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INTEGRAL SERIES SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE HELIUM ATOM*

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In the preceding Letter,¹ a method for obtaining analytic solutions of the nonrelativistic Schrödinger equation for the two-electron atom of infinite nuclear mass was described. The solution for the spatial wave function $\psi(r_1, r_2, r_{12})$ of the simplest type of S state can be written in the form of an infinite power series in the interelectron distance r_{12} ,

$$\psi = \sum_{n=0}^{\infty} r_{12}^n \mathcal{W}_n \psi_0 \quad (1)$$

In this equation $\psi_0(r_1, r_2)$ is the corresponding eigenfunction of the unperturbed Hamiltonian \mathcal{H}_0 in which the electron repulsion term is absent, and the \mathcal{W}_n are integrodifferential operators satisfying three-term recursion relations, which depend implicitly on the energy E . The eigenvalue can be found by multiplying the Schrödinger equation $(\mathcal{H}_0 + V)\psi = E\psi$ by ψ_0 and integrating to obtain

$$E = E_0 + \langle \psi_0, V\psi \rangle / \langle \psi_0, \psi \rangle, \quad (2)$$

and then solving this implicit equation for E iteratively.

The power series solution (1) has the theoretical advantage of being almost certainly uniformly convergent, as compared with the variational forms of Hylleraas² or Pekeris,³ which are only convergent in the mean. However, it suffers from the practical disadvantage of almost certainly converging slowly for most configurations of the electrons. It is therefore necessary to sum at least some of the terms to obtain a potentially useful solution. The purpose of the present Letter is to describe an alternative approach which achieves such a summation implicitly, and which avoids the assumption of a power series form. In this preliminary communication, we shall merely sketch the method without attempt at rigor.

We partition⁴ the Hamiltonian for the two-electron atom with atomic number Z into⁵ $\mathcal{H} = \mathcal{H}' + \Lambda$ where, in Z -reduced atomic units (energy unit = Z^2 Hartree, length unit = Z Bohr),

$$\mathcal{H}' = -\frac{1}{2} \left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} \right] - r_1^{-1} - r_2^{-1} + \lambda r_{12}^{-1}, \quad (3)$$

$$\Lambda = - \left[\frac{\partial}{\partial r_{12}} + \frac{2(1+\mathcal{D})}{r_{12}} + 2r_{12}\mathcal{D}' \right] \frac{\partial}{\partial r_{12}}, \quad (4)$$

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

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

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

The Schrödinger equation $(\mathcal{H} - E)\psi = 0$ may then be written in the form

$$\Lambda\psi = (E - \mathcal{H}')\psi. \quad (6)$$

Let Λ^{-1} denote the inverse (Green's operator) of Λ in the subspace complementary to that of the functions φ satisfying the homogeneous equation $\Lambda\varphi = 0$. Then Eq. (6) can be rewritten as the integral-type equation

$$\psi = \varphi_0 + \Lambda^{-1}(E - \mathcal{H}')\psi, \quad (7)$$

where φ_0 is the appropriate solution of $\Lambda\varphi = 0$. Clearly, as $\lambda \rightarrow 0$, $\varphi_0 \rightarrow \psi_0$, and a perturbation analysis¹ proves that we can take $\varphi_0 = \psi_0$. In contrast to the reduced resolvent $(E_0 - \mathcal{H}_0)^{-1}$, the inverse Λ^{-1} can be realized explicitly as a double integral, by using the theory of characteristics of partial differential equations.⁶ Thus, when operating on a function of the coordinates $x = r_1^2 + r_2^2$, $y = r_1^2 - r_2^2$, and $u = r_{12}$, the inhomogeneous part may be written in the form

$$\Lambda^{-1}f(x, y, u) = -\frac{1}{4}u^2 \int_0^1 \int_0^1 \alpha^{1/2} f(x - u^2(1-\alpha)\beta, y, u(\alpha\beta)^{1/2}) d\alpha d\beta, \quad (8)$$

where α and β are dummy integration variables.

Assuming convergence, the solution of Eq. (7) can be written in a formally closed, wave operator

form

$$\begin{aligned}\psi &= [1 - \Lambda^{-1}(E - \mathcal{K}')]^{-1} \psi_0 \\ &= \{1 - [1 - \Lambda^{-1}(E - \mathcal{K}')]^{-1} \Lambda^{-1} V\} \psi_0 \\ &= \mathcal{W} \psi_0,\end{aligned}\quad (9)$$

where $V = \lambda r_{12}^{-1}$. In practice, ψ has to be expanded as the infinite series

$$\psi = \psi_0 - \Lambda^{-1} V \psi_0 - \Lambda^{-1} (E - \mathcal{K}') \Lambda^{-1} V \psi_0 - \dots, \quad (10)$$

where each term can be realized as a definite integral. By expanding each term in powers of r_{12} we recover the power series form (1). The eigenvalue can be found by substituting (10) into Eq. (2) and solving iteratively⁷ for E .

The crucial practical question is: How rapidly does the integral series (10) converge? The only information on this point available at present is for the Hooke's law model atom,^{8,9} in which the electrons are attracted to the nucleus by a parabolic potential well, but repel each other Coulombically. In this case the terms of Eq. (10) converge at least as rapidly as the successive orders of Rayleigh-Schrödinger perturbation theory in powers of λ . If this is also true for the actual two-electron atom it is highly satisfactory: The ground-state eigenvalue of helium is given to within 2 parts in 10^6 by the first six terms of the perturbation series.^{10,11}

The Λ^{-1} technique can also be applied to the Schrödinger equation for the two-electron diatomic molecule, hydrogen.¹² It is hoped it may be useful in the direct nonvariational solution of the pair equations of the Bethe-Goldstone type for many-electron atoms and diatomic molecules. Computations are in progress to find how rapidly Eq. (10) converges. In the event that convergence is too slow, it

may be necessary to consider the series obtained by inverting $\Lambda + V - L$, where L is a number. This also appears to be possible explicitly,¹³ but is considerably more complicated than the Λ^{-1} method outlined above.

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¹W. Byers Brown and R. J. White, preceding Letter [Phys. Rev. Letters **18**, 1037 (1967)].

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

³C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **126**, 1470 (1962).

⁴We are using the term partition loosely in order to relate our approach to P. O. Löwdin, J. Math. Phys. **3**, 969 (1962).

⁵The operator \mathcal{K}' is defined for fixed r_{12} , not fixed angle θ_{12} between \hat{r}_1 and \hat{r}_2 . Neither \mathcal{K}' nor Λ is Hermitian with respect to functions belonging to the domain of \mathcal{K} .

⁶R. Courant, Methods of Mathematical Physics (Interscience Publishers, Inc., New York, 1962), Vol. 2, p. 62.

⁷Note that, since Λ is not self-adjoint, the denominator of Eq. (2) cannot in general be set equal to unity. Furthermore, the bracketing theorem of Löwdin (Ref. 4), which is valid when \mathcal{W} is the true Brillouin-Wigner wave operator, does not appear to hold when \mathcal{W} is defined by Eq. (9).

⁸N. R. Kestner and O. Sinanoglu, Phys. Rev. **128**, 2687 (1962).

⁹R. J. White and W. Byers Brown, University of Wisconsin Theoretical Chemistry Institute Report No. WIS-TCI-116, 1965 (unpublished).

¹⁰R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963).

¹¹J. Midtdal, Phys. Rev. **138**, A1010 (1965).

¹²W. Byers Brown and R. J. White, to be published.

¹³An approximate treatment based on this idea, omitting the coupling terms in Λ , has been given by P. Pluvinage, Ann. Phys. (Paris) **5**, 145 (1950). See also M. Delves, Australian J. Phys. **18**, 101 (1965).