REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

Interpretation of the Rapid Convergence of Correlated Wave Functions*

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THE following comments are concerned with the effect of correlation on the functional form of the wave function. More specifically, they pertain to the structure of the Coulomb hole and the question of why correlated wave functions are better suited for an accurate description of the Coulomb hole than a superposition of configurations.

It is a well-known fact, first pointed out by Hylleraas[1,2] and recently reiterated by a number of workers,[3–6] that a superposition of configurations converges much more slowly than a correlated wave function. The numerical results for the ground state energy of He serve to emphasize this point. The correlation energy for He is $E_{\text{corr}} = E_{\text{HF}} - E_{\text{exact}} = -2.861680 + 2.903724 = 0.042044$ atomic units.[7,8] Using a correlated wave function containing only three terms, Hylleraas was able to recover 96.95% of this correlation energy.[2] Six-, ten-, and fourteen-term correlated wave functions recover 98.85, 99.71, and 99.95%, respectively.[2,9,10] By contrast, 20 and 35 configurations are required to obtain comparable results of 97.56 and 98.75% of the correlation, respectively.[5,11]

The greater efficiency of correlated wave functions has been attributed to the fact that they are better suited for describing short-range correlation effects, in particular, to their obvious superiority for representing the cusp at $r_{12} = 0$.[3–6] There is reason for questioning this interpretation. There is evidence to support the claim that the contribution to the correlation error from a poor representation of the wave function in the neighborhood of the cusp is relatively small and that the superiority of correlated wave functions is due to the fact that the entire Coulomb hole (which has a radius comparable to the atomic radius) has a much simpler structure relative to the electron than it does relative to a fixed reference point.

The most convincing part of the evidence may be found in a paper by Coulson and Neilson.[12] They compute the pair distribution function

$$f(r_{12}) \equiv \int |\psi(1,2)|^2 dv_1 dv_2/dr_{12} = \pi^2 r_{12} \int_{r_{12}}^{\infty} ds \times \int_{-r_{12}}^{r_{12}} dt (s^2 - t^2) |\psi(1,2)|^2 \qquad (1)$$

for the ground state of He using a number of approximate wave functions. (The variables in the second equality are $s = r_1 + r_2$ and $t = r_1 - r_2$.) They find that the relation between the error in the total energy and the quantity

$$\langle r_{12}^{-1} \rangle \equiv \int_0^{\infty} r_{12}^{-1} f(r_{12}) dr_{12}$$

is approximately linear with a slope which differs by only a few percent from 0.5 (in the proper units).[13] This empirical result implies that the error in the electron–nucleus part of the potential energy is negligible and justifies the use of the quantity $\Delta = \int r_{12}^{-1} \Delta(r_{12}) dr_{12}$ as a measure of the correlation error, where $\Delta(r_{12}) = f_{\text{exact}}(r_{12}) - f_{\text{HF}}(r_{12})$ is the difference between the exact pair distribution function and the pair distribution function calculated with the Har-

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* Based on work performed under the auspices of the U S Atomic Energy Commission.

[1] E. Hylleraas, Z. Physik **48**, 469 (1928).

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

[3] C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960).

[4] R. E. Watson, Phys. Rev. **119**, 170 (1960).

[5] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[6] C. Schwartz, Phys. Rev. **128**, 1146 (1962).

[7] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[8] C. L. Pekeris, Phys. Rev. **115**, 2161 (1959); **126**, 1470 (1962).

[9] S. Chandrasekhar, D. Elbert, and G. Herzberg, Phys. Rev. **91**, 1172 (1953).

[10] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[11] One could, presumably, improve this convergence by constructing the determinants from orbitals which were chosen to give the best polydeterminant wave function (by a procedure analogous to the Hartree–Fock method for determining the best orbitals for a single-determinant wave function). However, it is unlikely that this is sufficient to make a superposition of configurations converge more rapidly than a correlated wave function. The results of Davidson and Jones on the convergence of the natural spin-orbital expansion for H_2 [E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962)] support this last statement. See also, H. Shull and P. O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

[12] C. A. Coulson and A. H. Neilson, Proc. Phys. Soc. (London) **78**, 831 (1961).

[13] I am indebted to Professor Coulson for pointing out this fact and its implications. The argument utilizes the virial theorem and the fact that both the exact and approximate wave functions satisfy the virial condition.

tree–Fock wave function. The forms of the functions $\Delta(r_{12})$ and $r_{12}^{-1}\Delta(r_{12})$ are shown in Figs. 1 and 2. (Figure 1 is a replot of Fig. 4 in the Coulson–Neilson article. Figure 2 was calculated from their figure and, hence, should be regarded as only a qualitative representation of the true form. The qualitative form is sufficient for the purpose of this discussion.) The 6-term correlated wave function of Hylleraas was used for the "exact" wave function. A strong point of the argument is that f $(r_{12} \backsim r_{12}^2$ when $r_{12} \approx 0$ so that[14]

$$\lim_{r_{12}\to 0} r_{12}^{-1}\Delta(r_{12}) = 0 \,.$$

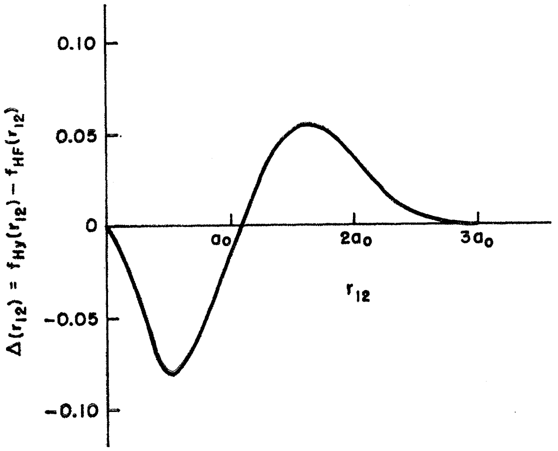

FIG. 1. The unweighted Coulomb hole, calculated by Coulson and Neilson[12] with the six-term correlated wave function of Hylleraas.

It is clear from Fig. 2 that the size of the Coulomb hole is comparable with the dimensions of the atomic orbital, as pointed out by Coulson and Neilson, and that the dominant contribution does not come from the neighborhood of the cusp but from an extended region which is comparable to the dimensions of the orbital. Although it may be true that a good cusp is important for extremely accurate results, it does not appear to be reasonable to ascribe the more rapid convergence of correlated wave functions primarily to the ease with which they can reproduce the Coulomb hole in the neighborhood of the cusp. A more likely explanation is that the Coulomb hole has a rather simple structure when viewed relative to one of the electrons (so that a description in terms of the variable r_{12} leads to simple and rapidly converging functions) while it has a rather complex structure when viewed relative to a fixed set of axes (so that a description in terms of a superposition of configurations is complicated and slowly convergent).

Additional evidence may be found by examining the cusps of correlated wave functions. Values of the cusp for the 10- and 14-term correlated wave functions of Chandrasekhar and Herzberg are given in Table I. We see that the cusp can be in error by an appreciable amount even when the total energy is correctly given to five significant figures.

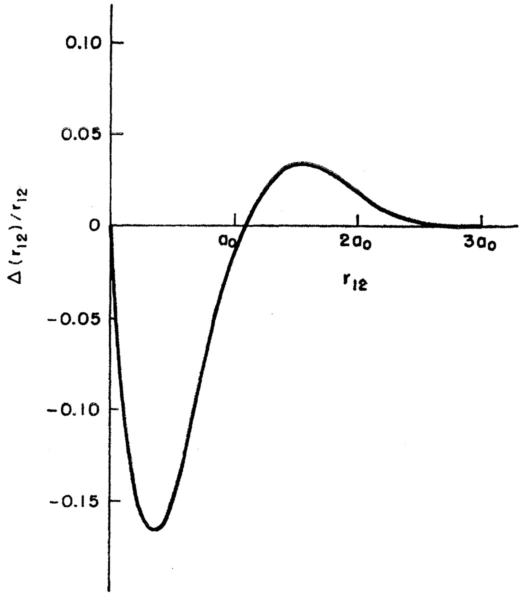

FIG. 2. The Coulomb hole, calculated by Coulson and Neilson[12] with the six-term correlated wave function of Hylleraas.

As a further check of our conjecture that the Coulomb hole has a simple structure when viewed relative to the instantaneous position of the electron,

TABLE I. Cusp values for the 10- and 14-term correlated wave functions of Chandrasekhar and Herzberg.[9,10] Cusp $= \partial \log \psi/\partial r_{12}|_{r_{12}=t=0} = (\beta + \chi_6 s)/(1 + \delta s + \epsilon s^2 + \chi_{11}s^3)$ where $s = r_2 + r_1$, $t = r_2 - r_1$, and β, δ, ϵ, χ_6, and χ_{11} are numerical constants. The last column gives cusps for third-degree polynomials fitted to the calculated points of the correlation function shown in Fig. 3. The exact energy is $E = -2.903724$ atomic units.[8] The exact value of the cusp is $\frac{1}{2}$.

	Cusp		
s	14-term correlated wave function	10-term correlated wave function	Cubic fit to correlation function
0.5	0.431	0.384	. . .
1.0	0.459	0.418	. . .
2.0	0.498	0.490	0.372
4.0	0.506	0.619	0.313
6.0	0.462	0.672	0.223
E	−2.903701 a.u.	−2.903603 a.u.	. . .

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[14] I am indebted to Dr. Lars Hedin for bringing this point to my attention.

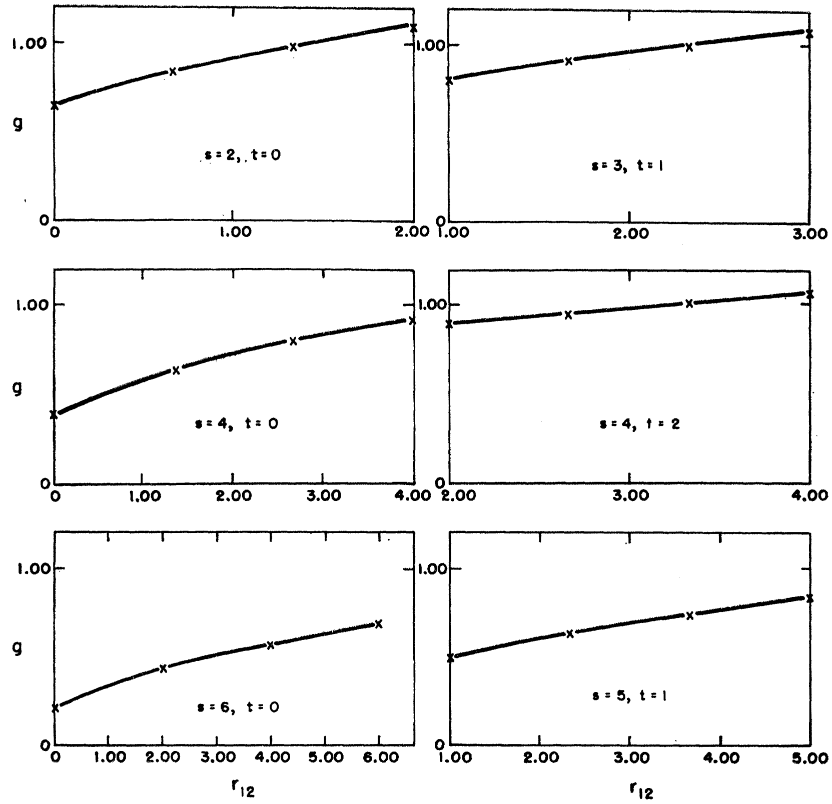

FIG. 3. The detailed structure of the Coulomb hole relative to an electron, taken from calculations by Simpson and McColl.[15] [$g(r_{12},s,t) = \psi_{\text{exact}}(1,2)/\psi_{\text{HF}}(1,2)$ where ψ_{exact} is represented by a 10-term correlated wave function.[9]]

it is useful to examine the dependence of the correlation function $g(r_{12},s,t) = \psi_{\text{exact}}(1,2)/\psi_{\text{HF}}(1,2)$ on the variable r_{12} for various values of s and t. Curves which exhibit this dependence are shown in Fig. 3.[15] The 10-term correlated wave function of Chandrasekhar and Herzberg was used to calculate the points indicated on these curves. The curves are smooth, approximately linear, and do not change very drastically as s and t are varied. This simple behavior is more precisely demonstrated by the rapid convergence of simple polynomial approximations chosen to fit the calculated points of the correlation function (indicated by crosses). Sample polynomials are

$$g(r_{12},2,0) = 0.68286 + 0.25390r_{12} - 0.017651r_{12}^2 - 0.001468r_{12}^3 ,$$

$$g(r_{12},4,0) = 0.48900 + 0.15322r_{12} - 0.013840r_{12}^2 + 0.000032r_{12}^3 ,$$

$$g(r_{12},6,0) = 0.22235 + 0.049557r_{12} - 0.004449r_{12}^2 + 0.000000r_{12}^3 .$$

These polynomial approximations do not, of course, reproduce the structure of the Coulomb hole in the neighborhood of the cusp where a small dip (not shown) may be expected. We infer this from the rather small cusp values obtained from the polynomials (see Table I, third column). However, the polynomials do reproduce the over-all structure of the correlation hole within the region where the function $r_{12}^{-1}\Delta(r_{12})$ is large and, hence, within the region where the dominant contribution to the correlation energy should occur.

In summary, the Coulomb hole in helium extends over a distance comparable to the atomic radius, is approximately spherical, smoothly dependent on position and representable by a rapidly converging series in r_{12}. These properties obviously favor a correlated wave function, quite independently of the suitability of correlated functions for representing the cusp. It should be emphasized, however, that the simple structure of the Coulomb hole has been demonstrated only for the $1s^2$ configuration. If our arguments are correct, then the success of correlated wave functions for helium cannot be extrapolated to heavier atoms. The Coulomb hole for a pair of electrons in a $2s^2$ configuration, for example, will be nonspherical because angular correlation can occur much

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[15] O. C. Simpson and D. McColl (unpublished calculations, Argonne National Laboratory). I am indebted to Dr. Simpson for permission to reproduce these curves.

more readily than radial correlation.[16,17] The Coulomb hole of an electron in an orbital φ_{nlm} with $n > 1$ and $l > 0$ may have a very complicated structure which will require an expansion in θ_{12} as well as r_{12} and which may not be rapidly convergent.

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[16] L. Szasz, Phys. Letters **3**, 263 (1963).

[17] R. McWeeny and B. T. Sutcliffe, Proc. Roy. Soc. (London) **273A**, 103 (1963).

REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

On the Spatial Correlation of Electrons in the Ground State of Helium

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IN the ground state of helium, it is well known that the greatest part of the electronic repulsion is taken into account by giving to the nucleus an effective charge such that each electron moves independently in a screened Coulomb central field. The wave function is then a product of two exponentials, the variables being only the distances r_1 and r_2 of the two electrons from the center of forces. Finer details on the correlation of the electrons and better values of the computed energy can be gained by multiplying by a power series, where the interelectronic distance r_{12} plays a dominant part. The screening constant is then replaced by an adjustable parameter. This is the way opened by the classical work of Hylleraas with considerable numerical success. Another way is the so-called method of superposition of configurations which has been discussed in particular by Löwdin and Shull[1] and combined with the first by Löwdin and Rèdei.[2] These authors have also studied the correlation between the electrons and we shall follow their notations. We intend to give here some results on the correlation as it appears after the recent developments along the Hylleraas line of thought. The unnormalized wave function has the form

$$\psi = \exp\left[-\epsilon(r_1 + r_2)\right]\varphi\,.$$

ϵ is not an adjustable parameter but has the value $(-E)^{\frac{1}{2}}$, E being the energy eigenvalue. φ is not at first a power series but a series of polynomials. In the work of Pekeris,[3] the variables are the linear combinations $\epsilon(r_2 + r_{12} - r_1)$, $\epsilon(r_1 + r_{12} - r_2)$, $2\epsilon(r_1 + r_2 - r_{12})$. In our own work[4] the variables entering into the polynomials are

$$x = 2\epsilon(r_1 + r_2)\,,\quad \rho = r_{12}/(r_1 + r_2)\,,$$
$$\tau = (r_1 - r_2)/(r_1 + r_2)\,.$$

φ is called the correlation factor. It modifies the global properties of the wave function. Table I gives some mean values computed with φ and without φ in our 27-term approximation. For the comparison of the norms, we have defined the arbitrary factor in φ by the condition

$$\varphi(x,\rho,\tau) = 1 \quad \text{for} \quad x = \rho = \tau = 0\,.$$

The exponential of the 27-term approximation or of approximations of any rank is not the best way to express an independent-electron model. The best exponential is known to be $\exp\left[-Z'(r_1 + r_2)\right]$ with $Z' = 27/16$. The difference with our $\exp\left[-\epsilon(r_1 + r_2)\right]$ is not very great, the computed total energy being -2.8477 instead of -2.8474.

To get a more detailed idea of the correlation effect, we have to study the local properties of the function φ and then of the function ψ. We meet here with a difficulty of convergence. It is true that by the Pekeris method and by our own method, one gets an "exact solution" of the Schrödinger equation, in the sense that the substitution of the series of polynomials results in recurring linear equations with a limited number of terms. The linear system is solvable within any degree of accuracy. But for isolated values of the variables the series can be only semiconvergent or perhaps divergent. For instance, the solution of Pekeris is certainly not absolutely convergent for $r_1 = r_2 = r_{12} = 0$, because no power

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[1] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956); see also Louis C. Green, Marjorie M. Mulder, C. W. Ufford, E. Slaymaker, Eleanor Krawite, and R. T. Mertz, Phys. Rev. **85**, 65 (1952).

[2] P. O. Löwdin and L. Rèdei, Phys. Rev. **114**, 752 (1959).

[3] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).

[4] P. Pluvinage, J. Phys. Radium, **16**, 675 (1955); G. Munschy and P. Pluvinage, J. Phys. Radium, **18**, 552 (1957), and **23**, 184 (1962).