

NEW APPROXIMATE HARTREE—FOCK MODEL

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A new approximate Hartree—Fock theory is put forward. The main point of the theory is the replacement of the exact exchange term with an approximate one. This approximate exchange potential is spin-dependent but it is the same for all of the electronic shells in the system.

The theory has been applied to the atom argon and the agreement of the exact and approximate Hartree—Fock theories is very good.

Introduction

An approximate exchange potential has been suggested by SLATER [1] to simplify the Hartree—Fock theory by replacing the exchange term by a simpler one. This term is proportional to the one-third power of the local electronic density. After this replacement, approximate Fock-equations have been derived and solved by the self-consistent field method. Later the author of this paper has given a modified version of the above theory in which the exchange potential is two thirds of that mentioned above [2]. SLATER [3] has shown that the exchange term may be considerably improved by introducing a factor α which replaces unity in the Slater type exchange term and which is dependent on the atomic number if determined by adjusting the total energy of the theory to the total energy of the Hartree—Fock theory [4]. It was shown later [5] that a natural intrinsic explanation may be given to this atomic number dependent α .

In this paper we are introducing and discussing an average exchange term, which has been mentioned in [5]. This exchange term is introduced in a self-consistent manner and it may be extended to atoms, molecules and solids as well. It is applied to an atomic system, and the agreement with the exact Hartree—Fock theory is excellent.

The Approximate Hartree—Fock model

In an atomic system the electron density is

$$\rho = \rho^\dagger + \rho^\ddagger \quad (1)$$

where

$$\rho^\dagger = \sum_{j^\dagger} n_j u_j^\dagger u_j \quad \text{and} \quad \rho^\ddagger = \sum_{j^\ddagger} n_j u_j^\ddagger u_j \quad (2)$$

denote the density of the electrons with spins up and down resp., $u_j - s$ are spin-orbitals and $n_j - s$ are occupation numbers of these spin-orbitals.

The total energy is given in the form

$$E = \sum_i n_i \int u_i^*(1) f_1 u_i(1) dv_1 + \frac{1}{2} \int \varrho(1) \varrho(2) g_{12} dv_1 dv_2 + \frac{1}{2} \int [\varrho_\uparrow U_\uparrow(1) + \varrho_\downarrow(1) U(1)] dv_1 \quad (3)$$

where f_1 is the sum of one-electron operators and $g_{12} = e^2/r_{12}$ the two particle interaction. In the last term, which is the exchange term, $\frac{1}{2} U$ is the exchange energy density of the swarm of electrons with a given spin.

By a variational method we get from Eq. (3) the approximate Fock equations

$$m[-\nabla_1^2 + V_C(1) + V_{X\uparrow}(1)] u_{i\uparrow}(1) = \varepsilon_{ix\uparrow} u_{i\uparrow}(1) \quad (4)$$

and a corresponding equation for the electrons with spin down. In Eq. (4)

$$V_C(1) = \int \varrho(2) g_{12} dv_2 + \sum_i \frac{Z_i}{r_i} \quad (5)$$

is the Coulomb potential of the electrons and the nuclei and V_X is the exchange potential of the electrons and is connected to the energy density U by the equation

$$V_{X\uparrow}(1) = \frac{1}{2} \left\{ U_{X\uparrow}(1) = \varrho_\uparrow(1) \frac{\delta U_{X\uparrow}(1)}{\delta \varrho_\uparrow(1)} \right\}. \quad (6)$$

The derivative in the last term is the functional derivative of U_\uparrow according to ϱ_\uparrow . By integrating Eq. (6) we get the relation

$$U_{X\uparrow}(1) = \frac{2}{\varrho_\uparrow(1)} \int_0^{\varrho_\uparrow} V_{X\uparrow}(\varrho'_\uparrow) d\varrho'_\uparrow \quad (7)$$

where $V'_{X\uparrow}$ is the same functional of ϱ'_\uparrow as $V_{X\uparrow}$ is that of ϱ_\uparrow . Eq. (7) gives us the possibility of finding an exchange energy density after the proper definition of an exchange potential.

The new exchange potential

When the exchange potential is evaluated, it turns out that each electron is surrounded by a hole i.e. a small region, where the other electrons with the same spin projection avoid being present with great probability [6]. The number of electrons missing from this region is one and the potential of this missing electron is the so called exchange potential. This potential is localized to a great extent and so may be a functional of the total charge ϱ in that point of reference and the density of the electron in question v .

In a region where the potential field is slowly changing the electrons of density ρ exert an exchange potential

$$V_{Xt}(l) = -8F(\eta) \left[\frac{3}{4\pi} \rho_t(l) \right]^{1/3}, \tag{8}$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right|. \tag{9}$$

The Fermi energy of the system of electrons is

$$E_{Ft} = k_{Ft}^2 = (6\pi^2 \rho_t)^{2/3} \tag{10}$$

where k_{Ft} is the Fermi momentum. The relative momentum of the electron in question is

$$\eta = k/k_F \tag{11}$$

If we average the exchange potential in (8) in the momentum space over a thin shell near the Fermi-momentum and that region of momentum space contains ν electrons, we get the exchange potential

$$V_{X\text{SHELL}t}(l) = -6 \left[\frac{3}{4\pi} \rho_t \right]^{1/3} \frac{\rho_t}{\nu_t} \left\{ 1 - \frac{1}{2} \eta^3 - \frac{1}{2} \eta + \frac{1}{4} [1 - \eta^2]^2 \ln \left| \frac{1+\eta}{1-\eta} \right| \right\} \tag{12}$$

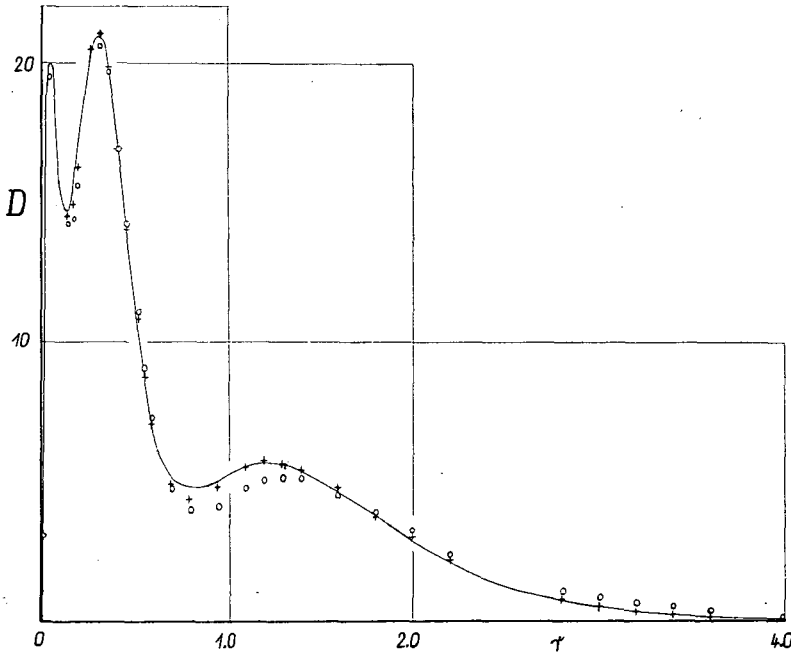


Fig. 1. The total density of the argon atom as calculated by the new method —, the method of Hartree o o o o and the method of Hartree-Fock + + + +

which is different for each shell, and where

$$\eta = \left(1 - \frac{v_t}{\rho_t}\right)^{1/3} \quad (13)$$

This exchange potential depends from the position of the electron in a complicated way. A drawback of this potential is that it is not the same for all electrons and so the resulting self-consistent orbitals are not orthogonal and they need to be orthogonalized separately. This may be avoided by a further averaging which gives

$$\bar{V}_{xt} = \frac{\sum_i N_{it} V_{x\text{SHELL}it}}{\sum_i N_{it}} \quad (14)$$

This potential field is still quite general and can be determined in a self-consistent way. There is no parameter in this theory which has to be adjusted to another theory or to be determined semiempirically.

Results and discussion

For testing the above theory, we have calculated the electronic structure of the argon atom. The electronic configuration of the argon atom is $(1s)^2(2s)^2(2p)^6$. The approximate Fock equations have been solved and the total particle density has been calculated. In Fig. 1 we have displayed this curve with the Hartree and the Hartree—Fock curves. The agreement of the exact Hartree—Fock theory and the approximate one is surprisingly good. Other applications of the theory are in preparation.

References

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НОВАЯ ПРИБЛИЖЁННАЯ МОДЕЛЬ ТЕОРИИ ХАРТРИ—ФОКА

P. Gaunap

Описано новое приближение теории Хартри—Фока. Главной особенностью теории является замена точного обменного члена на приближённый. Приближённый потенциал зависит от спина, но одинаков для всех электронных оболочек систем.

Теория применена к атому аргона. Результаты точной и приближённой теории Хартри—Фока находятся в хорошем согласии.