

Montana Tech Library

## Digital Commons @ Montana Tech

---

Center for Advanced Mineral and Metallurgical  
Processing (CAMP)

Faculty Scholarship

---

6-12-1967

### Analytic Power-Series Solution of the Schrödinger Equation for the Helium Atom

W. Byers Brown

*University of Wisconsin - Madison*

Ronald White

*Montana Tech of the University of Montana*

Follow this and additional works at: <https://digitalcommons.mtech.edu/camp>

 Part of the [Chemistry Commons](#), and the [Physics Commons](#)

---

#### Recommended Citation

W.B. Brown and R.J. White. Analytic power series solution of the Schrödinger equation for the helium atom. *Phys. Rev. Letters* 18:1037-1038, 1967.

This Article is brought to you for free and open access by the Faculty Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Center for Advanced Mineral and Metallurgical Processing (CAMP) by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact [sjuskiewicz@mtech.edu](mailto:sjuskiewicz@mtech.edu).

# PHYSICAL REVIEW LETTERS

VOLUME 18

12 JUNE 1967

NUMBER 24

## ANALYTIC POWER-SERIES SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE HELIUM ATOM\*

W. Byers Brown and Ronald J. White

Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin

(Received 27 April 1967)

The object of this Letter is to report the discovery of analytic solutions of the Schrödinger equation for the two-electron atom. In this preliminary communication we confine attention to the nonrelativistic Schrödinger equation<sup>1</sup> for a fixed nucleus of atomic number  $Z$ , and to the simplest  $S$  states (singlets or triplets) of the atom.

The Schrödinger equation in  $Z$ -reduced units (energy unit =  $Z^2$  Hartree units, length unit =  $Z$  Bohr radii) is

$$(\mathcal{H}_0 + \lambda r_{12}^{-1} - E)\psi = 0, \quad (1)$$

where  $\lambda = Z^{-1}$  and

$$\mathcal{H}_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - r_1^{-1} - r_2^{-1}. \quad (2)$$

For  $S$  states the spatial wave function  $\psi$  depends only on three variables which we take to be  $r_1$ ,  $r_2$ , and  $r_{12}$ , the interparticle distances. When operating on functions of these variables, the unperturbed Hamiltonian can be written

$$\mathcal{H}_0 = \mathcal{H}_0' - \left[ \frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{2\mathcal{D}}{r_{12}} \frac{\partial}{\partial r_{12}} + 2\mathcal{D}' r_{12} \frac{\partial}{\partial r_{12}} \right], \quad (3)$$

where

$$\mathcal{H}_0' = -\frac{1}{2} \left[ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right] - r_1^{-1} - r_2^{-1}, \quad (4)$$

and

$$\mathcal{D} = \frac{1}{4}(r_1^2 - r_2^2) \left( \frac{1}{r_1} \frac{\partial}{\partial r_1} - \frac{1}{r_2} \frac{\partial}{\partial r_2} \right),$$

$$\mathcal{D}' = \frac{1}{4} \left( \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_2} \frac{\partial}{\partial r_2} \right). \quad (5)$$

We assume a solution in the form of a power series in  $r_{12}$ , starting with the arbitrary power  $\sigma$ :

$$\psi = \sum_{n=0}^{\infty} r_{12}^{\sigma+n} \varphi_n(r_1, r_2), \quad (6)$$

with coefficients  $\varphi_n$  which are functions of  $r_1$  and  $r_2$  to be determined. This is a somewhat more general form than that proposed by Hylleraas<sup>2</sup> or by Kinoshita.<sup>3</sup> In spirit it is similar to the approach of Pluvineau.<sup>4</sup> By substituting (6) into Eq. (1), and using the independence of the powers of  $r_{12}$  within the range  $(|r_1 - r_2|, r_1 + r_2)$  to equate the coefficients to 0, we find that we must take  $\sigma = 0$ . The remaining equations then become

$$(\mathcal{D} + 1)\varphi_1 = \frac{1}{2}\lambda\varphi_0, \quad (7)$$

$$\left[ \mathcal{D} + \frac{1}{2}(n+1) \right] \varphi_n = \frac{\lambda}{2n} \varphi_{n-1}$$

$$+ \left[ \frac{1}{2n} (\mathcal{H}_0' - E) + \left( \frac{2}{n} - 1 \right) \mathcal{D}' \right] \varphi_{n-2} \quad (8)$$

for  $n = 2, 3, \dots$ . Hence if  $\varphi_0(r_1, r_2)$  is known, all the higher functions  $\varphi_n$  can be obtained iteratively by inverting the operators on the left-hand sides of Eqs. (7) and (8). Further, since  $\mathcal{D}$  is a first-order partial differential operator, the inversion can be carried out analytically by a single integration.

The key problem at this point is the form of the starting function  $\varphi_0$ . When the coupling parameter  $\lambda$  goes to 0,  $\psi$  approaches the cor-

responding eigenfunction  $\psi_0$  of the unperturbed Hamiltonian satisfying  $(\mathcal{H}_0 - E_0)\psi_0 = 0$ , whose form is known explicitly. If we limit discussion to the simplest S states, which correlate with the singly excited nondegenerate unperturbed configuration  $(1s)(ns)$ , then<sup>5</sup>  $\psi_0 = \psi_0(r_1, r_2)$ . Hence when  $\lambda \rightarrow 0$ ,  $\varphi_0 = \psi_0$  and all the other  $\varphi_n$  vanish. In the absence of further information about  $\varphi_0$ , it seems likely that we can take  $\varphi_0 = \psi_0$  for all  $\lambda$  (ignoring a normalization constant depending on  $\lambda$ ). This result may be proved by a perturbation analysis in powers of  $\lambda$ , which is known to be valid if  $\lambda$  is small enough.<sup>6</sup> The first-order treatment,<sup>7</sup> which led to the present work, shows that the only term independent of  $r_{12}$  in the first-order wavefunction is some multiple of  $\psi_0$ ; the same is true for the higher order wavefunctions. Therefore, provided the perturbation series converges for the value of  $\lambda (=Z^{-1})$  of interest,<sup>8</sup> we can take  $\varphi_0 = \psi_0$ .

To carry out the integrations, Eqs. (7) and (8) are most naturally written in terms of coordinates introduced by Gronwall<sup>9</sup> and Fock,<sup>10</sup>  $x = r_1^2 + r_2^2$  and  $y = r_1^2 - r_2^2$ , so that  $\mathcal{D} = y\partial/\partial y$ ,  $\mathcal{D}' = \partial/\partial x$ . Integrating the first two equations with respect to  $y$ , we get

$$\varphi_1 = \frac{1}{2}\lambda \int_0^1 \psi_0(x, \alpha y) d\alpha, \quad (9)$$

$$\varphi_2 = \frac{1}{4} \int_0^1 [\lambda^2(1 - \alpha^{1/2}) + (E_0 - E)\alpha^{1/2}] \psi_0(x, \alpha y) d\alpha, \quad (10)$$

where  $\alpha$  is a dummy integration variable. In terms of the Hylleraas variables  $s = r_1 + r_2$  and  $t = r_1 - r_2$ ,  $\varphi_1(s, t)$  for the ground state ( $\psi_0 = \pi^{-1} e^{-s}$ ) takes the form

$$\varphi_1 = \frac{1}{2} \lambda \psi_0 - \frac{\lambda t^2}{4\pi s} \int_0^1 (1 - \beta)^{1/2} \exp[-(s^2 + \beta t^2)^{1/2}] d\beta, \quad (11)$$

and  $\varphi_2$  is given by a similar type of expression. The next member  $\varphi_3$  can also be reduced to a single integral over  $\psi_0$  and its derivatives, and this is probably true for all the higher  $\varphi_n$ . The functions  $\varphi_n(s, t)$  may be expanded in powers of  $t^2$ , and most terms are then found to involve inverse powers of  $s$ . The possibility of a formal solution of the Hylleraas type,<sup>2</sup> provided inverse powers of  $s$  are included, was pointed out by Kinoshita.<sup>3</sup> There are no signs of logarithmic terms<sup>10-12</sup> in  $x$  or  $s$  in the early members, in agreement with the conclusion of Kinoshita<sup>13</sup>; nor of fractional powers<sup>14</sup> of  $s$  in the  $t^2$  expansions. Further details

will be given in a subsequent paper.

The above techniques also yield analytic solutions of the Schrödinger equations for the two-electron atom in the presence of a uniform electric field, and for the two-electron diatomic molecule, hydrogen.<sup>15</sup> The applications to arbitrary states of the two-electron atom and to the general three-body problem are being considered. It is interesting to note that in the case of the lithium atom, where interparticle coordinates can also be used, the obvious generalization of Eq. (6) to a triply infinite power series in  $r_{12}$ ,  $r_{23}$ , and  $r_{31}$  leads to an inconsistency (of order  $\lambda^2$ ) if only positive powers are allowed.

The practical weakness of the power-series solution (6) is that it almost certainly converges slowly. A more powerful approach leading to a more rapidly convergent analytic solution is proposed in the following Letter.<sup>16</sup>

We are grateful to Dr. Saul Epstein for discussions and helpful comments.

\*This research was supported by the National Aeronautics and Space Administration, Grant No. NsG-275-62.

<sup>1</sup>H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press, Inc., New York, 1957).

<sup>2</sup>E. A. Hylleraas, Z. Physik, **54**, 347 (1929).

<sup>3</sup>T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

<sup>4</sup>G. Munschy and P. Pluvinage, J. Phys. Radium **23**, 184 (1962).

<sup>5</sup>For S states correlating with doubly excited unperturbed configurations with principal quantum numbers  $n$  and  $n'$  ( $n \leq n'$ ), which are  $n$ -fold degenerate,  $\psi_0(r_1, r_2, r_{12})$  is a polynomial of degree  $n-1$  in  $r_{12}^2$ .

<sup>6</sup>T. Kato, Trans. Am. Math. Soc. **70**, 196 (1951).

<sup>7</sup>R. J. White and W. Byers Brown, to be published.

<sup>8</sup>For the ground state, the radius of convergence of the perturbation series appears to be determined by a branch point at  $\lambda = 1.118 \pm 0.003$ , as deduced by F. H. Stillinger, J. Chem. Phys. **45**, 3623 (1966). This includes the largest value of interest,  $\lambda = 1$  for  $H^-$ .

<sup>9</sup>T. H. Gronwall, Phys. Rev. **51**, 655 (1937).

<sup>10</sup>V. A. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954) [translation: Kgl. Norske Videnskab. Selskabs, Forh. **31**, 138 (1958)].

<sup>11</sup>J. H. Bartlett, Phys. Rev. **51**, 661 (1937).

<sup>12</sup>K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

<sup>13</sup>See Ref. 3, footnote 14, p. 1493.

<sup>14</sup>C. Schwartz, Phys. Rev. **128**, 1147 (1962).

<sup>15</sup>W. Byers Brown and R. J. White, to be published.

<sup>16</sup>W. Byers Brown and R. J. White, following Letter [Phys. Rev. Letters **18**, 1039 (1967)].