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COMMENT

The validity of Kinoshita's expansion for S-state eigenfunctions of the helium atom

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Abstract. The incorrectness of an assertion by Kinoshita of having found a set of variables in which helium atom eigenfunctions are analytic is demonstrated by making explicit an earlier statement of Fock. Some other flaws in Kinoshita's article are pointed out.

In 1929 E Hylleraas introduced a simple coordinate system for expressing the S-state eigenfunctions of the non-relativistic helium atom:

$$s = r_1 + r_2, \qquad t = r_2 - r_1, \qquad u = r_{12} \tag{1}$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, the subscripts refer to electrons 1 and 2, and distances are measured from an infinitely massive nucleus (Hylleraas 1929). Soon after this it was suggested that the S-state helium eigenfunctions are not analytic in these variables (Bartlett *et al* 1935). This conclusion depends on the assumption that the coefficient c_{000} is non-zero. These results also apply to any two-electron ion.

In 1957 Kinoshita used a modification of Hylleraas' variables to express a trial function for the helium atom:

$$s = r_1 + r_2, \qquad p = u/s, \qquad q = t/u \tag{2}$$

(Kinoshita 1957, p 1492). He asserts that the exact eigenfunctions of the helium atom can be written as a power series in s, p, and q, and he purports to give a proof of this assertion (see pp 1500–1). Kinoshita notices (p 1493) earlier works (Bartlett 1937, Fock 1954) which suggest that helium atom eigenfunctions are not analytic in his variables, but he dismisses these conclusions with the remark, 'It is to be noted that the logarithmic terms are not necessarily required by the structure of the Schrödinger equation itself.'

Unfortunately Bartlett's paper is now largely forgotten, and Fock's statement, that an expansion analytic in $(r_1^2 + r_2^2)^{1/2}$ is inadequate (Fock 1954, p 167), is not accompanied by a proof. Additionally, Bartlett's argument involves a numerical integration of questionable accuracy to show that a certain integral is non-vanishing (Bartlett 1937, pp 668–9), although it has been proved recently that Bartlett's conclusion is correct (Morgan 1976, 1978). The belief that the eigenfunctions of the helium atom are expressible as a power series in s, p, and q is proliferating throughout the literature of atomic calculations (Klahn and Bingel 1977, p 42). Therefore it may

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be appropriate to present a very brief proof of the non-analyticity of helium atom eigenfunctions in Kinoshita's variables and to point out other errors in his appendix.

We should begin by remarking that Kinoshita's proof of the alleged validity of his expansion (Kinoshita 1957, p 1500) is flawed. He argues that since 'there are ∞^3 equations to determine ∞^3 quantities $c_{l,m,m'}$', his equation (A.1) has 'formal solutions ... with ∞^2 arbitrary parameters.' Presumably this is supposed to be some sort of extension of the 'folk theorem' that 'a system of N linear equations for N unknowns has a non-trivial solution' to transfinite numbers. Since this 'folk theorem' is false, for the determinant of the coefficients must vanish in order for a non-trivial solution to exist (Murdoch 1957, pp 48–9), we should not put much faith in the validity of an argument which is the 'limit' of a sequence of incorrect statements.

To demonstrate that Kinoshita's conclusion is false, we could refer to Bartlett's (1937) article and to the making rigorous of his plausible contention that a certain integral is non-vanishing (Morgan 1976, 1978). Instead, a proof of Fock's statement of the inadequacy of an expansion analytic in $R^{1/2} = (r_1^2 + r_2^2)^{1/2}$ will be presented.

Fock's expansion (3.04) is

$$\psi = \sum_n R^{n-1} \psi_n(\alpha, \theta), \qquad n = 1, \tfrac{3}{2}, 2, \tfrac{5}{2}, \ldots \tag{3}$$

where $\sin(\alpha/2) = r_2/R^{1/2}$, $\cos(\alpha/2) = r_1/R^{1/2}$, and $(1 - \sin\alpha \cos\theta)^{1/2} = r_{12}/R^{1/2}$. Upon substituting (3) into Schrödinger's equation (3.03), one obtains

$$\square^* \psi_n + (n^2 - 1)\psi_n = \tfrac{1}{2} U \psi_{n-\frac{1}{2}} - \tfrac{1}{2} E \psi_{n-1}, \tag{4}$$

where

$$\square^* = \frac{1}{\sin^2\alpha}\left[\frac{\partial}{\partial\alpha}\left(\sin^2\alpha \frac{\partial}{\partial\alpha}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right)\right] \tag{5}$$

and

$$U = -Z\left(\frac{1}{\cos(\alpha/2)} + \frac{1}{\sin(\alpha/2)}\right) + (1 - \sin\alpha\cos\theta)^{-1/2}. \tag{6}$$

For $n = 1$ we have the equation $\square^* \psi_1 = 0$, whose solution is $\psi_1 = 1$. For $n = 3/2$ we have the equation

$$\square^* \psi_{3/2} + (5/4)\psi_{3/2} = \tfrac{1}{2} U \psi_{10} = \tfrac{1}{2} U, \tag{7}$$

whose solution is

$$\psi_{3/2} = -Z(\cos(\alpha/2) + \sin(\alpha/2)) + \tfrac{1}{2}(1 - \sin\alpha\cos\theta)^{1/2}. \tag{8}$$

For $n = 2$ we have the equation

$$\begin{aligned}\square^* \psi_2 + 3\psi_2 &= \tfrac{1}{2} U \psi_{3/2} - \tfrac{1}{2} E \psi_1 \\ &= \frac{1}{2}\left[-Z\left(\frac{1}{\cos(\alpha/2)} + \frac{1}{\sin(\alpha/2)}\right) + (1 - \sin\alpha\cos\theta)^{-1/2}\right] \\ &\quad \times [-Z(\cos(\alpha/2) + \sin(\alpha/2)) + \tfrac{1}{2}(1 - \sin\alpha\cos\theta)^{1/2}] - \frac{E}{2}.\end{aligned} \tag{9}$$

Two linearly independent solutions of the homogeneous equation are $\cos\alpha$ and $\sin\alpha\cos\theta$; in order for a solution of (9) to exist, the right-hand side of (9) must be orthogonal to both functions. The right-hand side of (9) is orthogonal to $\cos\alpha$ since it is symmetric about $\alpha=\pi/2$ whereas $\cos\alpha$ is antisymmetric about this point. We must then determine if

$$\int_0^\pi d\alpha\,\sin^2\alpha\int_{-1}^1 d(\cos\theta)\Big\{\frac{1}{2}\Big[-Z\Big(\frac{1}{\cos(\alpha/2)}+\frac{1}{\sin(\alpha/2)}\Big)+(1-\sin\alpha\cos\theta)^{-1/2}\Big]$$
$$\times[-Z(\cos(\alpha/2)+\sin(\alpha/2))+\tfrac{1}{2}(1-\sin\alpha\cos\theta)^{1/2}]-\frac{E}{2}\Big\}\sin\alpha\cos\theta$$
$$=-\frac{Z}{2}\int_0^\pi d\alpha\,\sin^2\alpha\int_{-1}^1 d(\cos\theta)\Big[\frac{1}{2}\Big(\frac{1}{\cos(\alpha/2)}+\frac{1}{\sin(\alpha/2)}\Big)(1-\sin\alpha\cos\theta)^{1/2}$$
$$+(\cos(\alpha/2)+\sin(\alpha/2))(1-\sin\alpha\cos\theta)^{-1/2}\Big]\sin\alpha\cos\theta$$
$$=-\frac{Z}{2}\int_0^\pi d\alpha\,\sin\alpha\int_{-1}^1 d(\cos\theta)(\cos(\alpha/2)+\sin(\alpha/2))$$
$$\times[(1-\sin\alpha\cos\theta)^{1/2}+\sin\alpha(1-\sin\alpha\cos\theta)^{-1/2}]\sin\alpha\cos\theta$$
$$=-Z\int_0^\pi d\alpha\,\Big(\frac{1}{5}[(1-\sin\alpha)^{5/2}-(1+\sin\alpha)^{5/2}]$$
$$-\frac{1-\sin\alpha}{3}[(1-\sin\alpha)^{3/2}-(1+\sin\alpha)^{3/2}]$$
$$-\sin\alpha[(1-\sin\alpha)^{1/2}-(1+\sin\alpha)^{1/2}]\Big)(\cos(\alpha/2)+\sin(\alpha/2)) \qquad (10)$$

vanishes. Since $\cos(\alpha/2)+\sin(\alpha/2)=(1+\sin\alpha)^{1/2}$, it is straightforward to verify that (10) is non-zero. Hence (9) has no solution with $\psi_1\neq 0$ and $\psi_{3/2}\neq 0$, so expansion (3) is inadequate.

No claim of originality is made for this proof, for undoubtedly it is the procedure Fock used nearly twenty-five years ago.

Since no expansion analytic in $R^{1/2}$ can describe the eigenfunctions of the helium atom and $R=\frac{1}{2}(s^2+t^2)=\frac{1}{2}s^2(1+p^2q^2)$ implies $R^{1/2}$ is analytic in s, no expansion analytic in s can satisfy Schrödinger's equation for the helium atom. Hence Kinoshita's expansion is invalid.

Furthermore, we can point out that equation (A.9) of Kinoshita's article is incorrect, for upon inserting (2.11) into (A.5) he neglected to differentiate the exponential and for some peculiar reason set the right-hand side of (A.5) equal to zero.

A few words out to be said concerning Kinoshita's appendix D. The fact that a function $f(x)$ is not orthogonal to every power of x on the interval $(0,1)$ does not imply that $f(x)$ has a well defined power series expansion in x, i.e., that f is analytic; the function $f(x)=-x\ln x$ provides a simple counter-example. Hence this section has little to do with Kinoshita's manipulations in the previous sections of his appendix, for these require analyticity to be valid.

Finally, it should be noted that there is a great deal of variation in some of Kinoshita's expansion coefficients when he goes from a 39-term trial function to a 80-term trial function (Kinoshita 1959, pp 367–8). This fluctuation is especially strong in the coefficients $c_{l,m,n}$ with $l\geqslant 2$ and $|l-m|\leqslant 2$. Such behaviour is precisely what would be expected if the exact wavefunction is not analytic in Kinoshita's variables. The coefficients of the expansions of successively more accurate trial functions cannot tend to a limit, for if they did, the exact eigenfunction would be analytic.

It is remarkable that these features of Kinoshita's paper apparently have not been noticed previously in the literature.

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