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Effect of Correlation on the One-Electron Wave Function in Atoms*

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The effect of correlation on the wave function of a single electron in an atom is discussed in an approximation where the exact nonlocal mass operator for the electron is approximated by a Hartree-Fock-Slater exchange potential plus a local static correlation potential. The correlation potential has been taken from recent calculations by Hedin for the electron gas over a large range of densities. The effect of such a correlation potential has been calculated in a few cases by numerical integration in first-order perturbation theory, using the functions tabulated by Herman and Skillman as zero-order solutions. The results show a small but distinct contraction of the radial wave functions and give non-negligible corrections to certain single-particle properties such as one-electron energies and the contribution to the diamagnetic susceptibility.

IN this paper we shall find the effect of a correlation potential taken from recent calculations of Hedin[1] for the electron gas on the one-electron wave functions of neon, argon, and krypton. We use as starting functions those tabulated by Herman and Skillman,[2] and shall confine ourselves to orbitals which are occupied in the ground state of the atom. The methods of many-body theory for extended systems have recently been applied to problems in atomic structure. Kelly[3] and Kelly and Sessler[4] have recently investigated the correlations in the ground state of atoms by such methods. Methods closely related to the random-phase approximation have been used by Brandt and Lundqvist[5] and Altick and Glassgold[6] for investigating the effect of correlations on dipole spectra. Recently, an extensive discussion of the one-electron problem in atoms, molecules, and solids has been given by Hedin,[1] using field-theoretic methods. Hedin applies the theory to alkali atoms with emphasis on the effect of core polarization on the valence-electron spectrum.

The wave amplitude $\phi(\mathbf{x})$ and energy ϵ of a single electron bound in an atom are solutions of the eigenvalue equation

$$\{\epsilon-h(\mathbf{x})-V(\mathbf{x})\}\phi(\mathbf{x})-\int M(\mathbf{x},\mathbf{x}',\epsilon)\phi(\mathbf{x}')d^3\mathbf{x}'=0\,, \qquad (1)$$

for a discrete energy value ϵ. $h(x)$ is the one-electron part of the Hamiltonian

$$h(\mathbf{x})=-(\hbar^2/2m)\nabla^2-(Ze^2/|\mathbf{x}|)\,, \qquad (2)$$

and $V(\mathbf{x})$ is the Hartree potential

$$V(\mathbf{x})=e^2\int\frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}d^3x'\,, \qquad (3)$$

where $\rho(\mathbf{x})$ is the electron density at $\mathbf{x}$. The self-energy operator $M(x,x',\epsilon)$ contains the combined effects of exchange and correlation. A series expansion in terms of the unscreened Coulomb interaction gives as the first term the Hartree-Fock exchange potential, and the higher terms describe the effect of correlations in the system.

To get an estimate of the effect, we neglect the energy

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* Supported by the National Science Foundation.

[1] L. Hedin, Phys. Rev. (to be published).

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

[3] H. P. Kelly, Phys. Rev. **131**, 684 (1963); **136**, B896 (1964).

[4] H. P. Kelly and A. M. Sessler, Phys. Rev. **132**, 2091 (1963).

[5] W. Brandt and S. Lundqvist, Phys. Rev. **132**, 2135 (1963).

[6] P. L. Altick and A. E. Glassgold, Phys. Rev. **133**, A632 (1964).

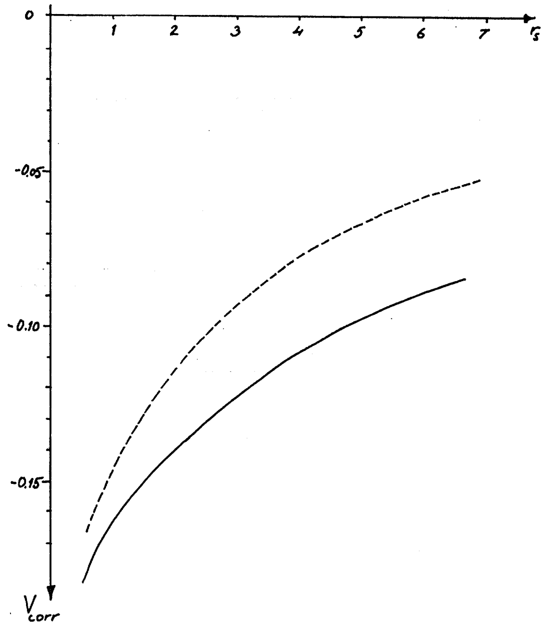

FIG. 1. Correlation potential (in Ry); ---- from Carr and Maradudin (Ref. 8); ——— from Hedin (Ref. 1).

dependence in M and further introduce a local approximation

$$M(\mathbf{x},\mathbf{x}',\epsilon)=\{V_{\mathrm{exch}}(\mathbf{x})+V_c(\mathbf{x})\}\delta(\mathbf{x}-\mathbf{x}')\,, \tag{4}$$

where the exchange is approximated by a local potential, e.g., in the form used in Ref. 2. The correlation potential $V_c(\mathbf{x})$ can be estimated from the various interpolation formulas given for the energy density $E_c(r_s)$ of an electron gas, where r_s measures the volume per electron and is related to the electron density ρ through the formula $r_s=(3/4\pi)^{1/3}\rho^{-1/3}$. The correlation potential is then found to be[7]

$$V_c(r_s)=E_c(r_s)-\tfrac{1}{3}r_s(dE_c(r_s)/dr_s)\,. \tag{5}$$

Hedin has calculated the self-energy operator to lowest

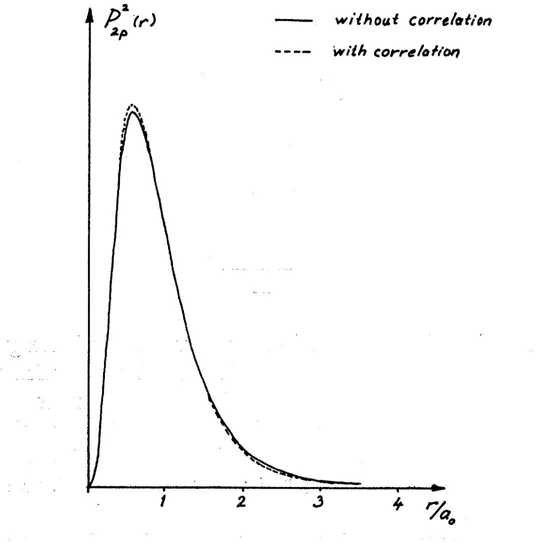

FIG. 2. Radial density of $2p$ electrons in Ne. $\int P_{2p}^2(r)dr=1$.

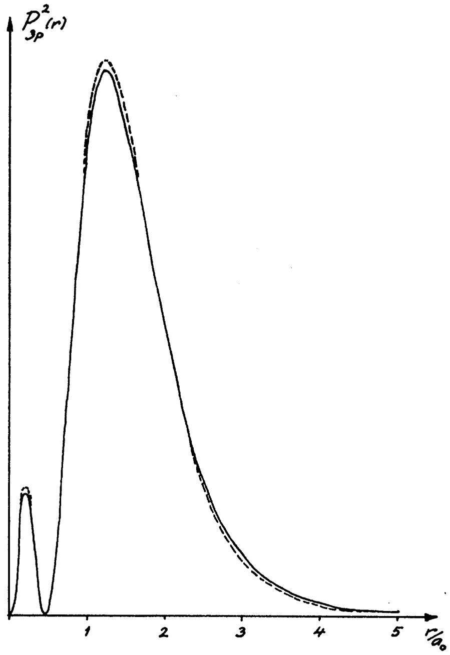

FIG. 3. Radial density of $3p$ electrons in Ar. $\int P_{3p}^2(r)dr=1$.

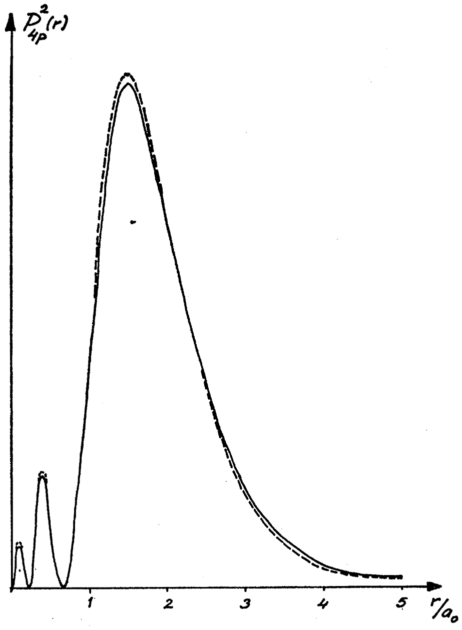

FIG. 4. Radial density of $4p$ electrons in Kr. $\int P_{4p}^2(r)dr=1$.

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[7] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. IX.

TABLE I. The diamagnetic susceptibility χ_{mol} (in units of 10^{-6} cgs units).

	Ne	Ar	Kr
Calculated	-6.9	-18.6	-28.4
Observed	-6.7	-18.1	-28.0

TABLE II. One-electron energies (in Ry).

	$2p$ Ne	$3p$ Ar	$4p$ Kr
Herman-Skillman, ϵ_{HS}	-1.471	-1.065	-0.952
First-order correction, ϵ_1	-0.181	-0.138	-0.155
Total energy, $\epsilon_{\mathrm{HS}}+\epsilon_1$	-1.652	-1.203	-1.107
Experimental	-1.587	-1.163	-1.045

order in the screened dynamic interaction and we have calculated the corresponding $V_c(r_s)$ in the interval $r_s \leqslant 6$ from his results. Around and beyond $r_s=6$ the results in Hedin's calculation have probably not much significance and we just made a graphical extrapolation in order to connect smoothly to the low-density results. In Fig. 1 we have compared the correlation potential thus obtained with that obtained from the recent interpolation formula for the energy density $E(r_s)$ given by Carr and Maradudin.[8] We feel no strong preference for one or the other, and they both seem to serve the purpose equally well to illustrate the effects we are discussing. The potential based on Hedin's work was used in our calculations, and the potential used by Herman and Skillman was chosen to represent the remaining potential. This choice was made in order to use their wave functions as the zeroth-order approximation in a perturbation approach.

With the approximations just discussed, implying that both exchange and correlation are represented by a local and static potential, the problem is reduced to solving the ordinary differential equations for the radial motion of the electrons, which are of the form

$$\{-(d^2/dr^2)+(l(l+1)/r^2)+V_{\mathrm{HS}}(r)+V_c(r)\} \times P_{nl}(r)=\epsilon_{nl}P_{nl}(r)\,, \quad (6)$$

where V_{HS} is the potential used by Herman and Skillman. In their calculations $\int P_{nl}^2(r)dr=1$. Writing $\epsilon_{nl}=\epsilon_{nl}^0+\epsilon_{nl}^1$ and $P_{nl}(r)=P_{nl}^0(r)+P_{nl}^1(r)$, where P_{nl}^0 and ϵ_{ne}^0 satisfy the equation with no correlation potential, thus

$$\{-(d^2/dr^2)+(l(l+1)/r^2)+V_{\mathrm{HS}}(r)\} \times P_{nl}^0(r)=\epsilon_{nl}^0P_{nl}^0(r)\,, \quad (7)$$

we obtain the first-order change in the wave function by solving

$$\{(d^2/dr^2)-(l(l+1)/r^2)-V_{\mathrm{HS}}(r)\} \times P_{nl}^1(r)=\{\epsilon_{nl}^1-V_c(r)\}P_{nl}^0(r)\,, \quad (8)$$

where $\epsilon_1=\int V_c(r)\rho^0(r)d^3r$ is the first-order correction to the single-particle energy.

Equation (8) was solved numerically for p electrons in the outer shell of Ne, Ar, and Kr. The resulting change in the density, as measured by $P_{np}^2(r)$, is illustrated in Figs. 2–4. The results show a decrease in the amplitude and density in the outer region of the atom and an increase as well as a slight sharpening of the principal peak for the p shells. Quantitatively, the decrease in $\langle r^2\rangle$ relative to the values calculated from the Herman-Skillman tables amount to 3.2% for Ne, 3.5% for Ar, and 3.4% for Kr. The change in the wave function is small but is significant in many cases where high accuracy is essential. Assuming the same contractions for the outer s electrons and that the effect of correlation on the inner shells can be neglected, we obtain for the molar diamagnetic susceptibility χ_{mol} the results given in Table I, which are in close agreement with the experimental values.

The first-order shifts ϵ_1 in the single-particle energies are given in Table II, together with the Herman-Skillman values ϵ_{HS}, and the total energy obtained from ionization potentials. The first-order correction is of appreciable magnitude, but is seen to overcorrect the Herman-Skillman values, giving, however, a better agreement with the experimental values. Part of the overcorrection can be traced to the fact that the exchange calculated for the electron gas turns out to be more negative than the modified Slater exchange used in Herman and Skillman's calculations. The remaining discrepancies must be attributed to the inaccuracy of a local approximation and the neglect of the finite gap in the spectrum for the electrons in the approximation for V_c. Such effects are outside the scope of this discussion.

We conclude that the self-energy effects on the motion of a single electron seem to be of sufficient magnitude to deserve attention. Our estimates show a considerable effect on the single-particle energies and an effect on the single-particle wave function, which although smaller, is of significance for those properties where accurate one-electron amplitudes are needed.

We are indebted to Dr. L. Hedin for stimulating discussions and to S. Bergström for carrying out the numerical calculations.

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[8] W. J. Carr and A. A. Maradudin, Phys. Rev. **133**, A371 (1964).