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

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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 equation¹ 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 ψ 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 σ :

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

with coefficients φ_n which are functions of r_1 and r_2 to be determined. This is a somewhat more general form than that proposed by Hylleraas² or by Kinoshita.³ In spirit it is similar to the approach of Pluvineau.⁴ 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 φ_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 φ_0 . When the coupling parameter λ goes to 0, ψ approaches the cor-

responding eigenfunction ψ_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 $(1s)(ns)$, then⁵ $\psi_0 = \psi_0(r_1, r_2)$. Hence when $\lambda \rightarrow 0$, $\varphi_0 = \psi_0$ and all the other φ_n vanish. In the absence of further information about φ_0 , it seems likely that we can take $\varphi_0 = \psi_0$ for all λ (ignoring a normalization constant depending on λ). This result may be proved by a perturbation analysis in powers of λ , which is known to be valid if λ is small enough.⁶ The first-order treatment,⁷ which led to the present work, shows that the only term independent of r_{12} in the first-order wavefunction is some multiple of ψ_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,⁸ 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 Gronwall⁹ and Fock,¹⁰ $x = r_1^2 + r_2^2$ 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 α 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 φ_2 is given by a similar type of expression. The next member φ_3 can also be reduced to a single integral over ψ_0 and its derivatives, and this is probably true for all the higher φ_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,² provided inverse powers of s are included, was pointed out by Kinoshita.³ There are no signs of logarithmic terms¹⁰⁻¹² in x or s in the early members, in agreement with the conclusion of Kinoshita¹³; nor of fractional powers¹⁴ 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.¹⁵ 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 λ^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.¹⁶

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