ELECTRON CORRELATION IN THE RELATIVISTIC THEORY OF ATOMS

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An expression is obtained for the correlation energy of a relativistic atom in the second order of perturbation theory with respect to the electron interaction. The Gell-Mann and Low formula is used to calculate the energy level shift.

1. INTRODUCTION

THE traditional problem of the theory of atoms is to find better methods of calculating energy levels. The present status of this problem is as follows. For the lightest atoms we can assume the exact solution of the nonrelativistic problem to be known, and the matter reduces to calculation of the relativistic corrections of different orders, and also corrections for the motion and structure of the nucleus[1-4]. For light atoms, with $Z \leq 10$ electrons, the principal problem is to obtain as exact a solution of the Schrödinger equation as possible, or else to take into account the electron correlation[5]. Beyond $Z \approx 10$, the relativistic effects become comparable with the correlation[6]. For internal electrons in heavy atoms, the nonrelativistic approximation is in general unsuitable, and the interaction, to the contrary, is small, of the order of $1/Z$. Methods of calculating relativistic corrections in this case are discussed in[7-10]. The corrections for the motion and structure of the nucleus for heavy atoms are negligibly small.

It follows from the foregoing that for a consistent refinement of the calculations of the energy levels of multielectron atoms it is necessary to take into account simultaneously the correlation and the relativistic corrections. The principal scheme of such calculation is the topic of the present article.

2. FORMULATION OF PROBLEM

We consider an atom as an aggregate of electrons interacting with one another and moving in the field of a nucleus, which is assumed to be infinitely heavy. The Hamiltonian of the atom is of the form

$$H = H_0 + H_{int}, \tag{1}$$

$$H_0 = \int \Psi^+(\mathbf{x}) h(\mathbf{x}) \Psi(\mathbf{x})\, d\mathbf{x}, \tag{2}$$

$$h(\mathbf{x}) = \alpha \mathbf{p} + \beta m - eU(\mathbf{x}), \tag{3}$$

where H_{int} is the Hamiltonian of the interaction with the electromagnetic field, $\mathbf{p} = -i\nabla$, α and β are Dirac matrices, m is the electron mass, and $U(\mathbf{x})$ is the potential of the nucleus. We use a system of units with $\hbar = c = 1$.

As the initial approximation, it is convenient to use a relativistic variant of the Hartree-Fock self-consistent field method[11-58]. To this end, we represent H in the form

$$H = H_0' + H_{int}' = (H_0 + H') + (H_{int} - H'), \tag{4}$$

where

$$H' = \int \Psi^+(\mathbf{x})\, eV^{\mathrm{X}\Phi}(\mathbf{x})\, \Psi(\mathbf{x})\, d\mathbf{x}, \tag{5}$$

$$V^{\mathrm{HF}}(\mathbf{x}) f(\mathbf{x}) = \sum_{n=1}^{N} \int \psi_n^*(\mathbf{x}') \frac{e^2}{|\mathbf{x}-\mathbf{x}'|} \psi_n(\mathbf{x}')\, d\mathbf{x}'\, f(\mathbf{x})$$

$$- \sum_{n=1}^{N} \int \psi_n^*(\mathbf{x}') \frac{e^2}{|\mathbf{x}-\mathbf{x}'|} f(\mathbf{x}')\, d\mathbf{x}' \psi_n(\mathbf{x}), \tag{6}$$

where $f(\mathbf{x})$ is an arbitrary function. The function $\psi_n(\mathbf{x})$ are the eigenfunctions of the operator

$$h^{\mathrm{X}\Phi}(\mathbf{x}) = h(\mathbf{x}) + V^{\mathrm{X}\Phi}(\mathbf{x}), \tag{7}$$

$$h^{\mathrm{X}\Phi}(\mathbf{x}) \psi_n(\mathbf{x}) = E_n \psi_n(\mathbf{x}). \tag{8}$$

The wave function of the atom Φ^0 represents at the zeroth approximation an antisymmetrized product of the first N eigenfunctions of the operator (7) (N—number of electrons in the atom), and the zeroth-approximation energy is

$$E^0 = \sum_{n=1}^{N} E_n. \tag{9}$$

The operator h^{HF} is self-adjoint and has a complete system of eigenfunctions, which will henceforth be used as the basis system.

2. SHIFT FORMULA

We shall calculate the atomic energy-level shift under the influence of a perturbation directly in terms of the S matrix using the formula of Gell-Mann and Low[16]:

$$\Delta E = \lim_{\alpha \to 0} \frac{1}{\langle \Phi^0 | S_\alpha | \Phi^0 \rangle} \frac{i}{2} \alpha \lambda \frac{\partial}{\partial \lambda} \langle \Phi^0 | S_\alpha | \Phi^0 \rangle, \tag{10}$$

$$S_\alpha = \sum_{n=0}^{\infty} \lambda^n S_\alpha^{(n)}$$

$$= \sum_{n=0}^{\infty} \lambda^n (-i)^n \frac{1}{n!} \int_{-\infty}^{\infty} dt_1 \ldots \int_{-\infty}^{\infty} dt_n\, T(H_{1\alpha}(t_1), \ldots, H_{1\alpha}(t_n)),$$

$$H_{1\alpha}(t_k) = e^{iH_0 t_k} H_{int}' e^{-iH_0 t_k} e^{-\alpha |t_k|}. \tag{12}$$

Here λ denotes the coupling constant. We shall confine ourselves henceforth to calculation of corrections up to λ^4 inclusive. We therefore expand the numerator and the denominator in formula (10) in powers of λ and confine ourselves to terms of fourth order:

$$\Delta E = \lim_{\alpha \to 0} {}^1/_2 i\alpha \{ \langle \Phi^0 | S_\alpha^{(1)} | \Phi^0 \rangle \lambda + [2 \langle \Phi^0 | S_\alpha^{(2)} | \Phi^0 \rangle - \langle \Phi^0 | S_\alpha^{(1)} | \Phi^0 \rangle^2] \lambda^2$$

$$+[3\langle\Phi^0|S_\alpha^{(3)}|\Phi^0\rangle - 3\langle\Phi^0|S_\alpha^{(2)}|\Phi^0\rangle\langle\Phi^0|S_\alpha^{(1)}|\Phi^0\rangle + \langle\Phi^0|S_\alpha^{(1)}|\Phi^0\rangle^3]\lambda^3 + [4\langle\Phi^0|S_\alpha^{(4)}|\Phi^0\rangle - 4\langle\Phi^0|S_\alpha^{(3)}|\Phi^0\rangle\langle\Phi^0|S_\alpha^{(1)}|\Phi^0\rangle + 4\langle\Phi^0|S_\alpha^{(2)}|\Phi^0\rangle\langle\Phi^0|S_\alpha^{(1)}|\Phi^0\rangle^2 - 2\langle\Phi^0|S_\alpha^{(2)}|\Phi^0\rangle^2 - \langle\Phi^0|S_\alpha^{(1)}|\Phi^0\rangle^4]\lambda^4 + \ldots\}. \quad (13)$$

4. CLASSIFICATION OF DIAGRAMS

To calculate corrections of different orders, we can now use the usual Feynman technique in the Furry representation for a system of N electrons interacting with one another and with an additional external field with potential $-V^{HF}$. It is convenient in this case to use also a mixed gauge for the photon lines: a Coulomb gauge for photon lines beginning and ending at different electron lines, and a Lorentz (Feynman) gauge for photon lines beginning and ending with the same electron line or touching with at least one end a closed electron ring. We shall denote graphically the Coulomb interaction by means of a dashed line, and the interaction with the external field by a dashed line ending with a cross. It can then be stated that the effects of the electron with relativistic theory of the atom correspond to diagrams containing only Coulomb lines and interaction with the external field. These diagrams will thus be the subject of our study. We shall calculate all these diagrams up to fourth order (in the coupling constant $\lambda \equiv e^2$) inclusive, which will yield us the first nonvanishing correction to the energy of the atom in the Hartree-Fock approximation, i.e., the correlation energy. The remaining diagrams give the properly-relativistic and also the mixed correlation-relativistic corrections.

We agree to represent every time on the diagram as many electron lines (out of the total number N) as there are particles participating in the interaction process under consideration. Then in first order in e^2 we shall have one diagram (Fig. 1), in second order three diagrams (Fig. 2), in third order five diagrams (Fig. 3), etc. By virtue of the choice of the external potential $V \equiv -V^{HF}$, the diagram of Fig. 1, as well as the diagram of Fig. 2a, is a diagram of first order of smallness in the interaction between the electrons. Among the diagrams of second order in the interaction are those in Figs. 2b, 2c, 3a, 3b, and also the series of fourth-order diagrams shown in Fig. 4. It is these diagrams which give the energy of the correlation of the electrons in the atom in second in the interaction. The diagrams of Figs. 3c-e and also the remaining diagrams of fourth order in e^2, give correlation corrections of higher orders.

5. FORMULATION OF THE MATRIX ELEMENTS

To determine the matrix elements from the diagrams, we can use the following correspondence rules:

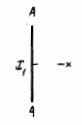

FIG. 1

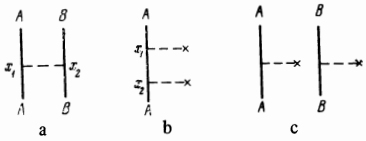

FIG. 2

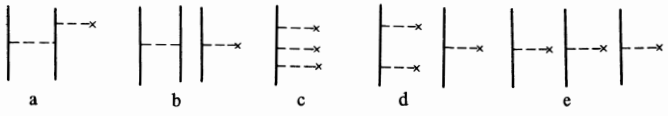

FIG. 3

to each external incoming fermion line there corresponds a function $\psi_A(x) = \psi_A(x)e^{-iEAt}$, where $\psi_A(x)$ is the solution of Eq. (8). To each incoming fermion lines there corresponds the function $\bar{\psi}_A(x) = \psi_A^*(x)\gamma_4$. To each internal fermion line there corresponds the propagator

$$S(x_1x_2) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\omega\, e^{i\omega(t_1-t_2)} \sum_n \frac{\psi_n(x_1)\bar{\psi}_n(x_2)}{E_n(1-i0)+\omega}. \quad (14)$$

The summation in (14) is carried out over the entire system of eigenfunctions of the operator (7). The Coulomb photon line corresponds to the propagator[17]

$$D_{\mu\nu}^c(k) = \frac{1}{k^2}\delta_{\mu4}\delta_{\nu4}, \quad (15)$$

or in the coordinate representation

$$D_{\mu\nu}^c(x_1x_2) = -i\frac{1}{r_{12}}\delta(t_1-t_2)\,\delta_{\mu4}\delta_{\nu4}, \quad (16)$$

where $r_{12} = |x_1 - x_2|$. The external photon lines correspond to the potentials

$$V_\mu(x) = -ieV^{HF}(x)\delta_{\mu4}, \quad (17)$$

and the vertices of the diagrams correspond to the factors $e\gamma_\nu e^{-\alpha|t|}$.

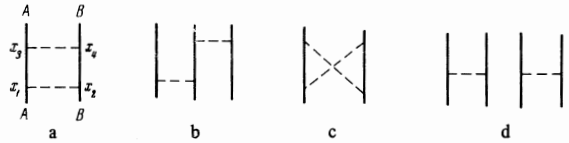

FIG. 4

6. CALCULATION OF THE CORRELATION DIAGRAMS

We begin with the calculation of the diagram of Fig. 1. The corresponding matrix element, in accordance with the correspondence rules, is of the form

$$M_1 = e\int dx_1(\bar{\psi}_A(x_1)\gamma_\mu V_\mu(x_1)\psi_A(x_1))e^{-\alpha|t_1|}. \quad (18)$$

Substituting here (17) and integrating with respect to t_1, we obtain

$$M_1 = -\frac{2i}{\alpha}e^2(V^{HF})_{AA}, \quad (19)$$

where

$$(F)_{AB} = \int\psi_A^*(x)F(x)\psi_B(x)\,dx. \quad (20)$$

We now consider the diagram of Fig. 2a:

$$M_{2a} = e^2\int dx_1\,dx_2(\bar{\psi}_A(x_1)\gamma_\mu\psi_A(x_1)) \times(\bar{\psi}_B(x_2)\gamma_\nu\psi_B(x_2))D_{\mu\nu}^c(x_1x_2)e^{-\alpha|t_1|-\alpha|t_2|}. \quad (21)$$

Substituting (16) and integrating with respect to t_1 and t_2, we obtain

$$M_{2a} = -\frac{i}{\alpha}e^2\left(\frac{1}{r_{12}}\right)_{ABAB}, \quad (22)$$

$$(F)_{A'B'AB}=\int\psi_{A'}^{*}(\mathbf{x}_1)\psi_{B'}^{*}(\mathbf{x}_2)F(\mathbf{x}_1\mathbf{x}_2)\psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2)\,d\mathbf{x}_1\,d\mathbf{x}_2. \quad (23)$$

Finally, let us calculate also the diagram of Fig. 4a:

$$M_{4a}=e^4\int dx_1\ldots dx_4(\bar\psi_A(x_3)\gamma_{\mu_3}S(x_3x_1)\gamma_{\mu_1}\psi_A(x_1))$$
$$\times(\bar\psi_B(x_4)\gamma_{\mu_4}S(x_4x_2)\gamma_{\mu_2}\psi_B(x_2))D^{c}_{\mu_1\mu_2}(x_1x_2)D^{c}_{\mu_3\mu_4}(x_3x_4)$$
$$\times\exp(-\alpha|t_1|-\alpha|t_2|-\alpha|t_3|-\alpha|t_4|). \quad (24)$$

Substituting in (24) formulas (14) and (16), we arrive at the expression

$$M_{4a}=\frac{1}{(2\pi)^2}e^4\int dt_1\,dt_3\,d\omega_1\,d\omega_2\sum_{n_1n_2}\frac{|(r_{12}^{-1})_{n_1n_2AB}|^2}{[E_{n_1}(1-i0)+\omega_1][E_{n_2}(1-i0)+\omega_2]}$$
$$\times\exp\{i(E_A+E_B+\omega_1+\omega_2)t_3\}\exp\{-i(E_A+E_B+\omega_1+\omega_2)t_1\}$$
$$\times\exp\{-2\alpha|t_1|-2\alpha|t_3|\}. \quad (25)$$

Integration with respect to t_1 yields

$$\int_{-\infty}^{\infty}dt_1\exp\{-i(E_A+E_B+\omega_1+\omega_2)t_1-2\alpha|t_1|\}$$
$$=\frac{4\alpha}{(\omega_1+\omega_2+E_A+E_B)^2+(2\alpha)^2}. \quad (26)$$

A similar factor is obtained from the integral with respect to t_3. It remains to integrate with respect to the frequencies:

$$\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2[(\omega_1+\omega_2+E_A+E_B)^2+(2\alpha)^2]^{-2}$$
$$\times[E_{n_1}(1-i0)+\omega_1]^{-1}[E_{n_2}(1-i0)+\omega_2]^{-1}$$
$$=(2\pi i)^2\{[E_{n_1}+E_{n_2}-E_A-E_B)^2+(2\alpha)^2]^{-2}$$
$$-(4i\alpha)^{-2}(E_{n_1}+E_{n_2}-E_A-E_B+2i\alpha)^{-2}$$
$$-2(4i\alpha)^{-3}(E_{n_1}+E_{n_2}-E_A-E_B+2i\alpha)^{-1}\}. \quad (27)$$

The other diagrams are calculated in similar fashion.

7. CALCULATION OF THE LEVEL SHIFT

We consider first the level shift in first order in the electron interaction. To this end it is necessary to take into account in formula (13) the diagrams of Fig. 1 and Fig. 2a. The contribution of the diagram of Fig. 1 to ΔE_1, with allowance for all the occupied single-electron states, is

$$\Delta E_1'=-e^2\sum_{A=1}^{N}(V^{\mathrm{HF}})_{AA}. \quad (28)$$

The contribution of the diagram of Fig. 2a with allowance for all the occupied single-electron states and exchange diagrams is

$$\Delta E_1''=\frac{1}{2}e^2\sum_{A,B=1}^{N}\left(\frac{1}{r_{12}}\right)_{AB;\,AB}, \quad (29)$$

where

$$(F)_{A'B';\,AB}=(F)_{A'B'AB}-(F)_{A'B'BA}. \quad (30)$$

Taking into account the definition of V^{HF} and Eq. (8), we obtain

$$E^0+\Delta E_1=\sum_{A=1}^{N}(h)_{AA}+\frac{1}{2}\sum_{A,B=1}^{N}\left(\frac{1}{r_{12}}\right)_{AB;\,AB}=E^{\mathrm{HF}}. \quad (31)$$

We thus arrive at the following result, which is known from nonrelativistic theory: the Hartree-Fock energy is obtained in first order of perturbation theory in the interaction.

We proceed to calculate the level shift in second order in the interaction. In this order there are diagrams (Figs. 2c and 4d) which give divergences of the type $1/\alpha$ on going to the limit as $\alpha\to 0$. Similar divergences are obtained also from certain terms of formula (13), due to the expansion of the denominator, and also the diagrams of Figs. 2b, 3a, 4a, and 4b when the intermediate electronic states coincide with the initial (final) ones. In particular, for the diagram of Fig. 4a, this is seen from formula (27) when $E_{n_1}+N_{e_2}=E_A+E_B$. It can be verified directly that all these divergences cancel each other. Leaving out the cumbersome calculations, we now present a final expression for ΔE_1, obtained by going to the limit with respect to α from the diagrams of Figs. 2b, 2c, 3a, 3b, and 4a–d, with allowance for all the topological and exchange variants. In this expression, account is taken also of certain cancellations that result from the choice of the potential $V=V^{\mathrm{HF}}$. We have

$$\Delta E_2=\frac{e^4}{4}\sum_{A,B}^{\leqslant N}\sum_{n_1n_2}^{>N}\frac{1}{E_A+E_B-E_{n_1}-E_{n_2}}\left|\left(\frac{\Lambda_1^{(+)}\Lambda_2^{(+)}}{r_{12}}\right)_{AB;\,n_1n_2}\right|^2$$
$$-\frac{e^4}{4}\sum_{A,B}^{\leqslant N}\sum_{n_1n_2}\frac{1}{E_A+E_B-E_{n_1}-E_{n_2}}\left|\left(\frac{\Lambda_1^{(-)}\Lambda_2^{(-)}}{r_{12}}\right)_{AB;\,n_1n_2}\right|^2$$
$$+\frac{e^4}{4}\sum_{A,B}^{\leqslant N}\sum_{n_1n_2}\frac{1}{E_B-E_A+E_{n_1}-E_{n_2}}\left(\frac{1}{2}\frac{\Lambda_1^{(+)}\Lambda_2^{(-)}-\Lambda_1^{(-)}\Lambda_2^{(+)}}{r_{12}}\right)_{An_2n_1B}$$
$$\times\left(\frac{1}{2}\frac{\Lambda_1^{(+)}\Lambda_2^{(-)}-\Lambda_1^{(-)}\Lambda_2^{(+)}}{r_{12}}\right)_{n_1BAn_2}-\frac{e^4}{4}\sum_{A,B}^{\leqslant N}\sum_{n_1n_2}\frac{1}{E_B-E_A+E_{n_1}-E_{n_2}}$$
$$\times\left(\frac{1}{2}\frac{\Lambda_1^{(+)}\Lambda_2^{(-)}-\Lambda_1^{(-)}\Lambda_2^{(+)}}{r_{12}}\right)_{An_2n_1A}\left(\frac{1}{2}\frac{\Lambda_1^{(+)}\Lambda_2^{(-)}-\Lambda_1^{(-)}\Lambda_2^{(+)}}{r_{12}}\right)_{n_1BBn_2}$$
$$-e^4\sum_{A,B,C}^{\leqslant N}\sum_{n}\frac{1}{E_A+E_B-E_C-E_n}\left[\left(\frac{\Lambda_2^{(-)}}{r_{12}}\right)_{ABCn}-\left(\frac{\Lambda_1^{(-)}}{r_{12}}\right)_{ABnC}\right]\left(\frac{1}{r_{12}}\right)_{ABCn}, \quad (32)$$

where $\Lambda^{(\pm)}$ represents the projector on the state with positive (negative) energy.

In formula (32), the first term corresponds to the usual expression of second order of nonrelativistic perturbation theory[18], while the remaining terms, which contain summation over the intermediate states with negative energy, arise in the relativistic theory. When $e^2Z\ll 1$, these terms play the role of small corrections. On the whole, expression (32) gives the correlation energy of the relativistic atom in second order of perturbation theory and the interaction between the electrons. We note that in the relativistic variant of the Hartree-Fock method, the Brillouin theorem is no longer satisfied, namely, singly excited configurations with transition of the electrons to states with negative energy give a nonzero contribution to the correlation energy.

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