

Correlation Factor for Ground State of Helium

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Received December 9, 1968

If a variational trial function of form $\exp(-ar_1 - ar_2)f(r_{12})$ is postulated for the ground-state of helium-like ions, then for a given a it is shown that the variation principle leads to an ordinary second order differential equation for f , the solution of which represents the "optimum" function f for use with a trial function of this type, in the sense that this solution minimises the expectation value of the Hamiltonian for the system. A solution to the differential equation may be found by the usual series expansion method.

Wenn ein Variationsansatz der Form $\exp(-ar_1 - ar_2)f(r_{12})$ für den Grundzustand von He-artigen Ionen vorausgesetzt wird, so wird gezeigt, daß (bei gegebenem a) das Variationsprinzip zu einer gewöhnlichen Differentialgleichung 2. Ordnung für f führt. Ihre Lösung stellt eine "optimale", den Erwartungswert des Hamiltonoperators des Systems minimisierende Funktion des angegebenen Typs dar. Eine Lösung der Differentialgleichung kann mit der gewöhnlichen Methode eines Reihenentwicklungs-Ansatzes gefunden werden.

Si l'on prend comme fonction variationnelle d'essai pour l'état fondamental des ions de type hélium: $\exp(-ar_1 - ar_2)f(r_{12})$ le principe variationnel mène pour a constant à une équation différentielle du second ordre pour f . La solution de cette équation représente la «meilleure» fonction f à utiliser avec une fonction d'essai de ce type, car elle minimise la valeur moyenne de l'hamiltonien. Cette solution peut être obtenue par la méthode ordinaire de développement en série.

Introduction

Variational calculations of the ground-state energy of helium-like ions frequently commence with a very simple configuration space trial function of the symmetric type

$$\begin{aligned}\varphi &= \exp(-ar_1 - ar_2)f(u), \\ u &= r_{12},\end{aligned}\tag{1}$$

where r_{12} is the distance between electrons 1 and 2, with the usual nomenclature. Obviously this is not the only type of trial function which may be utilised, and restricting φ to this limited form will certainly decrease our flexibility of choice, since the only variables at our disposal are the exponent a and the correlation factor f . Denoting the term in front of f by the title uncorrelated function, it would clearly be of interest to see whether for a particular form of the uncorrelated function (not necessarily restricted to the exponential form (1)), it would be possible to select some particular function f which would minimise the expectation value of the Hamiltonian, $\langle H \rangle$, more than any other function f . If such can be found, with a given uncorrelated function, then we should be justified in calling that f the "optimum" correlation factor corresponding to the chosen form of the uncorrelated part. Clearly again, we may vary both the uncorrelated and correlated parts of the trial function in order to minimise $\langle H \rangle$, and the usual method of doing this is to

ascribe pre-determined functional forms to both the correlated and uncorrelated portions, and to vary certain disposable parameters attached to these functions.

In theory the technique to be described can be applied to any helium-like trial function which is a function of the variables r_1 , r_2 and u , provided the part $f(u)$ is separated from the uncorrelated portion, as in (1), but to keep the mathematics to an absolute minimum so that we do not lose the wood for the trees, we shall restrict the discussion to our trial function (1).

Variational Method

The non-relativistic Hamiltonian for a helium-like ion, in atomic units, is

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{1}{r_{12}}, \quad (2)$$

with the usual notation, z being the nuclear charge. Using the trial configuration space function (1) (all spin functions have been factored off), we know that for this trial function the minimum value of the expectation value

$$\langle H \rangle = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \quad (3)$$

will yield an upper bound to the ground-state energy of the system. From (3) and (1) we see that the function f must be such that the normalization integral converges.

To evaluate the integrals in (3), it is convenient to use as integration variables the coordinates

$$\begin{aligned} s &= r_1 + r_2, \\ t &= r_1 - r_2, \\ u &= r_{12}, \end{aligned} \quad (4)$$

and to integrate first over s and t , leaving the u integration till last. In these coordinates the volume element for integration over the whole of configuration space for electrons 1 and 2 is

$$dV = 2\pi^2 (s^2 - t^2) u ds dt du,$$

where

$$\begin{aligned} 0 &\leq u \leq \infty, \\ 0 &\leq t \leq u, \\ u &\leq s \leq \infty. \end{aligned}$$

Substituting (1), (2) and (4) into (3) and integrating over s and t , with a little algebra we obtain

$$\langle H \rangle = 3a^2 - 4az + \frac{\int_0^\infty du F(u) h F(u)}{\int_0^\infty du F(u) F(u)}, \quad (5)$$

where

$$h = -\frac{d^2}{du^2} + G(u), \quad (6)$$

$$G(u) = \frac{16}{3}(z-a)\frac{y^4 \exp(-2y)}{Q(u)} + \frac{1}{u} + \frac{1}{4}P^2 + \frac{1}{2}\frac{dP}{du}, \quad (7)$$

$$Q(u) = \exp(-2y)u\left(\frac{4}{3}y^3 + 2y^2 + y\right), \quad (8)$$

$$P = \frac{1}{Q(u)}\frac{d}{du}Q(u), \quad (9)$$

$$F(u) = f(u)[Q(u)]^{\frac{1}{2}}, \quad (10)$$

$$y = au. \quad (11)$$

Now, from (5), the variational theorem tells us that the minimum value

$$\langle H \rangle_m = 3a^2 - 4az + k, \quad (12)$$

for a given a , is reached when F satisfies the eigenvalue equation

$$hF(u) = kF(u). \quad (13)$$

For a *bound* ground state we only seek those values of k which make (12) negative, so that we shall write

$$\langle H \rangle_m = -\alpha^2. \quad (14)$$

From (6–13), the following differential equation for f may be set up:

$$(4y^3 + 6y^2 + 3y)\frac{d^2f}{dy^2} + (-8y^3 + 4y^2 + 12y + 6)\frac{df}{dy} = f(Ay^3 + By^2 + Cy + D), \quad (15)$$

where

$$\begin{aligned} A &= \frac{16(z-a)}{a} - \frac{4k}{a^2}, \\ B &= \frac{4}{a} - \frac{6k}{a^2}, \\ C &= \frac{6}{a} - \frac{3k}{a^2}, \\ D &= 3/a, \end{aligned} \quad (16)$$

and we are only interested in those values of k which render (12) negative. Since we wish f to behave regularly at $y=0$, the usual method [1] of Frobenius for solving in series form leads to (since the point $y=0$ is a singular point for (15) we

neglect the unphysical solution which behaves as y^{-1} for $y \rightarrow 0$):

$$f = \sum_{n=0}^{\infty} d_n y^n, \quad (17)$$

where we choose

$$d_0 = 1.$$

Comparing coefficients of powers of y in the usual way:

$$d_1 = 1/2a, \quad (18)$$

and we obtain the five-term recurrence relation

$$3(n+1)(n+2)d_{n+1} + (6n^2 + 6n - D)d_n + [4(n-1)^2 - C]d_{n-1} - [8(n-2) + B]d_{n-2} - Ad_{n-3} = 0, \quad (19)$$

with

$$d_{-3} = d_{-2} = d_{-1} = 0.$$

Hence

$$d_2 = \frac{1-2k}{12a^2}, \quad (20)$$

$$d_3 = \frac{1}{18a} + \frac{(\frac{1}{4} - 2k)}{36a^3},$$

and so on.

Because (19) is a five-term recurrence relation, and not a two-term relation, we cannot determine the eigenvalue k in the usual way adopted in quantum mechanics [2], by restricting the asymptotic behaviour of f for large y . However, to normalize the trial wavefunction (1), we know that as $y \rightarrow \infty$, f must not increase as rapidly as $\exp(y)$.

By direct numerical solution of (15) (or, rather, of another differential equation from which to determine the correlation factor $f(u)$), at the same time optimising the parameter a so as to minimise (12), Green *et al.* [3] computed the following values for the helium atom ($z = 2$):

$$\alpha^2 = 2.89126, \quad (21)$$

$$a = 1.848.$$

Hence

$$k = 1.6474 \quad (22)$$

in this case.

Thus if these values for a and k are inserted into (19–20) for $z = 2$, then we can compute the numerical coefficients d_n in (17), and so obtain the power series for that optimum correlation factor for helium which corresponds to using the trial form (1). It should be noted that when the minimum expectation value (12) of the Hamiltonian is measured in the atomic units we have adopted, then the value (21) for α^2 is to be compared with the “exact” Pekeris [4] value for the minimum ground state energy of helium: -2.9037 a.u.

From (17) and (18) we note that as $u \rightarrow 0$, $f(u)$ behaves as

$$1 + \frac{1}{2}u, \quad (23)$$

so that it satisfies the orbital cusp condition [5]

$$\left(\frac{1}{f} \frac{df}{du} \right)_{u=0} = \frac{1}{2}. \quad (24)$$

The behaviour (23) shown by the correlation factor for very small values of the interelectronic distance is the same as that shown by the Slater [6] correlation factor

$$\exp\left(\frac{1}{2}u\right) \quad (25)$$

and the Conroy [7] correlation factor

$$E_1(u) = \sum_{n=0}^{\infty} \frac{u^n}{n!(n+1)!}, \quad (26)$$

where E_1 is the Bessel-Clifford function. It has been shown [8] that both (25) and (26) are, in fact, special cases of a whole class of correlation factors expressed in terms of confluent hypergeometric functions.

In the asymptotic case of $u \rightarrow \infty$, the leading terms in (15) give the equation

$$4 \frac{d^2 f}{dy^2} - 8 \frac{df}{dy} - Af = 0 \quad (27)$$

with possible solutions

$$f = \exp\left[y \left(1 \pm \frac{\alpha}{a} \right) \right], \quad (28)$$

where we have used (16) and (12) with (14). If the trial function (1) is to be normalised, however, we know that the plus sign in (28) is inadmissible, so that the asymptotic behaviour of f as $u \rightarrow \infty$ is characterised by (since $y = au$)

$$f(u) = \exp[(a - \alpha)u]. \quad (29)$$

Hence (23) and (29) summarize the behaviour of the correlation factor for very small and very large values, respectively, of u .

Acknowledgement. The author is indebted to Professor C. A. Coulson for very helpful correspondence on the problem.

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