \rangle / \langle \Psi | \Psi \rangle, \tag{19}$$

where

$$\Psi = \Psi_0^{(a)} + \tilde{\Psi}_1^{(a)} \tag{20}$$

and  $\tilde{\Psi}_1^{(a)}$  is obtained by the orthogonalization of  $\Psi_1^{(a)}$  to  $\Psi_0^{(a)}$ . The comparison of our results with their counterparts given in [2] shows that a considerable improvement

Table 2. First-order expectation values of some one-and two-electron operators

$\Omega$	$\langle \Omega \rangle_a^a$	This work <sup>b</sup> $\langle \Omega \rangle_1$	$L-S$ <sup>c</sup> $\langle \Omega \rangle_1$	HNSM <sup>d</sup> $\langle \Omega \rangle_a$	Exact <sup>e</sup>
$r_{12}^{-1}$	0.9540	0.9524	0.9558	0.9347	0.9458
$r_{12}$	1.4075	1.4105	1.4027	1.3512	1.4221
$r_1^{-1}$	1.7022	1.6982	1.7051	1.6875	1.6883
$r_1$	0.9174	0.9201	0.9158	0.8962	0.9295
$\delta(r_{12})$	0.1113	0.1109	0.1101	0.0090	0.1063
$\delta(r_1)$	1.8366	1.8263	1.8389	1.6962	1.8104

<sup>a</sup> See Eq. (18).

<sup>b</sup> See Eq. (19).

<sup>c</sup> Results of Lebeda and Schrader-obtained with formula (19).

<sup>d</sup> Ref. [13], calculated with formula (18).

<sup>e</sup> Ref. [14].

may be obtained. This is of course still more evident when one takes under consideration the results of the HSKM method, also given in the table.

The results presented in Tables 1 and 2 allow to hope that by a proper choice of the correlation factor a perturbation treatment of the many-electron problem may be formulated and it will have better convergence properties for the energy as well as for the expectation values of other properties.

*Acknowledgement.* The author would like to thank Professor D. M. Schrader from the Marquette University (USA) for sending him a preprint of his paper prior to publication. The author is also indebted to Dr. J. Wasilewski whose numerous advices allowed him to perform the calculations on the GIER computer.

### References

1. Pluvinae, P.: Ann. Physique (Paris) **12**, 101 (1950).
2. Lebeda, C. F., and D. M. Schrader: J. chem. Physics **49**, 2547 (1968).
3. Jankowski, K.: Acta physica polon. **31**, 421 (1967).
4. — In course of publication in Acta physica polon.
5. Hirschfelder, J. D., W. Byers-Brown, and S. T. Epstein: Advances in quantum chemistry, Vol. I, p. 261. New York: Academic Press 1964.
6. Scherr, Ch. W., and R. E. Knight: Rev. mod. Physics **35**, 436 (1963).

7. Jankowski, K., and W. Woźnicki: *Bull. Acad. polon. Sci., Sér. Math. Astron. Phys.* **13**, 249 (1965).
8. Hirschfelder, J. O.: *J. chem. Physics* **39**, 3145 (1963).
9. Walsh, P., and S. Borowitz: *Physic. Rev.* **115**, 1206 (1959).
10. Weiss, A. W., and J. B. Martin: *Physic. Rev.* **132**, 2118 (1963).
11. Lebeda, C. F., and D. M. Schrader: *Chem. Physic. Lett.* **2**, 91 (1968).
12. Remarker, D. E., G. L. Hagnauer, R. E. Carlson, R. F. Gaetano, H. Crain, and D. M. Schrader: *Int. J. Quant. Chem.* **2**, 509 (1968).
13. Knight, R. E., and C. W. Scherr: *Physic. Rev.* **128**, 2675 (1962).
14. Pekeris, C. L.: *Physic. Rev.* **115**, 1216 (1959).

Dr. K. Jankowski  
Katedra Fizyki Doświadczalnej  
Uniwersytet M. Kopernika  
Toruń 1, ul. Grudziądzka 5, Poland