RELATIVISTIC POLARIZATION POTENTIAL OF A MANY-ELECTRON ATOM

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An effective approximate calculation of the exchange-polarization second-order diagrams in the Rayleigh—Schrödinger perturbation theory with the use of the relativistic Thomas—Fermi approximation is described and used to obtain a new relativistic expression for the effective two-particle polarization interaction potential in a many-electron atom.

1. The need to solve such important problems as heavy plasma diagnostics, the creation of short-wave lasers on multiply-charged ions, etc., has stimulated interest in the study of the spectroscopic characteristics of highly ionized and heavy neutral atoms. The characteristic feature of calculations for these systems is the need for a systematic treatment of both relativistic and exchange-polarization effects in both one-particle and many-particle systems. In recent years these calculations have usually been performed using the relativistic density functional method (see [1-4], for example) and also methods similar to the relativistic model potential methods [5-8], in which the principal one-particle relativistic and correlation effects can be taken into account. However, two-particle and many-particle effects, which are just as important in precision calculations, as well as effects of higher order (beginning with second order) in perturbation theory must be taken into account by a direct calculation in perturbation theory. It is well known that such a calculation is very complicated and laborious and a practically impossible calculation of infinite sums in perturbation theory is required in order to obtain a correct description of such complicated effects as the pressure of the continuum and the rapid spreading of the initial state over a vast set of additional configurations. An alternative method is the use of many-particle relativistic exchange-polarization interaction potentials. The problem of how to construct these potentials has still not been solved completely [2-4]. In the present paper we use the relativistic Thomas—Fermi approximation to obtain a new relativistic expression for the effective two-particle interaction potential in a many-electron atom, which approximates the exact contribution of the exchange-polarization diagrams of second order in perturbation theory (these diagrams give the dominant contribution to the correlation). Atomic units are used throughout.

2. There are two basic types of diagrams in second-order relativistic perturbation theory diagrams with Hartree—Fock inserts (Fig. 1, A, B, C) and diagrams without them (Fig. 2, A, B, C, D). It has been shown by Tolmachev [9] (see also [10, 11]) that in perturbation theory with the Hartree—Fock or Dirac—Fock zeroth approximation, the contribution of all diagrams with Hartree—Fock inserts exactly cancels out in all orders of perturbation theory. Corrections to the energy from the so-called ladder diagrams (exchange D and direct C diagrams) can be taken into account almost completely in the zero-order one-particle approximation of perturbation theory [12, 13]. The polarization diagrams (A and B in Fig. 2) correspond to many-particle effects and cannot be taken into account in a one-particle treatment, even in principle [14-16].

We calculate the contribution of the direct polarization diagram A of Fig. 2. It describes the polarization interaction of two electrons in states ψ_1 and ψ_2 (or vacancies) through the polarizable medium (the other electrons of the system will be called core electrons). The exact contribution to the energy of the system can be represented in the form

$$E(A) = -2 \sum_{\kappa} (\delta V_1)_{0\kappa} (\delta V_2)_{0\kappa} / (E_{\kappa} - E_0), \tag{1}$$

where

$$\delta V_i(r) = \int dr' \rho_i(r') / |r - r'|, \quad \rho_i(r) = \psi_i^*(r) \psi_i(r); \quad i = 1, 2. \tag{2}$$
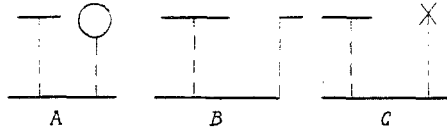
Fig. 1
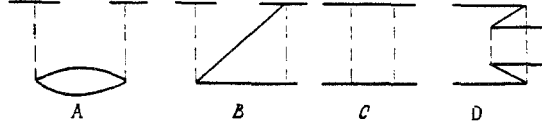

Fig. 2

The matrix elements $(\delta V_i)_{0K}$ in (1) are calculated between the ground state $|0>$ and the excited states $|\kappa>$ of the core. The expression for E(A) can be written in two equivalent forms:

$$E(A) = \int\int dr' dr'' \rho_1(r') \, \delta\rho_c^{(1)}(r''|2)/|r' - r''| = \int\int dr' dr'' \rho_2(r') \, \delta\rho_c^{(1)}(r''|1)/|r' - r''|. \tag{3}$$

The total density of the system is written as

$$\rho_c(r) = \rho_c^{(0)}(r) + \delta\rho_c^{(1)}(r|1) + \delta\rho_c^{(1)}(r|2) + ..., $$

where $\rho_c^{(0)}(r)$ is the electronic density distribution in the core; $\delta\rho_c^{(1)}$ is the first-order correction to $\rho_c^{(0)}$ due to the perturbation δV_i. To calculate $\delta\rho_c^{(1)}(r|i)$ we use the relativistic Thomas—Fermi method (see [1, 2]). In this approximation

$$\rho_c(r) \sim \left\{ [V(r) - \mu] + \frac{1}{2c^2}[V(r) - \mu]^2 \right\}^{3/2}, \tag{4}$$

where $V(r)$ is the total potential in the core, including δV_1 and δV_2; and μ is a constant. Linearizing (4) in the perturbation δV_i, we obtain

$$\delta\rho_c^{(1)}(r|i) \sim \rho_c^{(0)1/3}(r)\{1 + [3\pi^2\rho_c^{(0)}(r)]^{2/3}/c^2\}^{1/2} (\delta V_i(r) - \delta\mu). \tag{5}$$

The constant $\delta\mu$ can easily be determined from the conservation of charge condition:

$$\int dr \delta\rho_c^{(1)}(r|i) = 0. \tag{6}$$

Substituting (2) and (5) into one of the forms (3), we obtain the following expression for the direct polarization contribution to the energy E(A):

$$E(A) = \int\int dr_1 dr_2 \rho_1(r_1) \, V_{pol}^{(d)}(r_1, r_2) \rho_2(r_2)$$

with the effective two-particle interaction

$$V_{pol}^{(d)}(r_1, r_2) = X \{\int dr' \rho_c^{(0)1/3}(r')(1 + [3\pi^2\rho_c^{(0)}(r')]^{2/3}/c^2)^{1/2}/|r_1 - r'||r' - r_2| -$$
$$- [\int dr' \rho_c^{(0)1/3}(r')(1 + [3\pi^2\rho_c^{(0)}(r')]^{2/3}/c^2)^{1/2}/|r_1 - r'| \times \int dr'' \rho_c^{(0)1/3}(r'') \times$$
$$\times (1 + [3\pi^2\rho_c^{(0)}(r'')]^{2/3}/c^2)^{1/2}/|r'' - r_2|]/\int dr \rho_c^{(0)1/3}(r)(1 + [3\pi^2\rho_c^{(0)}(r)]^{2/3}/c^2)^{1/2}\}. \tag{7}$$

Here X is a numerical factor (see below). The second term in (7) arises because of $\delta\mu$ in (5). The exchange polarization diagram B of Fig. 2 is calculated in a similar way. We then obtain for the exchange part of the potential $V_{pol}^{(ex)}$

$$V_{pol}^{(ex)}(r_1, r_2) = -\frac{X}{2}(0.375)^{1/3}\{[\rho_c^{(0)1/3}(r_1)(1 + [3\pi^2\rho_c^{(0)}(r_1)]^{2/3}/c^2)^{1/2} +$$
$$+ \rho_c^{(0)1/3}(r_2)(1 + [3\pi^2\rho_c^{(0)}(r_2)]^{2/3}/c^2)^{1/2}]/|r_1 - r_2| - \int dr' \rho_c^{(0)-2/3}(r')(1 + \tag{8}$$

$$+ [3\pi^2 \rho_c^{(0)}(r')]^{2/3}/c^2)^{-1} [\rho_c^{(0)-1/3}(r_1)(1 + [3\pi^2\rho_c^{(0)}(r_1)]^{2/3}/c^2)^{-1/2}/|r' - r_1| +$$

$$+ \rho_c^{(0)-1/3}(r_2)(1 + [3\pi^2\rho_c^{(0)}(r_2)]^{2/3}/c^2)^{-1/2}/|r' - r_2|]/\int dr \rho_c^{(0)1/3}(r)(1 +$$

$$+ [3\pi^2\rho_c^{(0)}(r)]^{2/3}/c^2)^{1/2}\}.$$

As shown by numerical calculations, the contribution to the energy of the system from the exchange polarization diagram is usually two orders of magnitude smaller than the contribution from the direct diagram (see [12, 17], for example). Letting $c \to \infty$ in (7) and (8), we obtain the corresponding nonrelativistic expressions for $V_{pol}^{(d)}$ and $V_{pol}^{(ex)}$ (see [17]).

3. The coefficient X is found as follows. We consider the polarization interaction of two charged particles with charge distributions $\rho_1(r)$ and $\rho_2(r)$, where one of the particles is positively charged and localized at the nucleus, i.e., $\rho_1(r) = \delta(r)$. The contribution to the energy is then

$$E(A) = \int\int dr_1 dr_2 \rho_1(r_1) V_{pol}^{(d)}(r_1, r_2) \rho_2(r_2) = X \{\int\int dr_2 dr' \rho_c^{(0)1/3}(r')(1 +$$

$$+ [3\pi^2\rho_c^{(0)}]^{2/3}/c^2)^{1/2} \rho_2(r_2)/|r'| |r' - r_2| - [\int\int dr_2 dr' \rho_c^{(0)1/3}(r')(1 +$$

$$+ [3\pi^2\rho_c^{(0)}(r')]^{2/3}/c^2)^{1/2} \rho_2(r_2)/|r_2 - r'| \int dr'' \rho_c^{(0)1/3}(r'')(1 +$$

$$+ [3\pi^2\rho_c^{(0)}]^{2/3}/c^2])^{1/2}/r'']/\int dr \rho_c^{(0)1/3}(r)(1 + [3\pi^2\rho_c^{(0)}(r)]^{2/3}/c^2)^{1/2}\}. \tag{9}$$

The energy $E(A)$ can be estimated in this case without using the Thomas–Fermi method. The function $\rho_c^{(0)}(r)$ for a charge localized at the nucleus can be found analytically using Gauss' law:

$$\rho_c^{(0)}(r) = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 V_c(r, Z)), \tag{10}$$

where $V_c(r)$ is the potential. The deformation of the core caused by the additional unit charge is given by

$$\delta\rho_c(r|1) = -\frac{1}{r^2}\frac{\partial^2}{\partial Z\partial r}(r^2 \cdot \frac{\partial}{\partial r} V_c(r, Z)). \tag{11}$$

Substituting (11) into (3), we find for $E(A)$:

$$E(A) = -\int\int dr_1 dr_2 \frac{\rho_2(r_2)}{|r_1 - r_2|}\frac{1}{r_1^2}\frac{\partial^2}{\partial Z\partial r}\cdot\left(r_1^2 \frac{\partial}{\partial r_1} V_c(r_1, Z)\right). \tag{12}$$

Equating (9) and (12), we find the coefficient X. The potential (7) in this case imitates the interaction between a particle with $\rho_1(r) = \delta(r)$ and a particle with arbitrary $\rho_2(r)$. In general the quantity X is a functional of two arbitrary densities: $X[\rho_1(r), \rho_2(r)]$. In the case of arbitrary distributions ρ_1, ρ_2 the coefficient X is naturally defined in the form

$$X = X[\delta(r), \rho_1(r)]\cdot X[\delta(r), \rho_2(r)]/X[\delta(r), \delta(r)].$$

4. Earlier forms for V_{pol}, especially the relativistic analog of the Bottcher–Dalgaarno two-electron polarization potential V_{pol}^{BD} [18], have significant disadvantages in comparison with (7) and (8). The potential V_{pol}^{BD} depends on the dipole and quadrupole polarizabilities of the core, which must first be obtained in an independent calculation. The region of small $r_1 r_2$, where the use of V_{pol}^{BD} is incorrect, is excluded in V_{pol}^{BD} by introducing a cut-off factor. However, this region is very important for particles whose orbitals penetrate inside the core. The Rajagopal–MacDonald–Vosko relativistic exchange potential (see [2, 3], for example) is a one-particle potential, and therefore, cannot be used to describe many-particle effects, even in principle.

Finally, we note that the potentials (7) and (8) should certainly be used in precision systematic relativistic calculations of atoms and ions using relativistic perturbation theory for the Dirac equation with the inclusion of the Breit corrections to the Coulomb interaction potential due to retardation and magnetic interactions. In addition, the expressions obtained here give the polarization interaction energy as an effective parameter-independent functional depending only on the electronic densities. Hence, it can be used to improve the density functional theory (more exactly its relativistic variant).

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