Correlation in Helium-Like Atoms*

C. W. Ufford and Jeannette G. Thomas
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania
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In order to test the Z dependence of Wigner's correlation potential when applied to atoms, the effect of electron correlation has been calculated for the ground-state energy of helium-like atoms with $Z=1$ to 10, using hydrogen-like wave functions in first-order perturbation theory. The results are compared with the difference between the self-consistent field calculations and the observed values. The agreement is sufficiently good to show that this type of potential should give satisfactory results when used with a self-consistent field wave function in more complicated atoms.

WHENEVER calculations in atomic spectra fail to agree with experiment it is usually suggested that the discrepancy may be accounted for by the correlation between the electrons which has not been taken into account. Mitler[1] has considered the effect of a correlation potential given by Wigner,[2] on the ground-state energy of helium. Before extending calculations of this type to more complicated atoms, it is of interest to see whether this potential has the proper dependence on the atomic number Z.

Since we are interested in the dependence of the potential on the atomic number rather than in calculating a correct value of the correlation energy we use hydrogen-like radial wave functions for $1s^2$ for simplicity. We have to compute

$$\int V(r)P^2(1s)dr\,, \tag{1}$$

where

$$V(r)=0.576/(5.1+r_s)\mathrm{Ry}\,, \tag{2}$$

and

$$r_s=3^{1/3}[8\pi|u|^2]^{-1/3}. \tag{3}$$

The radial function, $P(1s)$ is normalized in the sense

$$\int P^2(1s)dr=1\,, \tag{4}$$

$$P^2(1s)=4\pi r^2|u|^2. \tag{5}$$

The radial function $P(1s)$ may be taken from Condon and Shortley[3]

$$P(1s)=-2Z^{3/2}re^{-zr} \tag{6}$$

in atomic units. The integral in (1) may then be written as

$$I=(0.576/10.2)\int_0^\infty[1+3^{1/3}(10.2Z)^{-1}e^{y/3}]^{-1}y^2e^{-y}dy. \tag{7}$$

With $Z=1$ to 10, we obtain the results for I given in Table I. The value of 0.0931 Ry for $Z=2$ compared to the value 0.0895 Ry of Mitler shows that the correlation energy is not excessively sensitive to the radial wave function used. Figure 1 shows a plot of the correlation energies of Table I against $1/Z$. We see that the correlation energy as given by (1) varies with $1/Z$ roughly as do the values calculated from the self-consistent field. There is no reason to believe that potentials of the type (2) should be excluded in future work on correlation energy in heavier atoms for lack of

TABLE I. Correlation energy in He-like atoms in rydbergs.

Z	Roothaan & Weiss[a]	Eq. (1)
1	0.07967	0.0803
2	0.08411	0.0931
3	0.08700	0.0986
4	0.08854	0.1017
5	0.08948	0.1037
6	0.09012	0.1050
7	0.09058	0.1061
8	0.09092	0.1068
9	0.09118	0.1074
10	0.09139	0.1080

[a] C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. 32, 194 (1960), Table V.

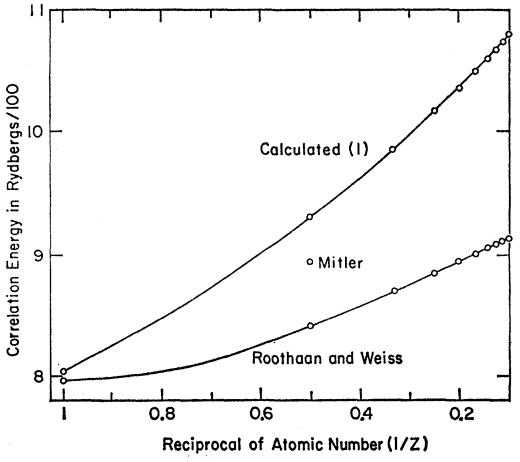

FIG. 1. Correlation energy in He-like atoms.

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[1] Henri Mitler, Phys. Rev. 99, 1835 (1955).
[2] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).
[3] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), Table 15.

proper Z dependence in two electron atoms. The absolute difference of the curves in Fig. 1 is not large. This much difference might well be expected from the type of potential and wave function used in this calculation where the purpose was to test the Z dependence of a particular type of correlational potential.

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Model for the Statistical Atom with Nonvanishing Angular Momentum*

JUDAH L. SCHWARTZ† AND SIDNEY BOROWITZ
Physics Department, New York University, New York, New York
(Received 4 April 1963)

In the first of the coupled integro-differential equations satisfied by the Green's functions of the many-body system the Hartree–Fock approximation is made for the two-particle Green's function. The resulting equation is written in a mixed position-angular momentum representation in such a way that use may be made of whatever empirical information about the angular momentum of the system is available. In the mixed position-angular momentum representation the one-particle Green's function appears as a sum of terms each of which corresponds to a different value of the angular momentum. For the principal groups of the periodic table in which the angular momentum of the atom is carried by either one, two, or three electrons added to or missing from a closed shell the appropriate terms in the expression for the one-particle Green's function are identified. The first of the coupled integro-differential equations for the Green's functions is then solved to lowest order in $\hbar$ in the manner indicated by Baraff and Borowitz. The result is a modified Thomas–Fermi model that differs from the previous results of Sessler and Foley for the same problem. The Sessler–Foley modification of the Thomas–Fermi atom is rederived in the spirit of the cranking model for the nucleus by spinning the potential. The present formalism is seen to lead to the Sessler–Foley result in the limit of many particles carrying the angular momentum. However, the region of validity of the cranking model in the nucleus lies far removed from the magic numbers where there are many nucleons outside a spherical core. Thus, the Sessler–Foley result may be interpreted as a kind of cranking model of the atom. In contrast to the previous work the present formalism yields a sign change for the quadrupole coupling constant on passing through closed shells and calculated values for the quadrupole coupling constant of the halogens are seen to be within an order of magnitude of the accepted values.

I. INTRODUCTION

THE model of Thomas[1] and Fermi[2] allows one to calculate a density distribution of electrons in an atom by assuming that at each point in the atom, the electrons constitute a degenerate Fermi gas. The energy of the system is written in terms of the density and minimized subject to the condition that the number of electrons is constant. One is naturally led to ask about the utility of this model for describing other properties of the atom, for example, the angular momentum.

One suspects that a straightforward inclusion of angular momentum in the Thomas-Fermi model will lead to unsatisfactory results. For one thing, the assumed density in momentum space in this model is symmetric with respect to the origin. It thus possesses no net linear or angular momentum. For another, the only angular momentum in a statistical system compatible with a fixed energy is a rigid rotation about a fixed axis. This model is at variance both with the assumed density and with the known angular momentum distribution in real atoms.

To overcome the first (but not the second) difficulty, Sessler and Foley[3] were led to displace the distribution in momentum space from the origin by a position-dependent amount. This assumption used in the procedure similar to the original derivation of the Thomas-Fermi model yields a spherical atom spinning rigidly about a fixed axis.[4] This result may also be derived by spinning the nuclear potential in analogy to the nuclear cranking model of Inglis.[5,6]

A satisfactory approach might be to restrict the phase-space density in the statistical model to a fixed energy and total value of the angular momentum. This is a difficult problem in the conventional formulation of the Thomas-Fermi model. Recently, however, Baraff and Borowitz[7] have derived the Thomas-Fermi model of the atom from the many-body Schrödinger equation

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† Present address: Lawrence Radiation Laboratory, University of California, Livermore, California.

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[2] E. Fermi, Z. Physik **48**, 73(1928).

[3] A. M. Sessler and H. M. Foley, Phys. Rev. **96**, 366 (1954).

[4] See, for example, L. Landau and Ya. Smorodinsky, *Lectures on Nuclear Theory* (Plenum Press, New York, 1959), Chap. 6 for an ample discussion of the fact that a spherical quantum mechanical system cannot rotate.

[5] D. Inglis, Phys. Rev. **96**, 1059 (1954).

[6] D. Inglis, Phys. Rev. **97**, 701 (1955).

[7] G. A. Baraff and S. Borowitz, Phys. Rev. **121**, 1704 (1961).