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Application of a Self-Consistent Scheme Including Exchange and Correlation Effects to Atoms*

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Self-consistent schemes including approximations to exchange and correlation proposed by Kohn and Sham are applied to computing atomic energies and densities. These quantities, with and without the correlation correction, are obtained and compared with the results of calculations using the Slater exchange hole or the Hartree-Fock method and with experimental values. The present method, without correlation, gives slightly better results for energies and substantially better results for densities than Slater's method. This was anticipated in the general theory. The correlation corrections of the present scheme are not very good, presumably because the electronic density in atoms has too rapid a spatial variation.

I. METHOD

A SELF-consistent-field method has been proposed by Kohn and Sham[1] which takes into account approximately exchange and correlation effects. We present here the calculation of some atomic properties using this scheme and compare the results with experimental measurements in the hope of throwing some light on the applicability of this self-consistent method to atoms. If, in this scheme, we take out terms corresponding to the correlation effect, we have an approximation to the Hartree-Fock method. Slater's exchange hole[2] presents another approximation. The difference between Slater's method and ours has been discussed in Ref. 1. Comparison of the numerical results of both methods with the Hartree-Fock calculation is presented here.

Our computation consists in solving the set of self-consistent equations (in atomic units):

$$\{-\tfrac{1}{2}\nabla^2+\varphi(\mathbf{r})+v_{\mathrm{xc}}(\mathbf{r})\}\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r}),\tag{1}$$

where the electrostatic potential for a nucleus with charge Z is given by

$$\varphi(\mathbf{r})=-\frac{Z}{r}+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}',\tag{2}$$

the density for an atom with N electrons is

$$n(\mathbf{r})=\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2,\tag{3}$$

and $v_{\mathrm{xc}}(\mathbf{r})$ represents the effects of exchange and correlation,[1]

$$v_{\mathrm{xc}}(\mathbf{r})=\mu_{\mathrm{x}}(n(\mathbf{r}))+\mu_{\mathrm{c}}(n(\mathbf{r})).\tag{4}$$

$\mu_{\mathrm{x}}(n)$ and $\mu_{\mathrm{c}}(n)$ are, respectively, the exchange and correlation contributions to the chemical potential of a system of interacting electrons with uniform density n. It is well known that

$$\mu_{\mathrm{x}}(n)=-(3n/\pi)^{1/3}.\tag{5}$$

For $\mu_{\mathrm{c}}(n)$, we interpolate between the low-density formula of Wigner and the high-density one of Gell-Mann and Brueckner.[3] The results as a function of r_s are shown in Fig. 1.

The total energy is given by

$$E=\sum_{i=1}^{N}\epsilon_i-\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\int n(\mathbf{r})\{\epsilon_{\mathrm{xc}}(n(\mathbf{r}))-v_{\mathrm{xc}}(n(\mathbf{r}))\}d\mathbf{r},\tag{6}$$

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[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

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

[3] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

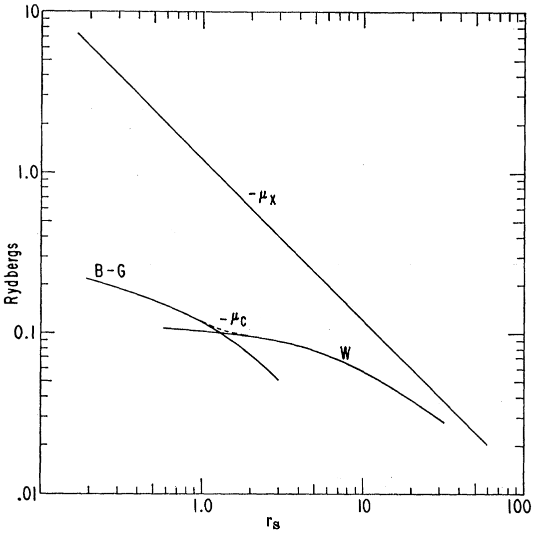

FIG. 1. Exchange and correlation contributions to the chemical potential of the homogeneous electron gas.

where $\epsilon_{\mathrm{xc}}(n)$ is the exchange and correlation energy per electron of the system of interacting electrons with uniform density n:

$$\epsilon_{\mathrm{xc}}(n)=\epsilon_{\mathrm{x}}(n)+\epsilon_{\mathrm{c}}(n)\,, \tag{7}$$

and

$$\epsilon_{\mathrm{x}}(n)=-\tfrac{3}{4}(3n/\pi)^{1/3}\,, \tag{8}$$

$\epsilon_{\mathrm{c}}(n)$ being obtained by an interpolation scheme as $\mu_{\mathrm{c}}(n)$.

Results of computation by the scheme described above will be designated by KS-XC. If we want to drop the correlation effects, then in place of Eq. (4) we use

$$v_{\mathrm{x}}(\mathbf{r})=\mu_{\mathrm{x}}(n(\mathbf{r})) \tag{9}$$

and in Eq. (6), ϵ_{xc} and v_{xc} have to be replaced by ϵ_{x} and v_{x}. This scheme will be denoted by KS-X. In the Slater approximation,

$$v_{\mathrm{x}}(\mathbf{r})=2\epsilon_{\mathrm{x}}(n(\mathbf{r}))=\tfrac{3}{2}\mu_{\mathrm{x}}(n(\mathbf{r}))\,. \tag{10}$$

This scheme will be denoted by S.

TABLE I. Total energies (in rydbergs).

Atoms	Expt	KS-XC	KS-X	S	HF
He	− 5.807	− 5.651	− 5.447	− 5.404	− 5.723356[b]
Ne	− 257.880	− 256.349	− 254.986	− 254.764	− 257.09396[b]
Ar	−1055.21	−1051.709	−1049.027	−1048.702	−1053.63410[b]
Kr		−5499.947	−5493.686	−5492.976	−5504.1086[b]
Li	− 14.956	− 14.656	− 14.349	− 14.303	− 14.865452[b]
Na	− 324.521	− 322.768	− 321.258	− 321.041	− 323.71714[b]
K	−1199.97	−1196.215	−1193.387	−1193.061	−1198.32894[b]
Rb		−5872.321	−5865.889	−5865.185	
Rb$^+$		−5872.002	−5865.618	−5864.930	−5876.440[c]
O	− 150.069[a]	− 148.861	− 147.851	− 147.696	− 149.5388[a]

[a] References 6 and 7. Averaged over spin multiplet.
[b] Reference 6.
[c] R. E. Watson and A. J. Freeman, Phys. Rev. **124**, 1117 (1961).

TABLE II. Exchange energies (in rydbergs).

Atoms	$E_{\mathrm{x}}=\int\epsilon_{\mathrm{x}}n d\mathbf{r}$	$\Delta E_{\mathrm{x}}=E_{\mathrm{HF}}-E_{\mathrm{KS\text{-}X}}$	$\dfrac{\Delta E_{\mathrm{x}}}{(E_{\mathrm{x}}+\Delta E_{\mathrm{x}})}$ (%)
He	− 1.707	−0.275	13.88
Ne	−21.873	−2.115	8.82
Ar	−55.551	−4.607	7.66
Be	− 4.557	−0.700	13.32
O	−14.388	−1.768	10.94
Li	− 2.961	−0.516	14.84
Na	−25.362	−2.464	8.86
K	−60.222	−4.942	7.58
Ne$^+$	−20.856	−2.198	9.53
Ar$^+$	−54.849	−4.607	7.75
Na$^+$	−25.182	−2.419	8.76
K$^+$	−60.063	−4.918	7.57

Herman and Skillman[4] have done extensive calculations using Slater's exchange and published the programs which they have used. We just modify their non-relativistic program for the appropriate $v_{\mathrm{xc}}(\mathbf{r})$ or $v_{\mathrm{x}}(\mathbf{r})$. It should be noted that we have *not* used the tail correction which Herman and Skillman proposed. It appears from independent calculations by Liberman et al.,[5] that in the case of KS-X, tail correction actually worsens agreement with the exact Hartree-Fock result for both total energy and density distribution.

II. RESULTS AND DISCUSSIONS

In Table I we present the total energies of several atoms and ions. The column marked Expt actually represents results of experimental values minus the relativistic correction, both taken from Clementi's

TABLE III. Correlation energies (in rydbergs).

Atoms	$-(E_{\mathrm{KS\text{-}XC}}-E_{\mathrm{KS\text{-}X}})$	$-E_{\mathrm{c}}$ (Clementi)[a]
He	0.204	0.0842
Ne	1.363	0.786
Ar	2.682	1.582
Kr	6.261	
Li	0.307	0.0906
Na	1.510	0.806
K	2.828	1.64
Rb	6.432	
O	1.010	0.530[b]
Ne$^+$	1.257	0.656
Ar$^+$	2.584	
Na$^+$	1.446	0.792
K$^+$	2.768	

[a] Reference 7. [b] Averaged over spin multiplet.

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[4] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[5] R. D. Cowan, A. Larson, D. Liberman, J. B. Mann, and J. Waber, following paper, Phys. Rev. **144**, 5 (1966).

TABLE IV. Ionization potential (in rydbergs) of one electron from a neutral atom.

Atoms	Experiment[a]	KS-XC	KS-X	Analytic Hartree-Fock[b]
He	1.807	1.938	1.834	
Ne	1.5848	1.657	1.551	1.4605
Ar	1.1582	1.183	1.085	1.0855
Kr	1.0289	1.06	0.973	0.9754
Li	0.3962	0.396	0.331	0.3926
Na	0.3777	0.387	0.325	0.3636
K	0.3190	0.330	0.271	0.2947
Rb	0.3070	0.32	0.272	

[a] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., pp. 7–14.
[b] Reference 6.

work.[6,7] The column HF denotes Hartree-Fock calculations with sources as indicated. Notice that the energies of KS-X are very close to, though slightly better than, those of those of S in comparison with HF. With some correlation effect taken into account, the energies of KS-XC are in fair agreement with experiment but are not as good as HF. Most of the error is due to our imperfect approximation of the exchange part present in KS-XC.

Let us denote by ES the electrostatic approximation in which $v_{xc}(\mathbf{r})$ is put equal to zero. This is not identical with the Hartree approximation except in the limit of large N, since $\varphi(\mathbf{r})$ in Eq. (2) includes the interaction of an orbital with itself. Let us define $E_{\text{HF}}-E_{\text{ES}}$ as the exchange energy. Then $E_{\text{KS-X}}-E_{\text{ES}}$ is our approximation to the exchange energy. This is approximately given by

$$E_{\text{KS-X}}-E_{\text{ES}}\approx\int n(\mathbf{r})\epsilon_x(n(\mathbf{r}))d\mathbf{r}, \tag{11}$$

where $n(\mathbf{r})$ is $n_{\text{KS-X}}(\mathbf{r})$. Table II shows that KS-X scheme approximates the exchange energy to within about 10%, better for larger atoms.

The correlation energy in KS-XC may roughly be taken as $E_{\text{KS-XC}}-E_{\text{KS-X}}$. Comparison with experiment is shown in Table III. Again, by experimental values, we mean the real ones minus the estimates of relativistic corrections. Our approximation is about a factor of 2 too large for small atoms, but better for larger atoms.

TABLE V. Ionization of oxygen atoms (in rydbergs).

Ionization process	Expt	KS-XC	SSM[a]	KS-X	HF[b]
$O \rightarrow O^{+}$	1.1646	1.215	1.009	1.115	1.0712
$O^{+} \rightarrow O^{2+}$	2.4401	2.469	2.581	2.361	2.3697
$O^{2+} \rightarrow O^{3+}$	3.9522	3.955	4.037	3.843	3.9085
$O^{3+} \rightarrow O^{4+}$	5.6878	5.644	5.691	5.530	5.6740
$O^{4+} \rightarrow O^{5+}$	8.3721	8.344	8.372	8.233	8.1594
$O^{5+} \rightarrow O^{6+}$	10.1519	10.004	10.155	9.898	10.1338
$O^{6+} \rightarrow O^{7+}$	54.3419	54.647	}118.392	54.456	54.2222
$O^{7+} \rightarrow O^{8+}$	64.0458	62.585		62.415	64.0000
$E_{\text{TOT}}(O) =$	−150.1564	−148.861	−150.237	−147.851	−149.5388

[a] Reference 8. [b] Reference 7.

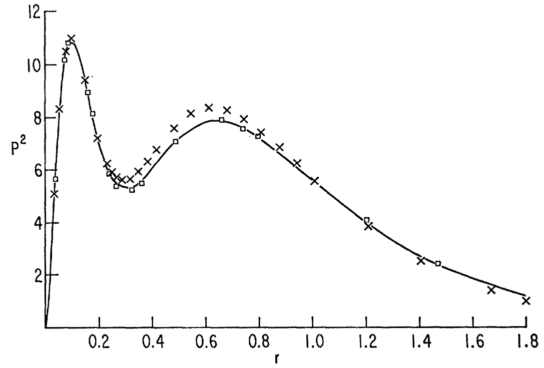

FIG. 2. Radial density of Ne atom. Solid line, KS-XC; □, HF from Ref. 10; ×, S.

The ionization energy of an atom can simply be obtained as the difference between total energies before and after ionization. Thus, the ionization energy on removing one electron from a neutral atom is $E(N)$-$E(N$-1). Results for several atoms are presented in Table IV. Here no attempt is made to remove estimates of relativistic effects from the experimental measurements since such effects in total energies change little on ionizing an atom.[6,8] Our approximation for the ionization energy appears to be in good shape. In Table V, we present the calculated ionization energies as we strip the oxygen atom of its electrons one by one. The experimental values[9] quoted are averaged over various spin multiplets. The column SSM represents semi-empirical results including relativistic effects.[8] That our approximation in Eqs. (4) or (9) is worse for smaller number of electrons is borne out in Table V.

TABLE VI. Expectation values $\langle r^2\rangle$ of r^2.

Atoms	Experiment[a]	KS-XC	KS-X	S	HF
He	2.4	2.597			2.386[b]
Ne	8.4 – 9.8	9.893	10.038		9.3682[c]
Ar	14.2 –24.9	26.460	26.810	23.307	26.03[d]
Kr	34.8 –36.9	39.847	40.331	35.570	39.530[e]
Li^+	0.88– 5.5	0.938		0.831	0.8924[b]
Na^+	6.3 –13.1	6.615	6.674	5.914	6.4130[c]
K^+	17.2 –23.4	19.658	19.825	17.806	19.5358[c]
Rb^+	27.2 –39.5	31.853	32.101	29.117	
Ar^+		20.272	20.459	18.278	20.1742[c]
Kr^+		31.995	32.266	29.139	

[a] Reference 15. Diamagnetic susceptibility $\chi=c\langle r^2\rangle$, where $c=7.927\times10^{-7}$ when χ is measured in (cm^3 mol^{-1}).
[b] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959); **126**, 143 (1962); **126**, 1470 (1962).
[c] P. S. Bagus, Phys. Rev. **139**, A619 (1965).
[d] Reference 13.
[e] *Added in proof.* J. B. Mann (private communication).

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[6] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962); E. Clementi, J. Chem. Phys. **38**, 996 (1963); **38**, 1001 (1963); **41**, 295 (1964); **41**, 303 (1964); IBM J. Res. Develop. **9**, 2 (1965).

[7] E. Clementi, J. Chem. Phys. **38**, 2248 (1963); **39**, 175 (1963); **42**, 2783 (1965); IBM J. Res. Develop. **9**, 2 (1965).

[8] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[9] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 1, Table 15–15.

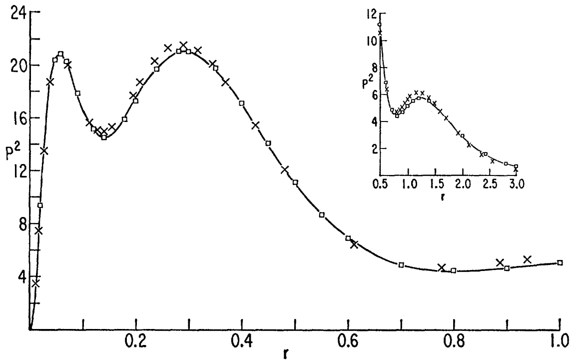

FIG. 3. Radial density of Ar atom. Solid line, KS-XC; □, HF from Ref. 12; ×, S.

In Figs. 2–4 are plotted the radial densities of Ne, Ar, and Kr; i.e.,

$$P^2(r)=4\pi r^2 n(r). \tag{12}$$

The densities calculated from the two schemes KS-XC and KS-X are so close as to be indistinguishable in the figures. In other words, our correlation term does not affect the density much. Our Ne curve agrees well with the HF calculation by Worsley[10] which is also presented in Fig. 2. Both depart somewhat from an earlier HF calculation by Brown.[11] Our density for Ar agrees well with HF.[12] Since our approximation should get better for larger atoms, our good density results for Ne and Ar encourage us to expect that our Kr density should be better still. However, our density for Kr does not have the same good agreement with the HF calculation by Worsley.[13] The small discrepancies show that either our expectation was not met or Worsley's results are not sufficiently self-consistent because of the large number of orbitals involved in the calculation.[14] Density distributions by the Slater scheme are peaked more near the nucleus as it should be since the Slater potential is more attractive. Also the tails fall more rapidly. Herman and Skillman's modification[4] nearly preserves the Slater curve with a minute flattening of the tail.

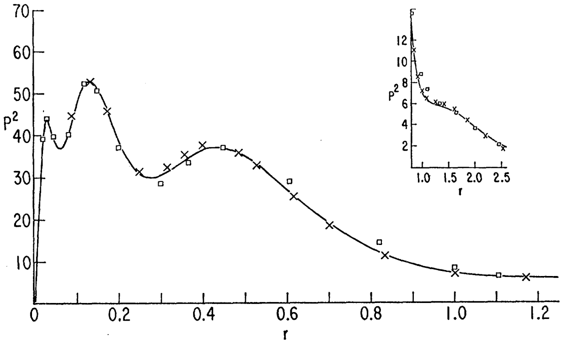

FIG. 4. Radial density of Kr atom. Solid line, KS-XC; □, HF from Ref. 13; ×, S.

A good measure of the shape of the density distribution is $\langle r^2\rangle$. This quantity is also proportional to the experimentally measurable diamagnetic susceptibility. Values in Table VI (see Ref. 15) confirm our conclusions in the preceding paragraph that (i) there is little difference between the densities from KS-XC or KS-X, (ii) there is good agreement between KS-X and HF, and (iii) $\langle r^2\rangle$ from S is smaller than that calculated by KS-X. Unfortunately, the uncertainties in experimental values of $\langle r^2\rangle$ are too great to permit any definite conclusion in comparing various calculations with experiment.

In conclusion, we can say that our computation is simple compared with Hartree-Fock and configuration-interaction schemes and that our results are quite good, especially for large atoms. Our exchange approximation is satisfactory. Comparison of numerical results of KS-X and S confirms the inference about these two schemes drawn in Ref. 1, namely, that the total energies are close but that our density should be a distinct improvement over that obtained by the Slater scheme. Our approximation to the correlation energy is poor. We are trying to understand precisely why this error is fractionally so much larger than that of the exchange energy.

ACKNOWLEDGMENTS

We are indebted to Professor W. Kohn for constant guidance. We thank Dr. D. A. Liberman and Dr. R. Cowan for sending their results on Kr for the KS-X scheme for checking with our own results.

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[10] B. H. Worsley, Can. J. Phys. **36**, 28 (1958).

[11] F. W. Brown, Phys. Rev. **44**, 214 (1933).

[12] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

[13] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).

[14] *Note added in proof.* Dr. J. B. Mann has since performed the Hartree-Fock calculation for the density of Kr whose agreement with our result is much improved as compared to Worsley's and is as good as the agreement between HF and KS-X for Ne. We are grateful to Dr. J. B. Mann for sending us his results.

[15] Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik* (Springer-Verlag, Berlin, 1950), 6 Auflage, Band 1.