THE

PHYSICAL REVIEW

Exchange Potential for Electrons in Atoms and Solids*

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(Received 27 November 1967)

The Hartree-Fock exchange potential for a uniform degenerate electron gas is adapted for use in atomic and solid-state calculations. Results are given for argon and mercury atoms. Energy eigenvalues are quite close to the Hartree-Fock values.

IN 1951 Slater[1] proposed a simple approximation for the exchange potential which appears in the Hartree-Fock one-electron equations. In terms of the Fermi wave number $k_F(r) = (3\pi^2\rho(r))^{1/3}$, his exchange potential is

$$V_{SX}(r) = -\tfrac{3}{2}(e^2/\pi)k_F(r).$$

Shortly afterward Gaspar[2] pointed out that the application of the variational method, as in Lenz's derivation of the Thomas-Fermi-Dirac equation, gave the smaller exchange potential

$$V_{GX}(r) = -(e^2/\pi)k_F(r).$$

Unfortunately Gaspar was not able to do the accurate self-consistent field calculations that were needed to show the relative merits of the two exchange potentials.

More recently Kohn and Sham[3] and also Cowan et al.[4] repeated Gaspar's derivation. Calculations were done[4,5] which compared V_{SX} and V_{GX} with the Hartree-Fock exchange potential. They showed that for atoms, at least, Gaspar's exchange potential produced orbital functions that were closer to those obtained from the Hartree-Fock equations, but that the energy eigenvalues were poorer than those based on V_{SX}.

Also, in the past few years, there have been a number of calculations with exchange potentials suggested by the form V_{SX}[6,7] but adjusted in one way or another to fit the results of Hartree-Fock calculations or experiment.

We want to suggest here still another exchange potential[8] which has the advantage of giving both good orbital functions and good eigenvalues and which also has a reasonable theoretical foundation.

The derivation is similar to Slater's in that it starts with the Hartree-Fock equations and proceeds to approximate the exchange term in them. Slater's derivation was in two parts: the replacement of the Hartree-Fock exchange potential by an average one, and then the approximation of this average by free-electron expressions. Our suggestion is simply to skip Slater's first step and to adapt the well-known Hartree-Fock exchange potential for a degenerate electron gas to the case of variable density.

The exchange potential for the electron gas may, because of translational invariance, be expressed as a local operator. It is

$$V_{FX} = -(e^2/\pi)k_F F(k/k_F),$$

where

$$F(\eta) = 1 + \frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|$$

and k is the magnitude of the wave vector of the electron state being considered. The similarity of V_{FX} to V_{SX} and V_{GX} leads one to try adapting V_{FX} to distributions of electron charge which are not constant by making k and k_F functions of position in an appropriate manner.

* 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. Acad. Sci. Hung. 3, 263 (1954).
[3] W. Kohn and L. J. Sham. Phys. Rev. 140, A1133 (1965).
[4] R. D. Cowan et al., Phys. Rev. 144, 5 (1966).
[5] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).
[6] I. Lindgren, Arkiv Fysik 31 59 (1966).
[7] R. D. Cowan, Phys. Rev. 163, 54 (1967).

[8] Since writing this paper we have been advised of two earlier suggestions of the exchange potential proposed here. They are L. J. Sham and W. Kohn [Phys. Rev. 145, 561 (1966)] and K. Yonei [J. Phys. Soc. Japan 22, 1127 (1967)]. We are indebted to L. J. Sham and F. Herman for this information.

The prescription that immediately suggests itself is that they be chosen to correspond to the values for a uniform electron gas in a constant potential which match the local density and potential:

$$k_F(\mathbf{r}) = (3\pi^2\rho(\mathbf{r}))^{1/3},$$

$$k(\mathbf{r}) = [2m(E - V(\mathbf{r}))/\hbar^2]^{1/2}.$$

This is, of course, just an application of the semiclassical approximation as in the Thomas-Fermi model. The approximation may be expected to be good where electron wavelengths are short compared to the distance in which the potential has a substantial fractional change. As is well known, in atoms this condition excludes the region very close to the nucleus and that at very large radii. If the atomic number is large enough, the region in between contains most of the charge density and the failure of the approximation at the two limits of large and small radii is not serious.

The failure of the semiclassical approximation manifests itself in our case most seriously at radii beyond the classical turning point where $\hbar^2 k^2 / 2m = E - V(\mathbf{r})$ is negative. At the classical turning point $F(k/k_F) = F(0) = 2$. We have somewhat arbitrarily used this value for all larger radii. Near the nucleus k/k_F exceeds 1, which is not consistent with the notion that the electrons may be considered locally as a degenerate electron gas. In our calculations we have, nontheless,

continued to use the above formula for F. It has been pointed out by Wood[9] that it might be better in this case to use for F the value it has when $k/k_F = 1$ which is just $F(1) = 1$.

A question which arises in the practical application of this exchange potential is how exchange is to be put into $V(\mathbf{r})$ when computing the magnitude of the local wave number, $k(\mathbf{r})$. It would seem to be more consistent to use V_{FX} itself in $V(\mathbf{r})$ at this point but easier to use V_{SX} or V_{GX}. The results reported here were obtained with the use of V_{FX}. Our first calculations used V_{GX} which gave somewhat poorer eigenvalues for the most loosely found electrons.

Several calculations for atoms have been done with a relativistic self-consistent field computer program[10] using V_{SX}, V_{GX}, and V_{FX}. These are compared with relativistic Hartree-Fock calculations done byMann[11] with a program devloped by Coulthard.[12] The agreement between the energy eigenvalues obtained with our free electron exchange potential and the Hartree-Fock energy eigenvalues is surprisingly good. Eigenvalues for argon and mercury are given in Table I.

The charge density is not as close to the Hartree-Fock charge density as that calculated with the Gaspar ex-

TABLE I. Energy eigenvalues (atomic units).

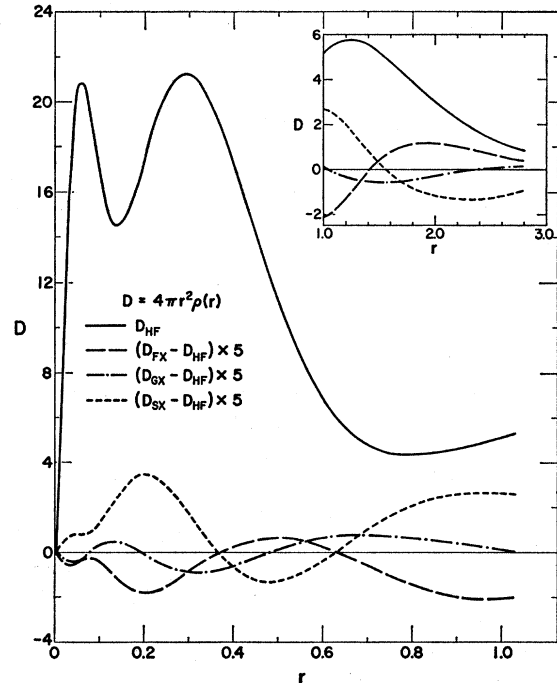| Orbital	E_{HF}	E_{FX}	E_{GX}	E_{SX}
		Argon		
$1s_{1/2}$	− 119.13	− 118.61	− 114.21	− 116.73
$2s_{1/2}$	− 12.41	− 12.32	− 10.81	− 11.48
$2p_{1/2}$	− 9.63	− 9.65	− 8.44	− 9.13
$2p_{3/2}$	− 9.55	− 9.56	− 8.35	− 9.04
$3s_{1/2}$	− 1.287	− 1.172	− 0.841	− 1.036
$3p_{1/2}$	− 0.5954	− 0.5356	− 0.3376	− 0.5083
$3p_{3/2}$	− 0.5878	− 0.5287	− 0.3311	− 0.5009
		Mercury		
$1s_{1/2}$	−3076.15	−3075.03	−3049.43	−3065.07
$2s_{1/2}$	− 550.54	− 550.44	− 540.00	− 545.13
$2p_{1/2}$	− 526.86	− 527.97	− 518.17	− 523.85
$2p_{3/2}$	− 455.15	− 455.66	− 446.66	− 451.49
$3s_{1/2}$	− 133.18	− 133.03	− 128.07	− 130.05
$3p_{1/2}$	− 122.64	− 122.85	− 118.23	− 120.32
$3p_{3/2}$	− 106.54	− 106.65	− 102.39	− 104.23
$3d_{3/2}$	− 89.43	− 89.71	− 86.08	− 87.98
$3d_{5/2}$	− 86.02	− 86.24	− 82.69	− 84.51
$4s_{1/2}$	− 30.67	− 30.45	− 28.08	− 28.95
$4p_{1/2}$	− 26.13	− 26.00	− 23.87	− 24.73
$4p_{3/2}$	− 22.19	− 22.04	− 20.04	− 20.82
$4d_{3/2}$	− 14.80	− 14.67	− 13.15	− 13.88
$4d_{5/2}$	− 14.05	− 13.93	− 12.43	− 13.14
$4f_{5/2}$	− 4.472	− 4.273	− 3.554	− 4.139
$4f_{7/2}$	− 4.311	− 4.109	− 3.400	− 3.975
$5s_{1/2}$	− 5.106	− 5.063	− 4.292	− 4.603
$5p_{1/2}$	− 3.538	− 3.509	− 2.897	− 3.188
$5p_{3/2}$	− 2.842	− 2.782	− 2.218	− 2.485
$5d_{3/2}$	− 0.6498	− 0.5925	− 0.3617	− 0.5626
$5d_{5/2}$	− 0.5743	− 0.5107	− 0.2942	− 0.4871
$6s_{1/2}$	− 0.3283	− 0.3667	− 0.2208	− 0.3218

FIG. 1. Radial charge density for argon atom. The solid-line curve is the Hartree-Fock radial charge density. The broken-line curves are the deviations of the radial charge densities computed with the various approximate exchange potentials from the Hartree-Fock values. The deviations have been multiplied by the factor 5.

[9] J. H. Wood (private communication).
[10] D. Liberman, J. T. Waber, and D. Cromer, Phys. Rev. **137**, A27 (1965).
[11] J. B. Mann (unpublished).
[12] M. A. Coulthard, Proc. Phys. Soc. (London) **91**, 44 (1967).

change potential, but is perhaps a little better than that obtained with the Slater exchange potential. Computed charge densities are shown in Fig. 1. Probably the same is true of the orbital functions.

Since V_{FX} depends through $k(\mathbf{r})$ on the particular orbital function to which it is applied, it cannot be expected that the orbital functions will be exactly orthogonal. To see if this lack of orthogonality is serious we have computed the overlap integrals for the two atoms for which data is presented. The largest of these for argon has the value 0.0036 and for mercury the value 0.0084, and most of them are very much less. Since the squares of the overlap integrals are the quantities which are relevant in calculations with the atomic wave functions, it is seen that lack of orthogonality is not significant.

Although the calculations presented here for atoms are interesting, our exchange potential is really intended for solid-state calculations where it is hoped it will make possible with present-day computers and existing programs something fairly close to a true Hartree-Fock calculation. Whether this hope will be borne out, and if it is, whether the results will be useful, remains to be seen.

ACKNOWLEDGMENT

The idea for the exchange potential described in this paper arose in a conversation with P. Lloyd while the author was on leave at the University of Bristol.

APPENDIX

A more mathematical derivation of our approximate exchange potential can be made as follows:

The exchange term in the Hartree-Fock one-electron equations is

$$V_X\psi = -\int \frac{e^2\rho(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi(\mathbf{r}')d\mathbf{r}',$$

where

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{n=1}^{N} \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')$$

is the single-particle density matrix.

The first step in the derivation of V_{FX} is the approximation of the density matrix by the statistical (Thomas-Fermi) method[13]:

$$\rho(\mathbf{r},\mathbf{r}') = \int_V \frac{d\mathbf{q}}{(2\pi)^3}\frac{1}{V}e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}, \quad q < k_F(\mathbf{R})$$

where $\mathbf{R}=\frac{1}{2}(\mathbf{r}+\mathbf{r}')$ (we have omitted spin functions for the sake of simplicity). With this approximation the exchange potential is still nonlocal and therefore still more complicated than is desired.

The next step is to write

$$\psi(\mathbf{r}') = [\psi(\mathbf{r}')/\psi(\mathbf{r})]\psi(\mathbf{r})$$
$$= \exp[i(S(\mathbf{r}')-S(\mathbf{r}))/\hbar]\psi(\mathbf{r}),$$

where it is our intention to approximate S by the classical action for which

$$(1/2m)(\nabla S)^2 + V(\mathbf{r}) = E.$$

The difference of the two action functions in the exponential may be written as

$$S(\mathbf{r}') - S(\mathbf{r}) = \int_{\mathbf{r}}^{\mathbf{r}'} \nabla S(\mathbf{x})\cdot d\mathbf{x}$$
$$= \nabla S(\boldsymbol{\xi})\cdot(\mathbf{r}'-\mathbf{r})$$
$$= \mathbf{k}(\boldsymbol{\xi})\cdot(\mathbf{r}'-\mathbf{r}),$$

where $\boldsymbol{\xi}$ is a point on the path of integration between $\mathbf{r}$ and $\mathbf{r}'$. Since $\rho(\mathbf{r},\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$, which appears in the exchange integral above, is rather sharply peaked about $\mathbf{r}=\mathbf{r}'$, it is reasonable to replace $\boldsymbol{\xi}$ with any convenient values nearby. We choose $\boldsymbol{\xi}=\mathbf{r}$ and for the same reason replace $\mathbf{R}=\frac{1}{2}(\mathbf{r}+\mathbf{r}')$ in the approximate expression for $\rho(\mathbf{r},\mathbf{r}')$ with $\mathbf{r}$ also.

One may now do the integrals on $\mathbf{r}'$ and $\mathbf{q}$ and get the expression for the exchange potential which was obtained on the basis of plausibility arguments in the text.

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[13] W. Heisenberg, Physik Z. **32**, 737 (1931).