PHYSICAL REVIEW A VOLUME 1, NUMBER 1 JANUARY 1970

Single-Parameter Free-Electron Exchange Approximation in Free Atoms*

E. A. Kmetko

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

(Received 13 June 1969)

The optimum scale factor for the Slater free-electron exchange approximation for atoms has been obtained by minimizing the total electronic energy. In general, the scale factor lies between the Slater and the Gaspar-Kohn-Sham limit of 1 and $\frac{2}{3}$, respectively. The variation that occurs as the different shells are populated is qualitatively understandable in terms of the inhomogeneity of the over-all charge distribution.

INTRODUCTION

Slater[1] suggested that the exchange portion of the Hartree-Fock potential in atoms and solids be approximated by

$$V_{xs} = -6[(3/8\pi)\rho(r)]^{1/3}, \tag{1}$$

where $\rho(r)$ is the charge density at r and the spins are matched. The derivation consisted of two steps: (i) the Hartree-Fock (HF) potential was replaced by an averaged potential, and (ii) this averaged potential was replaced by the expression for the exchange potential of a homogeneous free-electron gas. Later, Gaspar,[2] followed by Kohn and Sham,[3] applied the variational method to the Thomas-Fermi atom and derived a similar expression differing from Slater's only by a factor of $\frac{2}{3}$. Neither the Slater nor the Gaspar-Kohn-Sham (GKS) potential gives results that are in complete agreement with those of a true HF calculation or experiment, and it has become rather common to use a scaled, Slater free-electron approximation

$$V'_{xs} = \alpha V_{xs}, \tag{2}$$

where α is a fitting parameter. In almost all of the known cases, α lies between the Slater and GKS limits of 1 and $\frac{2}{3}$, respectively. Berrondo and Goscinski[4] have indicated that, in general, the virial theorem is not fulfilled by an approximate exchange potential of the Slater type. However, by introducing a scaling factor, α in Eq. (2), it is possible to obtain a solution having a lower total energy and thus satisfy the virial theorem. Wood[5] has optimized the scaled exchange potential [Eq. (2)] for elements of the iron group with gratifying results. Rosén and Lindgren[6] used two adjustable parameters in a modified free-electron expression and obtained total energies remarkably close to the HF results. More recently, however, Herman, Van Dyke, and Ortenburger[7] developed an improved expression for the free-electron exchange by adding an inhomogeneity correction term similar to that of Weizsäcker for the statistical atom model. Their treatment thus avoids the necessity for optimizing the scale factor. In spite of this most recent advance in treating the exchange potential, examination of the inhomogeneity in the charge distribution of free atoms in terms of the single-parameter expression, which would in essence give a lumped sum or averaged effect of the Herman-Van Dyke-Ortenburger inhomogeneity correction, appeared likely to be productive of useful information. It would be reasonable to expect that occupation of the various shells would result in an interesting variation reflecting the building up of the atomic system.

METHOD

The scale factor α was determined for all atoms from helium to lawrencium by minimizing the total electronic energy, thus optimizing the exchange potential. A modified Herman and Skillman[8] program provided the nonrelativistic self-consistent solutions of the Hartree-Fock-Slater equation, and an elaboration of Zare's[9] integral program was used to obtain the various energy integrals involving the self-consistent-field SCF functions. This method was followed for the case where Latter's self-energy correction was included to provide the correct one-electron potential at larger radii, as well as where it was omitted.

RESULTS AND DISCUSSION

The features and regularities in the variation of the scale factor with atomic number, evident in Fig. 1, are summarized as follows: (i) Addition of s or p electrons causes the scale factor to decrease, the former having the stronger effect, as is indicated by the rather sharp minima at the alkali and alkaline-earth atoms. On the other hand, d and f electrons generally cause α to increase. (ii) The scale factor is largest for helium ($\alpha = 1.004$), but seems to approach the GKS limit as the atomic number becomes large. (iii) Omission

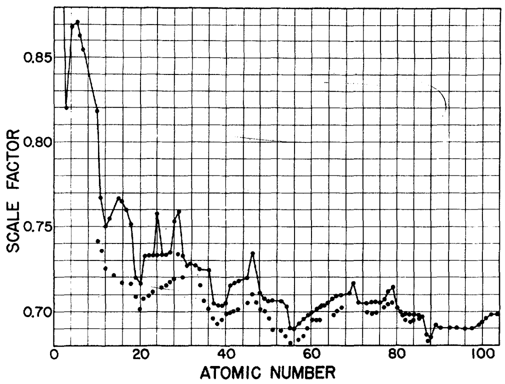

FIG. 1. Dependence of the optimum scale factor for the free-electron exchange versus the atomic number. The Latter self-energy correction to the potential was used to obtain those points connected by the solid line; the isolated points were calculated without this correction. The higher value shown for Cr ($Z=24$) is for the configuration $3d^4 4s^2$; the lower value corresponds to the ground state $3d^5 4s$.

of the Latter self-energy potential correction invariably results in smaller values for α.

The work of Herman *et al.*[7] indicates that inhomogeneity causes the local one-electron potential to increase in magnitude, and hence drive the average, as reflected by α, above the GKS limit. The over-all decrease in α with increasing Z thus shows that the electron gas becomes generally less inhomogeneous as the atomic number increases. With the exception of helium and the alkali and alkaline-earth elements, the distance from the nucleus to the outermost principal maximum in the charge distribution is rather uniform.[10] Thus, as more electrons are packed into a sphere of reasonably constant volume, the effect of the various nodes and antinodes is to smear out the charge distribution and make it increasingly smoother. There must be exceptions, however, when either d or f electrons with their sharp interior maxima are added, as is indicated in Fig. 1. Among the atoms studied, helium has by far the tightest and consequently the least homogeneous charge distribution, which is reflected in its large scale factor. As the higher s shells are populated, however, the charge becomes spread out and smoothed by virtue of the broad extents of both the outermost and principal maxima, and α decreases. The case of Cr is interesting because it has one less $4s$ electron than its neighbors. Both the loss of an s electron as well as the gain of a d electron act to increase the gradients in the charge distribution. The scale factor for Cr with the configuration $3d^5 4s$ is significantly larger than that of its neighbors as well as of the same atom in the configuration $3d^4 4s^2$, as seen in Fig. 1. The flatness of the curve of α versus Z at the beginning of the $5f$ series may reflect the fact that the $5f$ orbitals are not nearly so compact as the $4f$; typical rare-earth chemical behavior is not manifested until Cm is reached. The $5f$ shell, however, contracts more rapidly with increasing Z than does the $4f$ in the rare-earth series, with the result that the charge distributions of the $5f$ electrons may initially be rather ineffective in decreasing the homogeneity of the over-all charge distribution.

Omission of the Latter potential causes the one-electron potential to approach zero exponentially rather than Coulombically. The effect of the omission is to push the outer maxima slightly inward, as well as to diminish the amplitudes of the tails. This tends to homogenize the charge distribution in the outer reaches of the atom and to decrease α slightly toward the GKS limit, as shown in Fig. 1.

Optimization of the single-parameter free-electron exchange approximation in atoms, in spite of some shortcomings, nevertheless gives considerable insight into the way exchange is influenced by the electrons in the various subshells. It would seem that, where electrons of lower angular momentum are involved, the single-parameter approach still can provide a reasonably good approximation.

ACKNOWLEDGMENTS

The author is indebted to J. H. Wood and A. M. Boring of this Laboratory for much valuable counsel, and to F. W. Schonfeld for encouragement.

---

[*] Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. C. Slater, Phys. Rev. 81, 385 (1951).

[2] R. Gaspar, Acta Phys. Hung. 3, 263 (1954).

[3] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1966).

[4] M. Berrondo and O. Goscinski, University of Upsala, Report No. 198, 1967 (unpublished); Phys. Rev. (to be published).

[5] J. H. Wood, Intern. J. Quant. Chem. (to be published).

[6] A. Rosén and I. Lindgren, Phys. Rev. 176, 114 (1968).

[7] F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Letters 22, 807 (1969).

[8] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[9] R. N. Zare, Joint Institute for Laboratory Astrophysics, University of Colorado, Report No. 80, 1966 (unpublished).

[10] J. T. Waber and D. T. Cromer, J. Chem. Phys. 42, 4116 (1965).