RELATIVISTIC THEORY OF THE HEAVY ATOM

M. A. BRAUN, Yu. Yu. DMITRIEV, and L. N. LABZOVSKIĬ

Leningrad State University

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A method of calculating relativistic corrections, valid equally for both the outer and inner electrons in the atom, is formulated. The initial approximation is a relativistic variant of the self-consistent field method. All diagrams containing one virtual photon line are considered. After removal of all divergences a finite expression containing integrals over configuration space and sums over the intermediate electron states is obtained for the energy level shift; a variational principle is proposed for the calculation of these sums.

1. INTRODUCTION

THE relativistic description of the heavy atom is complicated not only by increase of the number of electrons but also by the fact that it is necessary to use completely different approximations to describe the outer and inner electrons in the atom. In view of the smallness of the parameter $Z_{eff}\alpha \ll 1$, where Z_{eff} is the effective charge of the nucleus and α is the fine-structure constant, the outer electrons are nonrelativistic. Therefore the relativistic corrections for these electrons may be obtained exactly as for light atoms by expanding in the parameters α and $Z_{eff}\alpha$. In the lowest order α^2Ry, these corrections are given, e.g., in [1] and in the order α^3Ry in [2]. For the internal electrons, since $Z_{eff}\alpha \sim 1$, the nonrelativistic approximation is completely invalid and it is necessary to use other methods. In view of the smallness of the parameter $1/Z_{eff}$ we may use as a starting point the approximation of relativistic electrons moving in the field of the nucleus but not interacting with each other. On the basis of this approximation a number of relativistic corrections for K-electrons in heavy atoms have been calculated.[3-5] We emphasize that these calculations and, especially, the procedure for renormalizing divergent expressions are connected in an essential way with the assumption of a Coulomb external field.

The purpose of the present work is to formulate a method equally valid for the description of all electrons in the atom. This method must satisfy two basic requirements: 1) not to use expansions in $Z_{eff}\alpha$, 2) to take account of the fact that the field in which each electron moves is not a Coulomb field. In addition it is desirable that the divergences appearing in the theory (both ultra-violet and infra-red) can be isolated and removed in the general form without using the specific form of the external potential. We shall be interested chiefly in the theoretical scheme of the calculations. After removal of all divergences the specific corrections considered are reduced to integrals in configuration (or momentum) space which must be calculated for specific atoms with definite wave functions. In this paper we leave on one side the question of the technical methods of evaluation of such integrals (which in some cases are fairly complicated). The expression for the level shift of a many-electron atom contains, as usual, sums over the intermediate one-electron states. We propose a variational method to calculate these sums.

2. FORMULATION OF THE PROBLEM

We consider the atom as an aggregate of electrons interacting with each other and moving in the field of the nucleus, which we shall assume to be infintely heavy. The Hamiltonian of the atom has the form

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

$$H_0 = \int \Psi^+(x) h(x) \Psi(x) d^3x, \tag{2}$$

$$h(x) = \alpha p + \beta m + eV^n, \tag{3}$$

where V^n is the potential of the nucleus and H_{int} is the Hamiltonian of the interaction with the electromagnetic field. Here and below we use the units $\hbar = c = 1$. Since we assume that the atom is in the ground state and is not radiating, the Hamiltonian of the free electromagnetic field is not included in H. In the absence of the interaction the wavefunction Ψ_a^0 of the atom is an antisymmetrized product of the first N eigenfunctions of the operator (3) (N is the number of electrons in the atom):

$$h(x)\psi_{n^0}(x) = E_{n^0}\psi_{n^0}(x) \tag{4}$$

The energy of the atom in this approximation is

$$E_{a^0} = \sum_{n=1}^{N} E_{n^0}. \tag{5}$$

In first order of perturbation theory the shift of level a under the action of the perturbation is equal to

$$\Delta E_a = \operatorname{Re}\langle a|M|a\rangle,$$
$$-2\pi i\delta(E_{a^0} - E_{b^0})\langle b|M|a\rangle = S_{ba}, \tag{6}$$

where S_{ba} is the matrix element of the S-matrix between states Ψ_b^0 and Ψ_a^0.

The initial approximation of non-interacting electrons is poor for all shells except the innermost; therefore we redefine the perturbation in the following way. We separate out the Coulomb interaction from H_{int}:

$$H_{int} = H'_{int} + H''_{int}, \tag{7}$$

where

$$H'_{int} = \frac{e^2}{2}\int \Psi^+(x)\Psi^+(x')\frac{1}{|x-x'|}\Psi(x')\Psi(x)\,d^3x\,d^3x', \quad (8)$$

and H''_{int} now contains only the interaction with transverse photons. As a new initial approximation it is reasonable to use the relativistic version of the Hartree-Fock self-consistent field method recently successfully developed in the theory of the atom.[7-12] For this we represent H in the form

$$H = H_0' + (H'_{int} - H') + H''_{int}, \quad (9)$$

$$H_0' = H_0 + H', \quad (10)$$

$$H' = \int \Psi^+(x)\,V^{HF}(x)\Psi(x)\,dx, \quad (11)$$

$$V^{HF}(x)f(x) = \sum_{n=1}^{N}\int \psi_n^*(x')\frac{e^2}{|x-x'|}\psi_n(x')\,d^3x'\cdot f(x) - \sum_{n=1}^{N}\int \psi_n^*(x')\frac{e^2}{|x-x'|}f(x')\,d^3x'\,\psi_n(x), \quad (12)$$

where f(x) is an arbitrary function. Now the wavefunction of the atom in the zeroth approximation is formed from the first N eigenfunctions of the operator

$$h^{HF}(x) = h(x) + V^{HF}(x), \quad (13)$$

$$h^{HF}(x)\psi_n(x) = E_n\psi_n(x). \quad (14)$$

The Hamiltonian now contains two perturbations: $H'_{int} - H'$ and H''_{int}. The correction to the energy of first order in the perturbation $H'_{int} - H'$, when added to the zeroth approximation energy, gives, as in the non-relativistic theory, the Hartree-Fock energy; corrections of the next orders begin to take account of electron correlation. We shall not consider here either these corrections or the mixed corrections in $H'_{int} - H'$ and H''_{int}, remarking only that in principle electron correlation may be taken account of by methods worked out for non-relativistic theory.[13] Below we shall consider only the perturbation H''_{int}.

3. GENERAL SCHEME OF THE CALCULATIONS

As far as possible we shall carry out the calculations in coordinate space since it is in this space that, as a rule, expressions for the wavefunctions of many-electron atoms are known. We may use the usual correspondence rules to formulate the matrix elements in terms of diagrams. To each external incoming fermion line corresponds a function $\psi_A(x) = \psi_A(x)e^{-iEAt}$, where $\psi_A(x)$ is the solution of Eq. (14). To each outgoing fermion line corresponds a function $\bar{\psi}_A(x) = \psi_A^*(x)\gamma_4$. To each internal fermion line corresponds the propagator:[14]

$$S(x_1x_2) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\omega\, e^{i\omega(t_1-t_2)}\sum_n \frac{\psi_n(x_1)\psi_n(x_2)}{E_n(1-i0)+\omega} \quad (15)$$

The summation in formula (15) extends to the region of both positive and negative energies. For the photon propagators we use a mixed gauge. Corresponding to each internal photon line beginning and ending at one and the same fermion line or resting with at least one end on a closed electron ring we have the propagator

$$D_{\mu\nu}(x_1x_2) = -\frac{i}{(2\pi)^4}\delta_{\mu\nu}\int \exp\{ikr_{12} - i\omega(t_1-t_2)\}\frac{d^3k\,d\omega}{k^2-\omega^2-i0}, \quad (16)$$

where $r_{12} = x_1 - x_2$. Corresponding to each internal photon line beginning and ending on different fermion lines is the propagator

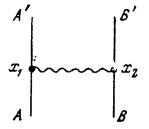

FIG. 1

$$D_{\mu\nu}(x_1x_2) = \frac{i}{(2\pi)^4}(1-\delta_{\mu4})(1-\delta_{\nu4}) \times\int \exp\{ikr_{12} - i\omega(t_1-t_2)\}\left(\delta_{\mu\nu} - \frac{k_\mu k_\nu}{k^2}\right)\frac{d^3k\,d\omega}{k^2-\omega^2-i0}. \quad (17)$$

Integration over k in (16) and (17) gives

$$D_{\mu\nu}(x_1x_2) = -\frac{i}{8\pi^2}\frac{\delta_{\mu\nu}}{r_{12}}\int_{-\infty}^{\infty}\exp\{i\omega(t_1-t_2)+i|\omega|r_{12}\}\,d\omega, \quad (18)$$

$$D_{\mu\nu}^t(x_1x_2) = \frac{i}{8\pi^2}\left\{\frac{\delta_{\mu\nu}}{r_{12}}\int_{-\infty}^{\infty}\exp\{i\omega(t_1-t_2)+i|\omega|r_{12}\}\,d\omega - \nabla_{1\mu}\nabla_{2\nu}\frac{1}{r_{12}}\int_{-\infty}^{\infty}\exp\{i\omega(t_1-t_2)\}\frac{\exp\{i|\omega|r_{12}\}-1}{\omega^2}d\omega\right\}(1-\delta_{\mu4})(1-\delta_{\nu4}), \quad (19)$$

where $r_{12} = |\mathbf{r}_{12}|$. The second integral in (19) formally diverges but the whole expression has meaning if the differentiation is carried out first. Finally, in a number of cases we need an expression for the free fermion propagators in the coordinate representation:

$$S^0(x_1x_2) = \frac{i}{8\pi^2}\int_{-\infty}^{\infty}\exp\{i\omega(t_1-t_2)\}\,F(x_1x_2;\omega)\,d\omega\,\gamma_4, \quad (20)$$

$$F(x_1x_2;\omega) \equiv \left[i\frac{\alpha r_{12}}{r_{12}^3} + \frac{\alpha r_{12}}{r_{12}^2}\sqrt{\omega^2-m^2} + \frac{\beta m}{r_{12}} - i\frac{\omega}{r_{12}}\right]\exp\{i\sqrt{\omega^2-m^2}\}. \quad (21)$$

In the following sections all one-photon diagrams (i.e., those containing one virtual photon line) in the above scheme will be considered.

4. ONE-PHOTON EXCHANGE

We shall consider the matrix element corresponding to the diagram in Fig. 1.

$$S_{A'B'AB} = \alpha\int d^4x_1\,d^4x_2(\bar{\psi}_{A'}(x_1)\gamma_u\psi_A(x_1)) \times(\bar{\psi}_{B'}(x_2)\gamma_v\psi_B(x_2))D_{\mu\nu}^t(x_1x_2). \quad (22)$$

We put expression (17) into (22) and integrate over the times t_1 and t_2;

$$\int dt_1\exp\{iE_{A'}t_1 - iE_At_1 + i\omega t_1\}\int dt_2\exp\{iE_{B'}t_2 - iE_Bt_2 - i\omega t_2\} = (2\pi)^2\delta(\omega + E_{A'} - E_A)\delta(\omega - E_{B'} + E_B).$$

Performing now the integration over ω, we obtain

$$S_{A'B'AB} = \frac{i\alpha}{2}\langle A'B'|\frac{\alpha_1\alpha_2}{r_{12}}\exp\{i|E_A - E_{A'}|r_{12}\} - (\nabla_1\alpha_1)(\nabla_2\alpha_2)\frac{1}{r_{12}}\frac{\exp\{i|E_A - E_{A'}|r_{12}\}-1}{(E_A-E_{A'})^2}|AB\rangle \times\delta(E_A + E_B - E_{A'} - E_{B'}). \quad (23)$$

The index i on the Dirac matrix α_i indicates that the matrix acts on the function $\psi(x_i)$. Taking into account all occupied one-electron states and exchange diagrams using formula (6) we obtain

$$\Delta E_a = -\frac{\alpha}{4\pi}\sum_{AB}\left[\langle AB|\frac{\alpha_1\alpha_2}{r_{12}} + \frac{1}{2}(\nabla_1\alpha_1)(\nabla_2\alpha_2)r_{12}|AB\rangle\right.$$

$$-\langle BA|\frac{\alpha_1\alpha_2}{r_{12}}\cos(E_A-E_B)r_{12}+\frac{1}{2}(\nabla_1\alpha_1)(\nabla_2\alpha_2)\frac{1}{r_{12}}\times\frac{\cos(E_A-E_B)r_{12}-1}{(E_A-E_B)^2}|AB\rangle\Big]. \quad (24)$$

Expression (24) may be simplified using the relation

$$\begin{aligned}\langle BA|(\nabla_1\alpha_1)(\nabla_2\alpha_2)f(r_{12})|AB\rangle&=-\langle BA|[h_1^{X\Phi}[h_2^{X\Phi}f(r_{12})]]|AB\rangle\\&=(E_A-E_B)^2\langle BA|f(r_{12})|AB\rangle.\end{aligned} \quad (25)$$

Then (25) is changed to the form

$$\Delta E_a=-\frac{\alpha}{8\pi}\sum_{AB}\Big[\langle AB|\frac{\alpha_1\alpha_2}{r_{12}}+\frac{(\alpha_1r_{12})(\alpha_2r_{12})}{r_{12}^3}|AB\rangle-\langle BA|\frac{1-\alpha_1\alpha_2}{r_{12}}\cos(E_A-E_B)r_{12}-\frac{1}{r_{12}}|AB\rangle\Big] \quad (26)$$

For the outer electrons, $|E_A-E_B|\sim m\alpha^2$, $r_{12}\sim 1/m\alpha$ and consequently the argument of the cosine is a small quantity of order α. Limiting ourselves to the lowest order terms in the expansion of the cosine we obtain for ΔE_α the usual Breit expression for the correction due to retardation.

5. ELECTRON SELF-ENERGY DIAGRAM

We shall consider the matrix element corresponding to the diagram in Fig. 2a (the electron self-energy). The double line depicts an electron in an external field $V=V^n+V^{HF}$ and the wave line depicts the photon. The diagram in Fig. 2a diverges in the region of high virtual photon energies. The technique of removing the divergences in this diagram was considered in the paper [5]. The electron propagator in the external field is expanded in powers of the external potential and the first two terms of this expansion are considered separately. The division of the diagram in Fig. 2a into the parts 2b, 2c and 2d corresponds diagrammatically to this expansion. In these diagrams a simple continuous line denotes a free electron and a dotted line an interaction with potential V. Divergences are contained only in diagrams 2b, c and we may use the usual covariant renormalization procedure to remove them.

The energy shift corresponding to diagram 2b can be written, using formula (6) and summing over the occupied states of the atom, in the form

$$\Delta E_a^{(1)}=-\frac{\alpha\pi}{2}\sum_A\int\bar\psi_A(\mathbf{p})\Sigma(\mathbf{p},E_A)\psi_A(\mathbf{p})\,d^3p, \quad (27)$$

where $\psi_A(\mathbf{p})$ are one-electron functions in the momentum representation and $\Sigma(\mathbf{p}, E_A)$ is the regularized self-energy part. We may borrow an expression for $\Sigma(\mathbf{p}, E_A)$ from, e.g., [15]

$$\Sigma(p)=i\hat p\Big(1-\frac{m^2}{p^2}\Big)+2m-m\Big(4+3\frac{m^2}{p^2}+\frac{p^2}{m^2}\Big)\ln\frac{p^2+m^2}{m^2}-2(i\hat p+m)\ln\frac{\lambda^2}{m^2}, \quad (28)$$

where $p\equiv(\mathbf{p}, iE_A)$ and λ is a fictitious photon mass,

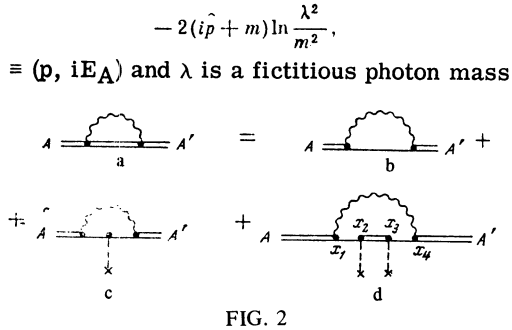

FIG. 2

which is introduced to remove the infra-red divergence. λ must be set to zero at the end of the calculations.

The energy shift corresponding to diagram 2c may be represented in the form

$$\Delta E_a^{(2)}=\frac{\alpha\pi i}{2}\sum_A\int\bar\psi_A(\mathbf{p})\Lambda_\nu(\mathbf{p},E_A;\mathbf{q},E_A)eV_\nu(\mathbf{p}-\mathbf{q})\psi_A(\mathbf{q})\,d^3q\,d^3p, \quad (29)$$

where $V_\nu\equiv(0,0,0,iV)$ and $\Lambda_\nu(\mathbf{p}, E_A; \mathbf{q}, E_A)$ is the regularized vertex part. An expression for Λ_ν is given in [15] and has the form

$$\Lambda_\nu(pq)=(a\gamma_\nu+bp_\nu+cq_\nu)(A\hat p+B\hat q+C\hat p\hat q)\times F(p^2,q^2,(p-q)^2)-2\gamma_\nu\ln(\lambda^2/m^2), \quad (30)$$

where $p\equiv(\mathbf{p}, iE_A)$ and $q\equiv(\mathbf{q}, iE_A)$. It is easy to see that the infra-red divergences in (27) and (29) are cancelled if ψ is an exact solution of Eq. (14), which in the momentum representation has the form

$$(\alpha p+\beta m-E_A)\psi_A(p)-e\int V(p-q)\psi_A(q)\,d^3q=0. \quad (31)$$

The diagram in Fig. 2d contains no divergences but computationally is much the most difficult since it contains a sum over all electron states in the external field. A variational method to remove this difficulty is proposed in the next section.

6. APPLICATION OF THE VARIATOINAL METHOD

We shall consider the matrix element corresponding to the diagram in Fig. 2d:

$$S_{AA'}=\alpha^2\int d^4x_1d^4x_2d^4x_3d^4x_4(\bar\psi_{A'}(x_4)\gamma_{\mu_4}S^0(x_4x_3)\gamma_{\mu_3}\times V_{\mu_3}(x_3)S(x_3x_2)\gamma_{\mu_2}V_{\mu_2}(x_2)S^0(x_2x_1)\gamma_{\mu_1}\psi_A(x_1))D_{\mu_1\mu_4}(x_1x_4). \quad (32)$$

Putting into (32) the expressions (15), (16) and (20), integrating over the times and frequencies and using formula (6) we arrive after certain manipulations at the expression

$$\Delta E_a^{(3)}=-\mathrm{Re}\frac{\alpha^2i}{2(4\pi^2)^3}\int_{-\infty}^{\infty}d\omega\sum_A\sum_n\frac{1}{E_n(1-i0)+\omega}\times\langle\psi_A^{(1)}(4)\psi_n^{(2)}(3)|G_A(\omega)-\alpha^{(1)}G_A(\omega)\alpha^{(2)}|\psi_n^{(1)}(2)\psi_A^{(2)}(1)\rangle, \quad (33)$$

where

$$G_A(\mathbf{x}_1\mathbf{x}_2\mathbf{x}_3\mathbf{x}_4;\omega)\equiv F^{(1)}(\mathbf{r}_{43};\omega)V(\mathbf{x}_3)V(\mathbf{x}_2)F^{(2)}(\mathbf{r}_{21};\omega)g_A(r_{14}), \quad (34)$$

$$g_A(r_{14})=r_{14}^{-1}\exp\{i|E_A-\omega|r_{14}\}, \quad (35)$$

and $F(\mathbf{r}_{43};\omega)$ is expressed by formula (21). The superscripts on the matrices and functions indicate which matrices act on which functions.

We consider the sum

$$\sum_n\frac{1}{E_n+\omega}\langle\psi_A^{(1)}(4)\psi_n^{(2)}(3)|G_A(\omega)|\psi_n^{(1)}(2)\psi_A^{(2)}(1)\rangle\equiv J_A(\omega). \quad (36)$$

Using Eq. (14) and the completeness of the system of eigenfunctions of the operator h^{HF}:

$$\sum_n(\psi_n^*(\mathbf{x}_2))_\alpha(\psi_n(\mathbf{x}_3))_\beta=\delta(\mathbf{x}_2-\mathbf{x}_3)\delta_{\alpha\beta}, \quad (37)$$

where α and β are spinor indices, we may represent the sum (36) in the form

$$J_A(\omega)=\langle\psi_A(4)|F(43;\omega)V(3)\delta(2-3)[h^{X\Phi}(2)+\omega]^{-1}\times V(2)F(21;\omega)g_A(14;\omega)|\psi_A^{(1)}\rangle \quad (38)$$

(the indices 1 and 2 may now be omitted). For the matrix element (38) we formulate a variational principle. We consider the functional

$$I_A[\psi_1, \psi_2] = \langle\psi_1(1234)|\delta(2-3)F(43;\omega)V(3)|\psi_A(4)\rangle + \langle\psi_2(1234)|V(2)F(21;\omega)g_A(14,\omega)|\psi_A(1)\rangle - \langle\psi_2(1234)|h^{X\Phi}(2)+\omega|\psi_1(1234)\rangle. \quad (39)$$

Varying this functional with respect to ψ_1 and ψ_2 we convince ourselves that its stationary value coincides with $J_A(\omega)$. The expression found must then be integrated in the complex ω-plane over the usual Feynman contour. The matrix element containing $\alpha^{(1)}G_A(\omega)\alpha^{(2)}$ can be treated analogously. As a result of applying the variational principle, the calculation of the infinite sum in (33) is reduced to the calculation of integrals in configuration space.

7. POLARIZATION OF THE VACUUM

The last one-photon diagram to be treated corresponds to polarization of the vacuum and is shown in Fig. 3a. This diagram is also divergent. Omitting here the detailed computations, we consider the removal of the divergences in this diagram. Again we expand the electron propagator in powers of the external potential and this time separate out the first four terms of the expansion. The diagrams 3b–3f are the diagrammatic equivalent of this expansion. The diagrams 3b and 3d give, by Furry's theorem, zero contribution. After renormalization the contribution of diagram 3c is equal to

$$\Delta E_a^{(1)} = -\frac{(2\pi)^4}{2\pi i}\sum_A \int \bar\psi_A(p)eV_\mu(k)\Pi_{\mu\nu}(k,0)D_{\nu\lambda}(k,0)\gamma_\lambda\psi_A(p+k)\,d^3p\,d \quad (40)$$

where $\Pi_{\mu\nu}(k)$ is the regularized photon self-energy part[14] and $D_{\nu\lambda}(k)$ is the photon propagator. The contribution of diagram 3e is

$$\Delta E_a^{(2)} = -\frac{1}{2\pi i}\sum_A \int \bar\psi_A(p)eV_{\mu_1}(k_1)eV_{\mu_2}(k_2)eV\,{}^{\nu}(k_3) \times I_{\mu_1\mu_2\mu_3\mu_4}(k_1 0;\, k_2 0;\, k_3 0)D_{\mu_4\mu_5}(k_1+k_2+k_3,0)\gamma_{\mu_5} \times\psi_A(p+k_1+k_2+k_3)\,d^3p\,d^3k_1\,d^3k_2\,d^3k_3, \quad (41)$$

where $I_{\mu_1\mu_2\mu_3\mu_4}(k_1k_2k_3)$ is the regularized photon-photon scattering tensor.

Diagram 3f does not contain divergences. Using the above method we may represent the contribution of this diagram to the energy shift in the form

$$\Delta E_a^{(3)} = -\mathrm{Re}\frac{2\alpha^3 i}{(4\pi)^6}\int_{-\infty}^{\infty} d\omega\,\mathrm{Sp}_{(2)}\sum_A\sum_n \frac{1}{E_n(1-i0)+\omega} \times\langle\psi_A^{(1)}(1)\psi_n^{(2)}(4)|(1-\alpha^{(1)}\alpha^{(2)})R^{(2)}(\omega)|\psi_A^{(1)}(1)\psi_n^{(2)}(5)\rangle, \quad (42)$$

where

$$R(x_1x_4x_5;\,\omega) = V(x_4)V(x_5)\int F(r_{32};\omega)V(x_3)F(r_{43};\omega)\frac{1}{r_{12}}F(r_{65};\omega) \times V(x_6)F(r_{26};\omega)\,d^3x_2\,d^3x_3\,d^3x_6. \quad (43)$$

Summing over the intermediate states may be avoided, as in the case of diagram 2d, by using the variation principle.

8. CONCLUSION

The suggested method makes it possible in principle to calculate any matrix elements. The method of removing divergences, considered for two examples, is general and leads to the elimination from the theory of all divergent expressions before the final state of the calculations. Application of the variational principle

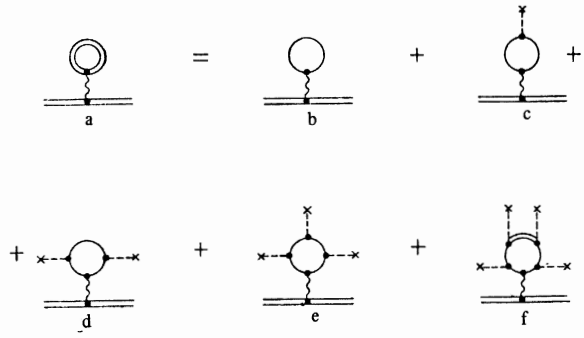

FIG. 3

to calculate expressions containing sums over the intermediate states also has the character of a general prescription. We use this method for cases with repeated summation.

We have not touched upon the question of the order of magnitude of the matrix elements corresponding to different diagrams. This depends on Z_{eff}, i.e., on which shell of the atom we are considering. For inner electrons the one-photon diagrams considered above give the main contribution to ΔE, of order α when compared with E^0. For the outer electrons the diagram in Fig. 1 gives a contribution of order α^2 and the diagrams in Figs. 2 and 3 a contribution of order α^3. Besides these a whole series of two-photon diagrams also gives a contribution of order α^3.[2] It can be said that, in the general case, the diagrams which must be taken into account are the same for all the electrons of a heavy atom as for the outer electrons.

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