

VISUALIZATION OF ELECTRON CORRELATION IN GROUND STATES OF He AND H⁻

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For the ground states of He and H⁻, conditional probability densities $d(r_2, \theta_{12} | r_1)$ for finding two electrons in different relative positions have been calculated for several wavefunctions including simple one-configuration wavefunctions and Hylleraas–Kinoshita type functions. The calculations, including graphing, were all carried out on a desktop computing calculator.

A long-standing goal in the interpretation of the electronic structure of atoms has been a means to portray the spatial effects of electron correlation. This note presents such a portrayal with examples drawn from H⁻ and He. The conditional probability density $d(r_2, \theta_{12} | r_1)$ for finding one electron at a distance r_2 with angle θ_{12} between the vectors r_1 and r_2 , when the other electron is at a distance r_1 from the nucleus, is the function chosen to depict the correlation of two electrons. With $d(r_2, \theta_{12} | r_1)$, we can compare wavefunctions of different qualities, see what roles long-range and short-range correlation play in various states, exhibit the relative importance of angular and radial correlation and compare correlation in different atomic systems. Many types of functions have been used to study electron correlation in atoms [1]; the strength of the conditional probability density lies in its retention of all information contained in $|\psi|^2$ about the *relative* positions of two electrons and the nucleus. Moreover it is cast in terms of variables which make correlation easy to see with traditional graphing techniques.

The discovery of a practical means for analytic reduction of approximations of $|\psi(r_1, r_2)|^2$ to the joint probability density $\rho(r_1, r_2, \theta_{12})$ has opened the way to efficient computing of $d(r_2, \theta_{12} | r_1)$ [2]. The computational exploration of the conditional probability density has been facilitated immeasurably by the availability of a fast, economical means [3] to compute accurate Hylleraas–Kinoshita [4] wavefunctions for the two-electron atoms.

The conditional probability $d(r_2, \theta_{12} | r_1)$ is obtained for $r_1 = r_1^0$ as

$$d(r_2, \theta_{12} | r_1^0) = \rho(r_1 = r_1^0, r_2, \theta_{12}) \times \left[\int_0^\pi r_2^2 dr_2 \int \sin \theta_{12} d\theta_{12} \rho(r_1 = r_1^0, r_2, \theta_{12}) \right]^{-1}$$

For the simple two-electron wavefunction of any angular momentum, if the angular dependence is expressed in terms of Euler angles or spherical polar angles, and if the radial dependence is in terms of a finite expansion of products of positive or negative powers of r_1 , r_2 , $r_1 + r_2$, and r_{12} then $\rho(r_1, r_2, \theta_{12})$ can be obtained exactly in closed form.

The following discussion explores correlation in the ground states of helium and the hydride ion. Elsewhere we examine correlation (primarily angular) for doubly-excited states of helium as a function of angular momentum and principal quantum number using very approximate wavefunctions [2]. A longer report will amplify the discussion of the ground states, and will consider the $1s2s\ ^1S$ and 3S bound states and the $(2s)^2$ and $(2p)^2$ Feshbach resonances of helium [5]. It is our intention to describe subsequently correlation in accurate representations of states of higher angular momentum.

The wavefunctions we have analyzed are of two types. One is the configuration interaction mixture (CI), based on atomic orbitals; for the CI functions for the ground state of helium, we used functions generated by Holþien [6]. The other is the Hylleraas–

Kinoshita type [4] generated for present purposes as a series from one to 26 terms. The program to generate the functions, which operates on a Hewlett-Packard 9825a desk-top calculator, was developed by Roothaan and England [3]. The 26 terms represent an arbitrary cut-off; most of the qualitative details seen in the graphs are clearly present after the inclusion of the most important eight terms. However, the 59-term series has been developed by Roothaan and England with this program. The 26-term function gives an energy of -2.903722 hartree for the ground state of helium while the value estimated by Pekeris [7] from extrapolation with a 1078-term function is -2.903724 . The difference is less than one part in 10^7 . For H^- , the 26-term function gives -0.527741 while the best estimate by Pekeris [7] is -0.527751 hartree, extrapolated from a 444-term function.

We turn now to the substantive results of the analysis. Fig. 1 a is a plot of $d(r_2, \theta_{12} | r_1)$ for the ground state of helium. The peak at the origin is characteristic of S-states and tends to obscure some of the important features of electron correlation; hence all further figures presented here show $r_2^2 d(r_2, \theta_{12} | r_1)$,

which includes the radial factor r_2^2 from the jacobian. Despite its strong peaking, the plot in fig. 1 a, based on our most accurate wavefunction, shows two important features of electron correlation: the kink in the function for $\theta_{12} = 0$ and $r_1 = r_2$, which we will term the "Coulomb hole", and a long-distance polarization effect, which appears as the lopsidedness of the curves of constant r_2 . We have not used previously quantified definitions of the Coulomb hole [8], but rather are relying on the intuitive concepts made obvious by series of graphs. For the helium ground state, as one electron is brought in from long distance the probability density of the remaining electron develops a distinct polarization (space limitations prevent presentation of a series of such graphs here). As the approaching electron begins to enter appreciable core density, the polarization remains relatively unaffected but something new appears in the density surface, a local cusp — our Coulomb hole. Fig. 1 b shows this cusp much more clearly than fig. 1 a. As electron 1 is moved through the polarized core density of electron 2, one can see the Coulomb hole move with it. Note that the Coulomb hole is a cusped dip

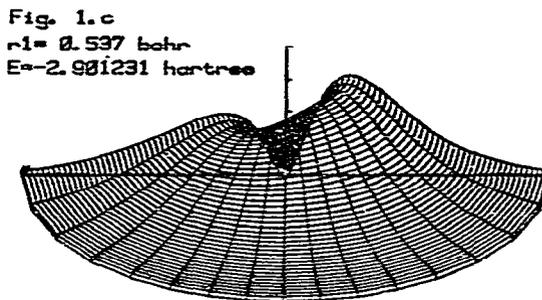
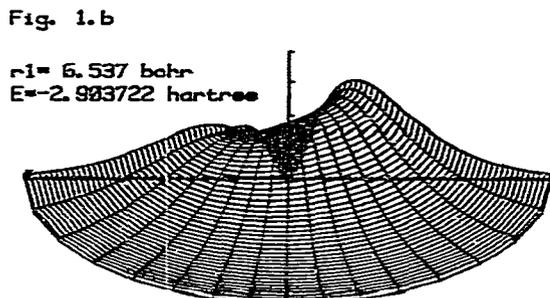
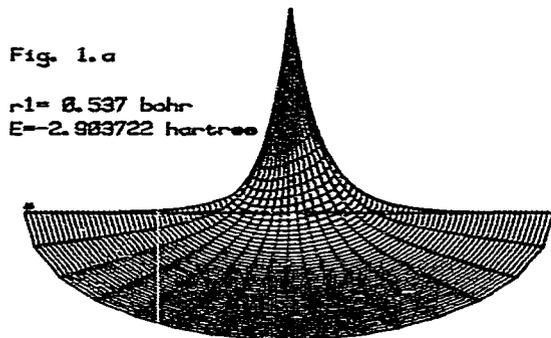


Fig. 1. Three representations of the conditional probability density d for the helium ground state with electron 1 fixed at its most probable value of 0.537 bohr. Both (a) and (b) are perspective projections of $d(r_2, \theta_{12} | r_1 = 0.537)$ in cylindrical polar coordinates for a 26-term Hylleraas-Kinoshita function with energy $= -2.903722$ hartree. The density is measured on the vertical axis in units of 1 for (a) and in units of 0.1 for (b). Distance is measured from the nucleus in units of 0.05 bohr out to a maximum of 2.5 bohr. The inter electronic angle sweeps from zero radians, denoted by an asterisk, at the left of the graph to π radians at the right. The curves are curves of constant r_2 and θ_{12} . (a) excludes the $r_2^2 \sin \theta_{12}$ jacobian factor. (b) is the same function as in (a) but with the r_2^2 jacobian factor included. (c) is Holáion's many-configuration function in the same projection as (b).

with finite, nonzero amplitude; that it has this form was shown analytically by Pluvineg [9] and by Roothaan and Weiss [10]. The wavefunction has a discontinuous derivative at $r_{12} = 0$ due to the repulsive Coulomb singularity in the hamiltonian at that point. Fig. 1c is the 20-configuration approximation to the helium ground state generated by Holþien [6]. Including hydrogenic configurations through the $(4d)^2$ configuration, one observes that this CI basis accounts well for the long-range polarization effects seen in fig. 1b, but is lacking in the high frequency terms necessary to approximate the hole region either qualitatively or quantitatively.

Fig. 2 shows cartesian plots of $d(r_2, \theta_{12} | r_1)$ for a succession of wavefunctions, essentially in order of improving quality, as measured by their energy expectation values. all for $r_1 = 1$ bohr. The first is the

$(1s)^2$ configuration which has no angular correlation and no Coulomb hole. The variationally determined exponent has the effect of introducing a small amount of radial correlation that pushes total electron density away from the nucleus and hence the two electrons away from each other. The second function is the simplest Hylleraas function, the $(1s)^2 + r_{12}$ "configuration". Aside from a marked improvement in the energy, one can see both a nascent kink at one bohr as well as marked long-range angular correlation; our limited experience with several states of He and the ground state of H^- suggests that functions with only a few terms introduce too much angular correlation. Fig. 2c is a CI function including a $(2p)^2$ term as well as $(1s)^2$ and $(2s)^2$. This function exhibits long-range angular correlation much better than the preceding function, but it again, like all CI functions, has a basis

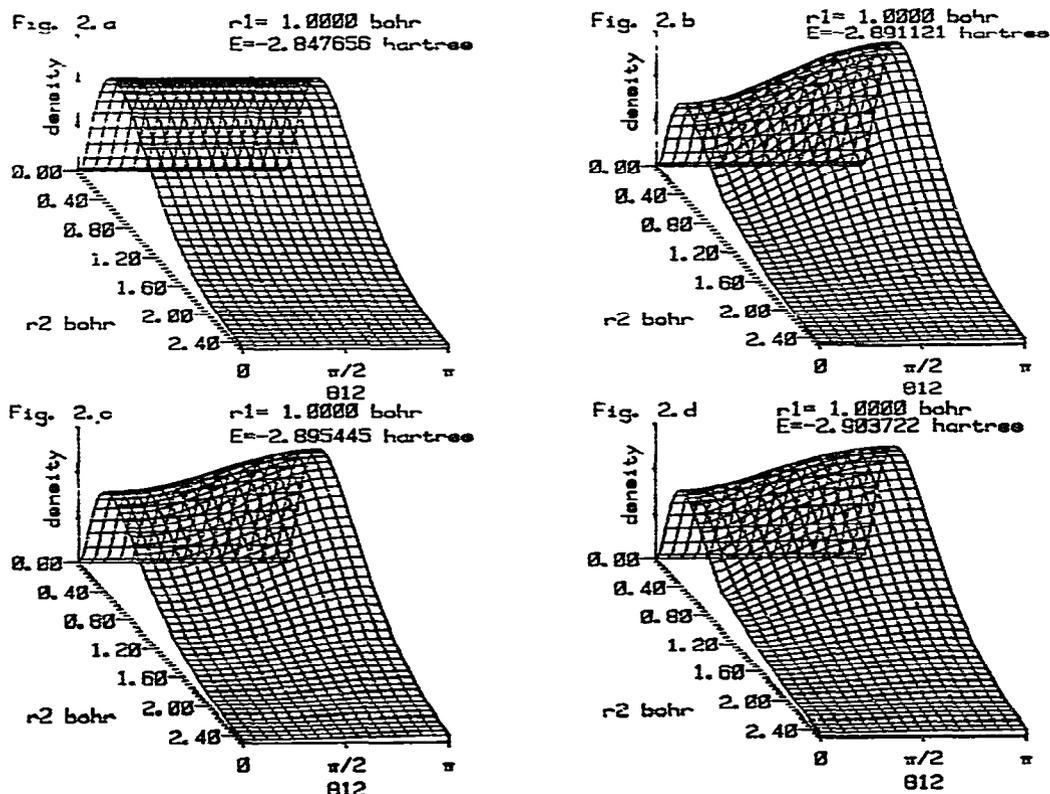


Fig. 2. Cartesian graphs of the conditional probability density for four different approximations to the ground state of helium. (a) is the $(1s)^2$ configuration showing no polarization, and no Coulomb hole. (b) which is the $(1s)^2 + r_{12}$ configuration and (c) which is the $(1s)^2 + (2s)^2 + (2p)^2$ function show how the inclusion of terms determine both of these properties to a large extent when compared with the "exact" 26-term result seen in (d).

of one-electron functions lacking the short wavelength terms that would be necessary to generate a Coulomb hole. (Anticipating ref. [5], we have found that the CI representation of the He $(2p)^2$ Feshbach resonance [6] does generate a large depression in $d(r_2, \theta_{12} | r_1)$ when r_1 is near its most probable value or greater. This large, broad depression, as well as the cusped Coulomb hole, occurs with the more accurate multiterm expansions of the Hylleraas–Kinoshita basis.) The additional terms that we add to those of fig. 2c to generate fig. 2d and reduce the energy from -2.895445 to -2.903722 hartree tend largely to reduce the angular correlation and to spread the conditional probability over a larger volume. The conditional probability in figs. 1b and 2d is probably indistinguishable to the eye from that of any more exact function.

The H^- ion is perhaps the most dramatic example in which electron correlation determines the properties of the species. Fig. 3 gives two graphs of the H^- ion, one where an electron is fixed at its expected value and another with the electron at its most probable value. The most striking characteristic of these graphs is the

Fig. 3.a

$r_1 = 1.176$ bohr
 $E = -0.527742$ hartree
 $S = 0.51729$

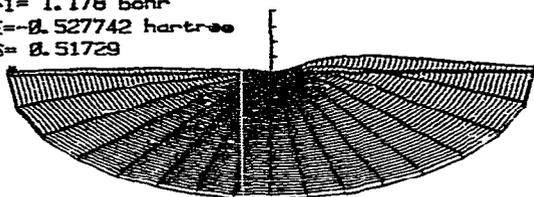


Fig. 3.b

$r_1 = 2.787$ bohr
 $E = -0.527742$ hartree
 $S = 0.29279$

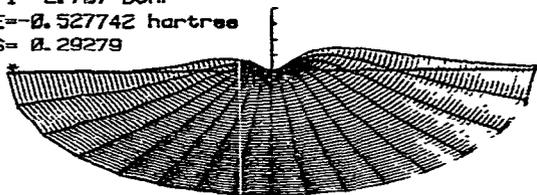


Fig. 3. Conditional probability densities for the H^- ion out to a maximum radial distance of 5 bohr. (a) fixes r_1 at its average value, $\langle r_1 \rangle$. The value, S , is proportional to the probability that an electron 1 actually attains the specified distance from the nucleus. Here the probability that an electron takes on its most probable value is 1.8 times larger than the probability that it takes on its expected value. The density on the vertical axis is in units of 0.1.

extreme spatial diffuseness of H^- relative to that of He. In his description of correlation in H^- , Chandrasekhar [11] showed graphically how some angular correlation would occur when one electron takes on its most probable value and the other (now inner) electron is at its most probable value conditional on the other electron being at the most probable r . (This calculation was based on a two-term function, $(1s)^2$ plus a Hylleraas r_{12} term.) Later, Roothaan and Weiss [9] developed a wavefunction for H^- that was used by one of us [12] as a basis to interpret H^- as being much like a polarized hydrogen atom with an extra electron, rather than being like a swollen helium atom. The graphs of fig. 3 tell us that the picture presented by Chandrasekhar, nearly correct as it is, fails to convey the diffuseness, the spread-out character of H^- . Specifically, by looking at fig. 3a where one electron is fixed at its most probable value, one can appreciate how little the conditional probability differs from the surface in fig. 3a when the electron is located at many other probable values. Moreover if we compare $d(r_2, \theta_{12} | r_1)$ of fig. 3a with fig. 1b we do see similar pictures differing basically in the swollenness of the hydride ion. When however the fixed electron is located at its expected value (fig. 3b), H^- represented with enough accuracy does look somewhat like a polarized hydrogen atom.

The conditional probabilities shown graphically here can, of course, be generated as numerical functions, and the information in them can be reduced to a few quantitative data such as distributions of r_2 and θ_{12} , moments of r_2, θ_{12}, r_{12} or joint moments. However, in our brief experience with these probabilities, we seem to gain more insights from graphs than from numerical tables. Such tables can be supplied upon request.

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