

more readily than radial correlation.^{16,17} The Coulomb

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

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

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.

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 Shull¹ 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

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

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 work⁴ 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

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

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 $\exp[-Z'(r_1 + r_2)]$ with $Z' = 27/16$. The difference with our $\exp[-\epsilon(r_1 + r_2)]$ 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

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

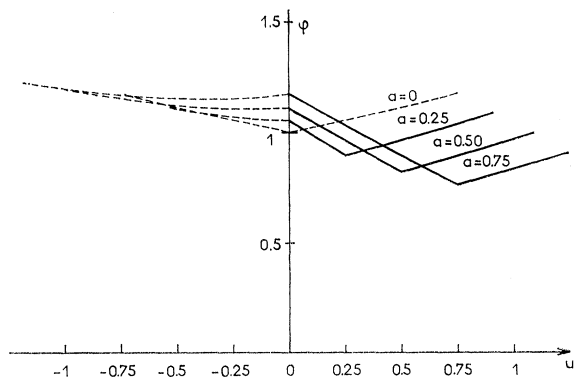


FIG. 1. The correlation factor φ for the electrons in line with the nucleus, one electron being fixed at the distance a atomic units (1 a. u. = 0.529 Å).

series in these variables is a formal solution. An inspection of our own numerical results⁴ shows that the convergence of our φ for the value $\rho = 1$ is at least weak.

With this restriction in mind we have computed the values of our 42-term approximation of φ in the following conditions: the position of the first electron is fixed on an axis $0u$ at the distance $r_1 = a$ from the nucleus. The second electron varies along the axis. In this configuration the correlation effect is clearly the strongest. Figure 1 shows four curves for

$$a = 0, \quad 0.25, \quad 0.50, \quad 0.75 \text{ a.u.}$$

For each value of a except zero, we see three regions:

$$\text{Region I. } u \leq 0, \quad x = 2\epsilon(a - u), \quad \rho = 1, \\ \tau = (a + u)/(a - u).$$

φ varies slowly. It seems that there exists a relative minimum if a is great enough. The branches of the curves are dotted, because the weakness of the convergence makes the numerical values somewhat uncertain.

$$\text{Region II. } 0 \leq u \leq a, \quad x = 2\epsilon(a + u), \\ \rho = \tau = (a - u)/(a + u).$$

The curves are nearly straight lines with negative slopes. For $a = 0$ the branch disappears. Table II gives the values of φ at the limits of the region.

$$\text{Region III. } a \leq u, \quad x = 2\epsilon(a + u), \\ \rho = -\tau = (u - a)/(a + u).$$

The curves are also nearly straight lines but the slopes are positive. They are interrupted rather

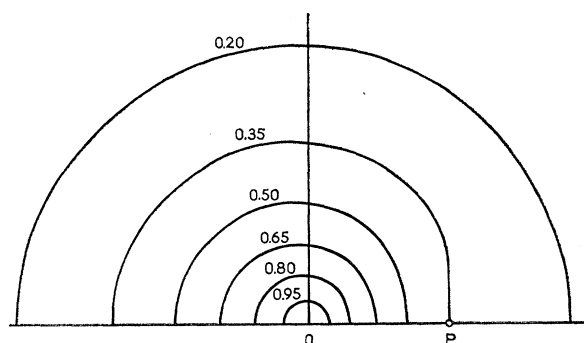


FIG. 2. Lines of equal ψ in a plane containing the nucleus and one electron fixed in P at the distance 0.50 a. u. from the nucleus. Relative values.

shortly because the convergence in x becomes soon too weak.

The three branches are separated by abrupt changes of slope. This feature is easily explained by the form of the derivatives. Thus we get a partial quantitative description of the "Coulomb hole" at the place occupied by the fixed electron.

In Fig. 2, we have selected the value $a = 0.50$, because it is not too far from the most probable value of r_1 and because the convergence in x is still strong enough. The second electron varies in the plane. Its polar coordinates are r_2 and the angle θ_{12} , which is the angle between r_2 and the $0u$ axis. We have computed the relative values of ψ and drawn some lines of equal values in the upper half of the plane. The lower half is symmetric. Without correlation, the curves would be circles with their centers at 0. With correlation, the curves are stretched in the direction opposite to the fixed electron; this feature is most marked when r_1 and r_2 are of the same order of magnitude.

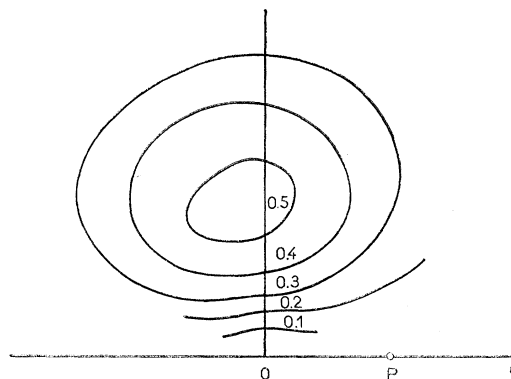


FIG. 3. Lines of equal probability of presence of the second electron at a position defined with respect to the first electron located at P . Relative values.

To get an exact idea of the probability of presence of the second electron, one must think of this graph as of the meridian section of a repartition around the Ou axis. Furthermore we have to compute ψ^2 and to multiply by the weight function $r_2^2 \sin \theta_{12}$. The lines of equal probabilities are represented in Fig. 3. Without correlation, they would be symmetric with respect to the axis $\theta_{12} = 90^\circ$. With correlation, the repelling action of the fixed electron is obvious. The conversion factor from relative to absolute values is a product

$$10^{-1}N^{-1}8\pi^2a^2 \exp(-2ea) = 0.67,$$

where 10^{-1} stands for the scale of the graph, N^{-1} for the normalization, $8\pi^2$ for the angular coordinates of the $r_1r_2r_{12}$ triangle in space, and $a^2 \exp(-2ea)$ for the density of probability of the first electron.

We thank G. Faivre for assistance in preparing Table I.

TABLE I. Mean values in atomic units without and with correlation in a 27-term approximation.

	without φ	with φ
norm	0.40312	0.53551
potential energy	-5.7511	-5.8074
$\langle r_1^{-1} \rangle$	1.7040	1.6883
$\langle r_{12}^{-1} \rangle$	1.0650	0.9458
kinetic energy	2.9037	2.9037
total energy	-2.8474	-2.9037
$\langle r_1 \rangle$	0.8803	0.9298

TABLE II. Maximum and minimum of the correlation factor for different positions of the first electron (a is in atomic units of length).

a	0	0.25	0.50	0.75
φ_0	1	1.053	1.111	1.175
φ_a	1	0.894	0.820	0.763

Discussion on The Hartree-Fock Approximation

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LÖWDIN: I would like to comment on some peculiarities with respect to the symmetry properties. In the original atomic Hartree calculations [D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928); Repts. Prog. Phys. **11**, 113 (1948); *Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957)] it was assumed that the resulting orbitals would be symmetry-adapted and, in the calculations, the corresponding self consistent field potentials would always be replaced by their spherically symmetric part. The scheme was essentially refined when Slater [J. C. Slater, Phys. Rev. **35**, 210 (1930)] and Fock [V. Fock, Z. Physik **61**, 126 (1930)] suggested that the total wave function Ψ should be approximated by a single determinant built up from spin-orbitals, and the application of the variation principle lead then to the famous Hartree-Fock equations [V. Fock, Z. Physik **61**, 126 (1930)]. It seems to have been generally assumed that, if the total Hamiltonian H for the many-electron system had a certain symmetry property then the Hartree-Fock functions will also automatically be symmetry-adapted.

Delbrück [M. Delbrück, Proc. Roy. Soc. (London) **A129**, 686 (1930)] proved that, if the total system is spherically symmetric and one requires the total determinant to have 1S character, then the associated orbitals are eigenfunctions of the orbital angular momentum and of the spin. In the case of more general types of symmetry occurring in molecular and solid-state systems, it has later been proven [C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960); P. O. Löwdin, J. Appl. Phys. Suppl. **33**, 251 (1962)] that the assumption that the Hartree-Fock functions are symmetry-adapted, i.e., form a basis for the irreducible transformation, is always *self-consistent* and corresponds to a specific minimum of the total energy. The question I would like to raise is whether this is really an *absolute minimum* or not?

The question whether the extreme values of $\langle H \rangle$ associated with the variation principle are maxima, minima, or terrace points has been studied in some detail [D. J. Thouless, Nuclear Phys. **21**, 225 (1960); W. H. Adams, Phys. Rev. **127**, 1650 (1962)]. Adams uses the term "absolute minimum" to denote a point where the second variation of the total energy is positive definite, whereas we have here used the term to denote the lowest one of all possible minima. So far, however, there has not been found any simple criterion which guarantees the occurrence of an absolute minimum lower than any other possible minima.