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Relativistic and radiative corrections to the energy of the ground state of an atom

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Feynman vacuum diagrams with a non-zero chemical potential renormalized in a certain manner are used to obtain relativistic and radiative corrections to the energy of the ground state of an atom. Corrections are obtained in the lowest (second) order of perturbation theory which are the sum of contributions of the Lamb shift, vacuum polarization and the Breit correction for the electrons of an atom in an effective external field. Numerical calculations are carried out for a number of neutral atoms using both the semiclassical and the nonrelativistic approximations.

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§1. INTRODUCTION

In connection with the increase in the accuracy of experimental investigations and the improvement of calculational methods recently there has been a growth in the interest in relativistic corrections to the theory of a many-electron atom. In their simplest form they are taken into account by means of the relativistic equations of the Hartree-Fock self-consistent field based on the Dirac equation (cf., for example, Ref. 1). A further improvement in the calculation requires the solution of two theoretical problems. Firstly, it is necessary to have a convenient apparatus for the calculation of the energy of a many-electron relativistic atom taking into account the retarded interaction between electrons. Secondly, it is necessary to carry out a renormalization of the mass and of the charge of the electron. These problems are interconnected, since a convenient calculation of the energy first of all presupposes just the possibility of carrying out a program of renormalization without operating in the intermediate stages with divergent nonphysical quantities.

It should be emphasized that no difficulties of principle exist in carrying out the program of renormalization for an atom. The corresponding many-electron Green's function in an external field can evidently be renormalized in the usual manner. However, to extract in a simple manner from such a Green's function the value of the energy of the atom appears to be possible only in the simplest cases of one- or two-electron atoms.[2,3] For a greater number of electrons the equations for the many-electron Green's function are very complicated and no one has succeeded in finding a simple algorithm for calculating the corrections to the energy using perturbation theory. We note in this connection that the well-known Gell-Mann–Low formulas[4] contain differentiation with respect to the bare charge and the obviously noncovariant time cut-off and are therefore inappropriate for use with renormalized quantities.

Earlier Labsovskiĭ and one of the authors of the present paper proposed a method of calculating the renormalized energy of the atom consisting of extracting from the renormalized many-electron Green's function the effective Hamiltonian for the interaction between electrons.[5] The interaction potential in this case turned out to be nonlocal and nonunique. The principal disadvantage of such a method, along with its certain artificiality, is associated with the fact that in this case each Feynman diagram is in fact counted twice: once as a contribution to the potential, and a second time as an iteration of the potential in the lowest order in determining the energy. This leads to a sharp increase in the amount of calculation. However, this method also has serious advantages—thus, it encounters no difficulty with degenerate ground states and enables one to determine also the excited energy levels.

For the calculation of the energy of a nondegenerate ground state of the electron shell of an atom a more natural and simple method of calculation appears to be one based on the quantum-field-theoretic technique with a given non-zero chemical potential μ. The renormalization and the determination of the energy for relativistic Fermi-systems in the case of zero external field and

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temperature were considered in Refs. 6, 7, and in the case of non-zero external field and temperature in Refs. 8, 9. In the present paper, which to a large extent is based on the results of Ref. 9, we apply the general theory for finding the energy of a relativistic Fermi-system to the case of an atom with filled shells. The expression for the energy of the ground state of an electron shell turns out to be renormalized and finite. In the lowest (second) order of perturbation theory it, as should be expected, consists of contributions from the Breit correction, the Lamb shift and the vacuum polarization calculated using the self-consistent atomic potential. In carrying out the numerical calculation we use the semiclassical approximation and an expansion in powers of $Z\alpha$ (Z is the nuclear charge, α is the fine structure constant). The values of the corrections obtained for neutral atoms with different values of Z are exhibited in Table I at the end of Sec. 4.

§2. THE ENERGY OF THE GROUND STATE OF A RELATIVISTIC ATOM

It is well known that an explicit expression for the energy of the nondegenerate ground state of a Fermi-system is given in perturbation theory by the sum of connected vacuum Feynman diagrams (up to the factor $2\pi i\delta(0)$).[10] In the relativistic case this expression is not renormalized, i.e., it contains the bare charge and mass of the electron, and, moreover, it diverges for large virtual momenta of the electrons and photons. The renormalization of the charge and of the mass of the electron in vacuum diagrams can be carried out by introducing the corresponding counterterms in the interaction Lagrangian. This corresponds to the elimination of divergences in the vacuum diagrams associated with the internal insertions of the polarization of the vacuum and of the proper mass of the electron (for details cf., Ref. 9). The sum of vacuum diagrams V^* obtained after such a renormalization, however, still remains infinite. The point is that the total energy of the system includes nonobservable contributions: the energy of the vacuum and the energy of the interaction between charges which renormalize the external field. The separation out of these contributions has been carried out previously.[9]

If, as is usually done, one associates with the energy E and the number of particles N the quantity $\Omega = E - \mu N$ (Ω is the thermodynamic potential of the system at a temperature equal to zero), then, as has been shown in Ref. 9, the observable part of Ω is expressed in terms of the renormalized sum of the vacuum diagrams V^* by the relations

$$\Omega(\mu, A^{(0)}) - \Omega(0, 0) = -(V + {}^1/_2 jD|_0 j), \tag{1}$$

$$V = V^* - V^*|_0 - {}^1/_2 A\,\partial^2 V^*/\partial A^2|_0 A, \tag{2}$$

$$j = -\partial V/\partial A. \tag{3}$$

Here $A^{(0)}$ and A are the renormalized external and total fields in the system. A symbolic method of recording is used in which all the quantities are regarded as matrices in the configuration space in terms of the vector indices of the photons. The symbol $|_0$ refers to zero chemical potential and external field. $D|_0$ is the renormalized total Green's function for the photon familiar in the usual quantum electrodynamics for vacuum. The quantity j has the physical meaning of the observable current in the system. The vacuum diagrams V^* must be evaluated in the external field A which satisfies the equation

$$D^{-1}|_0 A = D^{(0)-1} A^{(0)} + j, \tag{4}$$

where $D^{(0)}$ is the free photon propagator.

Since j itself is related to V^* by Eq. (3), it is clear that the system (2)–(4) represents a complex system of equations with respect to the unknowns V^*, A, and j.

We now turn to the specific problem of determining the shift in the energy of an atom as a result of taking relativistic effects into account. The interaction of electrons with a quantized electromagnetic field leads to an explicit change in V by an amount δV (addition of new diagrams to V^*). This is accompanied by a change also in the external field A by an amount δA. The total change in V is obtained by adding the explicit δV and the change due to the variation δA:

$$\delta V_{\text{tot}} = \delta V + \frac{\partial V}{\partial A}\delta A. \tag{5}$$

The quantity δA can be obtained from Eq. (4) in the form

$$\delta A = D|_0 \delta j + \delta D|_0 (j + D^{(0)-1} A^{(0)}). \tag{6}$$

Substituting (6) and (5) into expression (1) we obtain the shift $\delta\Omega$, which corresponds to adding new diagrams to V:

$$\delta\Omega(\mu, A^{(0)}) - \delta\Omega(0, 0) = -\delta V + j\delta D|_0 D^{(0)-1} A^{(0)} + {}^1/_2 j\delta D|_0 j. \tag{7}$$

In order to go over to the shift in the energy of the electron shell of an atom δE we subtract from (7) its value for $\mu = 0$ and make use of (8):

$$\delta E = \delta\Omega(\mu, A^{(0)}) - \delta\Omega(0, A^{(0)}) + \mu\delta N. \tag{8}$$

Then we have

$$\begin{aligned}\delta E = {} & \mu\delta N - \delta V(\mu, A(\mu)) + \delta V(0, A(0)) \\ & + [j\delta D|_0 D^{(0)-1} A^{(0)} + {}^1/_2 j\delta D|_0 j] - [\mu = 0].\end{aligned} \tag{9}$$

It can be seen that the shift in the energy is a sum of contributions of the additional vacuum diagrams themselves and of the contributions due to the change in the form of the photon propagator $\delta D|_0$. We shall utilize this formula also in subsequent discussion. It should be noted that the use of quantum-field perturbation theory to obtain V is possible only if the ground state of the atom is not degenerate. Therefore in future we shall consider only atoms with filled shells.

§3. RADIATIVE AND RELATIVISTIC CORRECTIONS TO THE ENERGY OF AN ATOM IN THE LOWEST ORDER OF PERTURBATION THEORY

We assume that the starting zero-order approximation for the description of the atom is the system of relativistic Hartree-Fock equations with Coulomb interaction between electrons. By relativistic and radiative corrections we respectively understand corrections due to the

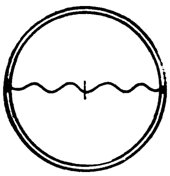

FIG. 1.

effects of magnetic interaction, retardation and self-action of electrons which are not contained in the relativistic Hartree-Fock equations. These corrections arise, on the one hand, as a result of the interaction of electrons with the transverse part of the quantized electromagnetic field, and on the other hand as a result of vacuum polarization. In the lowest order of perturbation theory they are described by the diagram of Fig. 1 for δV and by the diagram of Fig. 2 for $\delta D|_0$. The wavy line with a crossbar corresponds to the transverse part $D|_B^{(0)}$ of the photon propagator in the Coulomb gauge:

$$D_B^{(0)}(p)=-g_{\alpha s}g_{\beta q}\left(g^{sq}+\frac{p^s p^q}{\mathbf{p}^2}\right)\frac{1}{p^2}. \tag{10}$$

(In (10) $\alpha,\ \beta=0, 1, 2, 3$; $s,\ q=1, 2, 3$.) The solid double line corresponds to the electron propagator (with the chemical potential μ) in the external field $A(\mu)$, determined by Eq. (4).

In principle $A(\mu)$ can contain a vector potential. In the lowest order of perturbation theory the vector potential leads to corrections to the energy corresponding to a direct Breit interaction. For the filled shells under consideration, however, the vector potential and the direct Breit corrections vanish and in the Hartree-Fock equations it is sufficient to take into account the pure Coulomb interaction. We note that the term corresponding to the exchange (Coulomb) interaction between electrons does not appear in (4). It is artificially added to $A(\mu)$ and this corresponds to taking into account the diagram analogous to Fig. 1, but with the Coulomb (longitudinal) propagator $D_C^{(0)}(p)=g_{\alpha 0}g_{\beta 0}/\mathbf{p}^2$.

We turn to a detailed examination of (9). The diagram of Fig. 2 has been calculated repeatedly, and it remains for us to utilize the old results for $\delta D|_0$ (cf., for example, Ref. 11). In doing so we note that the fourth term in (9) describes the usual vacuum polarization in the field of the nucleus $A^{(0)}$, while the fifth term corresponds to the polarization in the field created by the charge of the electrons. The term $\mu\delta N$ is equal to zero since δE determined from (9) is much smaller than the spacing between the levels and the corresponding change in the number of particles is $\delta N=0$.

To establish the physical meaning of the difference $\delta V(\mu, A(\mu))-\delta V(0, A(0))$ we introduce the quantity

$$V_1^*(A(\mu))=V^*(0, A(\mu)).$$

We have of course

$$V^*|_0=V_1^*|_0,\quad \partial^2V^*/\partial A^2|_0=\partial^2V_1^*/\partial A^2|_0.$$

Therefore taking (2) into account we represent V in the form

$$V(\mu, A(\mu))=V^*(\mu, A(\mu))-V_1^*(A(\mu))+W(A(\mu)), \tag{11}$$

where the quantity $W(A(\mu))$ is determined by the formula

$$W(A(\mu))=V_1^*(A(\mu))-V_1^*|_0-{}^1/_2 A\partial^2V_1^*/\partial A^2|_0 A \tag{12}$$

and has the physical meaning of a renormalized energy corresponding to the external field $A(\mu)$ in vacuum.

Utilizing (11) we rewrite the contribution in which we are interested of the vacuum diagrams to the energy shift in the form

$$\begin{aligned}\delta V(\mu, A(\mu))-\delta V(0, A(0))=\delta V^*(\mu, A(\mu))-\delta V_1^*(A(\mu))\\ +\delta W(A(\mu))-\delta W(A(0)).\end{aligned} \tag{13}$$

Explicitly in the Furry representation[12] the electron propagator is given by

$$G^{(0)}(\mu, A(\mu))=\sum_n\frac{\psi_n\bar{\psi}_n}{\varepsilon_n-\varepsilon-i0\cdot\operatorname{sign}(\varepsilon_n-\mu)},$$

where ψ_n is the complete set of solutions of the Dirac equation in the external field $A(\mu)$ corresponding to the energy levels ε_n.

We break up $G^{(0)}(\mu, A(\mu))$ into two terms:

$$G^{(0)}(\mu, A(\mu))=G^{(0)}(0, A(\mu))+\Delta G^{(0)},$$

where

$$\Delta G^{(0)}=-2\pi i\sum_n\psi_n\bar{\psi}_n\theta(\mu-\varepsilon_n)\theta(\varepsilon_n)\delta(\varepsilon_n-\varepsilon). \tag{14}$$

The first difference in (13) can correspondingly also be broken up into two terms:

$$\delta V^*(\mu, A(\mu))-\delta V_1^*(A(\mu))=\delta V_L+\delta V_B,$$

where

$$\delta V_B=-\frac{\alpha}{2\pi}\operatorname{Sp}\{\Delta G^{(0)}\gamma_\alpha\Delta G^{(0)}\gamma_\beta D_B^{(0)\alpha\beta}\}, \tag{15}$$

$$\delta V_L=\frac{i}{2\pi}\operatorname{Sp}\{\Delta G^{(0)}\Sigma_1\}. \tag{16}$$

According to the renormalization procedure for V^* (cf., Ref. 9) the quantity Σ_1 is the usual mass operator of quantum electrodynamics in the lowest order of perturbation theory in the Furry representation less the subtractive term corresponding to the renormalization of the electron mass:

$$\Sigma_1(0, A)=\Sigma(0, A)-\Sigma|_0(\hat{p}=m).$$

Expression (16) is finite, since if we represent Σ_1 in the form

$$\Sigma_1(0, A)=\Sigma_r(0, A)+(\hat{p}-m-e\hat{A})\Sigma'|_0(\hat{p}=m),$$

then Σ_r is a finite expression for the proper mass of the electron in the field A, while the second term makes a

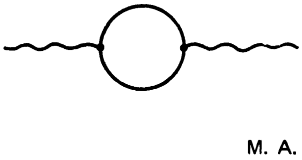

FIG. 2.

zero contribution to δV_L (in virtue of the properties of the functions ψ_n).

Taking into account the fact that in (14) summation is carried out only over the occupied levels in the atom ($\varepsilon_n < \mu$), it can be easily seen that δV_L is simply the sum of the Lamb shifts of the electrons of the atom, while δV_B is the sum of the exchange matrix elements corresponding to the magnetic interaction of the electrons taking retardation into account (the exchange correction due to Breit).

The quantity $\delta W(A(\mu))$ is the change in the energy of the field due to the interaction with the electron-positron vacuum (i.e., terms of the fourth, sixth, etc. order in the field). As can be shown, the contribution $\delta W(A(\mu)) - \delta W(A(0))$ is of the order $Z(Z\alpha)^7$ Ry and is negligibly small in comparison with the Lamb and the Breit corrections.

§4. EVALUATION OF THE CORRECTIONS IN THE SEMICLASSICAL APPROXIMATION

For a direct calculation of the contributions δV_L and δV_B we first of all consider the motion of the atomic electrons themselves to be nonrelativistic. Such an approximation is valid for all the electrons in the atom under the condition $Z\alpha \ll 1$. If $Z\alpha \sim 1$ then the nonrelativistic approximation does not hold only for the innermost electrons, which it is then necessary to take into account by a more rigorous method. In the nonrelativistic approximation one can in the usual manner make a transition from the Dirac bispinors to the Pauli spinors.

Further calculations are completely analogous to the calculation of the Lamb shift in a hydrogen-like atom and of the Breit correction to the interaction of two electrons.[13] As a result we obtain the following nonrelativistic expressions for the energy shifts $\delta E_L = -\delta V_L$ and $\delta E_B = -\delta V_B$ which represent simply sums of known expressions for the Lamb shift and the Breit correction for all the electrons in the atom:

$$\delta E_L = \frac{\alpha e}{4\pi m^2} K\left(\frac{4}{3}\ln\frac{m}{2\varkappa} + \frac{10}{9}\right) - \frac{2\alpha}{3\pi} B. \tag{17}$$

Here we have

$$B = m^{-2} \sum_{nn'} |\mathbf{p}_{nn'}|^2 (\varepsilon_{n'} - \varepsilon_n) \ln\frac{|\varepsilon_{n'} - \varepsilon_n|}{\varkappa}, \tag{18}$$

$$K = \sum_n \langle \Psi_n | \Delta\varphi | \Psi_n \rangle, \tag{19}$$

$$\Delta\varphi(r) = e[Z\delta^3(r) - \rho(r)]; \tag{20}$$

Ψ_n is the nonrelativistic wave function for the electron in level n; the sum over n includes only filled levels, and over n' only the unfilled ones; we set $\varkappa$ equal to $Z^2\alpha^2 m$; $\rho(r)$ is the density of the electrons in the atom; $\varphi(r)$ is the field in which the electrons move, i.e., the zero-order approximation for $A(\mu)$.

$$\delta E_B = \frac{\alpha}{2m^2} \sum_{nn''} \iint d^3r_1\, d^3r_2\, \Psi^*_{n''}(\mathbf{r}_1)\, \Psi_n^*(\mathbf{r}_2) \times \left[\frac{\Delta\mathbf{r}(\Delta\mathbf{r}\mathbf{p}_1)\mathbf{p}_2}{(\Delta r)^3} + \frac{\mathbf{p}_1\mathbf{p}_2}{\Delta r}\right] \Psi_n(\mathbf{r}_1)\, \Psi_{n''}(\mathbf{r}_2) + \frac{3\pi\alpha}{4m^2} \int d^3r\, \rho^2(r), \tag{21}$$

$$\Delta\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2.$$

In (21) n'', just as n, takes on only values corresponding to filled levels, while the summation over the spins has already been carried out. Everywhere the system of units $\hbar = c = 1$ is used in which $\alpha = e^2/4\pi$.

It is necessary to add to these shifts the analogous contribution from vacuum polarization (cf., (9)):

$$\delta E_P = -\frac{4Z\alpha^2}{15m^2}\rho(0) + \frac{2\alpha^2}{15m^2}\int d^3r\, \rho^2(r). \tag{22}$$

In going over from (9) to (22) we utilized the available expression $\delta D|_0 = 4\alpha\delta^3(r)/15m^2$ (cf., for example, Ref. 11).

For the calculation of $\rho(r)$ and also of the matrix elements appearing in (18), (19), and (21) and for the summation over the states we utilize the quasiclassical approximation. Of course, this approximation is too rough for the innermost electrons. However, we expect that for a general estimate of the contribution made by relativistic and radiative corrections to the energy of all the electrons the semiclassical approximation yields sufficiently sensible results (particularly since in principle one can improve the calculation by taking the lower levels into account more accurately). One should expect particularly good accuracy for the contribution to the corrections due to electron-electron interaction which is associated with the behavior of the wave functions in the region relatively far from the nucleus.

We consider the radial matrix element appearing in (18) of the form

$$\Phi_{n_r l, n'_r l\pm1} = \int_0^\infty dr\, \Phi(r)\chi_{n_r l}(r)\chi_{n'_r l\pm1}(r),$$

where $\chi_{n_r l}/r$ is the radial wave function for the electron, while $\Phi(r)$ is an arbitrary smooth function. If we approximate $\chi_{n_r l}$ by its semiclassical expression and utilize the saddle-point method for the evaluation of the integral then $\Phi_{n_r l, n_r', l\pm1}$ can be calculated explicitly.

Let $\varepsilon_{n'} > \varepsilon_n$, then $\Phi_{n_r l, n_r', l-1} = 0$, while

$$\Phi_{n_r l, n_r' l+1} = \Phi(r_0)(\pi m r_0)^{1/2} \frac{\cos(\sigma_{n_r l}(r_0) - \sigma_{n_r l+1}(r_0) - \pi/4)}{[\tau^{(0)}_{n_r l}\tau^{(0)}_{n_r' l+1} p_{n_r l}(r_0)\Delta\varepsilon]^{1/2}}. \tag{23}$$

Here the following notation has been introduced:

$$\Delta\varepsilon \equiv \varepsilon_{n'} - \varepsilon_n, \quad r_0^2 = (l+1)/m\Delta\varepsilon,$$
$$p^2_{n_r l}(r) = \left[\varepsilon_{n_r l} - e\varphi(r) - \frac{(l+{}^1/_2)^2}{2mr^2}\right]2m$$

(with $p^2_{n_r l}(r_0) = p^2_{n_r', l+1}(r_0)$),

$$\tau^{(0)}_{n_r l} = m\int_{r_{10}}^{r_{20}} \frac{dr}{p_{n_r l}(r)}, \quad \sigma_{n_r l}(r) = \int_{r_{10}}^{r} p_{n_r l}(r')\,dr';$$

r_{10} and r_{20} are the boundaries of the physical region.

Substituting the expression of the form (23) for the matrix elements into (18) we, remaining beyond this within the framework of the semiclassical approximation, replace the oscillating squares of the cosines by

$\frac{1}{2}$ and go over from a summation over the levels to integration over ε by using the relation

$$dn/\tau^{(0)}=d\varepsilon/\pi. \tag{24}$$

We succeed in carrying out a part of the integrations explicitly, while the remaining integration over the distance of the stationary point from the origin r_0 has to be carried out numerically. In the course of this r_0 varies over the region corresponding to the classical motion of the electrons in the given external field $\varphi(r)$ with the centrifugal energy $(l+\frac{1}{2})^2/2mr^2$. It is clear that this region is finite.

As regards the expressions for K, δE_B and δE_P, in order to calculate them it is sufficient to know only the electron density. After making the replacement (24) and carrying out the summation over l by the corresponding integration $\rho(r)$ in the physical region turns out to be equal to

$$\rho(r)=\frac{1}{3\pi^2}\left[2m(\mu-e\varphi(r))-\frac{1}{4r^2}\right]^{3/2}. \tag{25}$$

The contribution to (19) and (22) made by terms containing $\delta^3(r)$ and proportional to the electron density at the origin requires special consideration. Here the contribution is made only by the s-electrons. We sought the value of the wave function at the origin assuming that at small distances from the nucleus the wave function coincides with the Coulomb function with an accuracy up to the normalization constant which we determined in the semiclassical approximation. After this the summation over the levels was carried out by using (24). Finally, we calculated the contribution made by the first two terms to the expression (21) for the Breit correction in the approximation of weakly inhomogeneous plasma. In other words, we obtained its spatial density considering the electron distribution to be homogeneous, and then integrated it over the whole space taking into account the dependence of the Fermi momentum on the coordinate.

As a result of these calculations we obtained the following expressions for the corrections to the energy due to the Breit (exchange) interaction, vacuum polarization and the Lamb shift (cf., (17)):

$$\delta E_B=\frac{2\alpha}{3\pi^2m^2}J, \tag{26}$$

$$\delta E_P=\frac{8\alpha^2J}{135\pi^3m^2}-\frac{8Z^2\alpha^3}{15\pi}(\mu+2mZ^2\alpha^2-1.8m\alpha^2Z^{4/3}), \tag{27}$$

TABLE I. Relativistic and radiative corrections for neutral atoms with different Z.[1)]

Z	Lamb shift	Vacuum polarization	Breit interaction	Total shift due to all three corrections.
10	0.028	−0.002	0.034	0.060
12	0.051	−0.004	0.067	0.114
15	0.111	−0.011	0.147	0.247
18	0.192	−0.023	0,272	0.441
20	0.259	−0.037	0.405	0,627
25	0.445	−0.091	0.884	1.238
30	0.624	−0,194	1,661	2.091
36	0.564	−0.401	3.090	3,253
40	0.294	−0.624	4.456	4.126

[1)] Energy in Ry.

TABLE II. Contribution due to the electron-electron interaction.[1)]

Z	Lamb shift	Vacuum polarization	Z	Lamb shift	Vacuum polarization	Z	Lamb shift	Vacuum polarization
10	−0.011	0,0005	18	−0.054	0.004	30	−0.196	0.020
12	−0.017	0.0008	20	−0.071	0.005	36	−0.285	0.038
15	−0.033	0.002	25	−0.125	0.011	40	−0.359	0.053

[1)] Energy in Ry.

$$K=2m^3Z^4\alpha^3e\pi^{-1}(2-1{,}8Z^{-2/3})-\frac{e}{4\pi}\left(\frac{4}{3\pi}\right)^2J, \tag{28}$$

$$B=-\frac{2\alpha}{\pi m}\int dr\,r[\varphi'(r)]^2\left\{2(2mr^2[\mu-e\varphi(r)]-{}^1/_4)^{1/2}\ln(Z\alpha mr)\right.$$
$$\left.-\sum_{l=1}^{\nu}(2mr^2[\mu-e\varphi(r)]-(l+{}^1/_2)^2)^{1/2}\ln\left(\frac{l+1}{l}\right)\right\}, \tag{29}$$

$$J=\int r^2\rho^2(r)\,dr$$

$$\nu=E\{\max(2mr^2[\mu-e\varphi(r)])^{1/2}-{}^1/_2\}.$$

The integral J is taken over the region where $\rho(r)>0$, while the integrals in (29) are taken over the region where the expression under the radical are positive (from this condition it follows that the summation over l is limited by ν).

These formulas contain the potential $\varphi(r)$ in which the atomic electrons move. For the numerical calculations we restricted ourselves to neutral atoms ($\mu=0$) with $Z \leq 40$, having in mind the applicability of the nonrelativistic approximation. For $\varphi(r)$ we used the approximation due to Tietz[14]:

$$e\varphi(r)=-Z\alpha/r(1+0.606Z^{1/3}rm\alpha)^2.$$

The values that we have obtained for the energy shifts of the electron shell in Ry are exhibited in Table I.

The table shows results not only for atoms with filled shells. In the semiclassical approximation the effects associated with the incomplete filling of the shells are not taken into account, and conclusions can be regarded valid for any atoms with $Z \leq 40$. One should only keep in mind that for atoms with unfilled shells the corrections associated with the direct Breit interaction are different from zero and must be added to the corrections obtained here.

As has been pointed out earlier, the semiclassical approximation apparently can yield the greatest accuracy for the estimation of the contribution to the corrections made by the electron-electron interaction. In order to estimate the contribution made by the inter-electron interaction to the Lamb shift and to the vacuum polarization one can proceed in the following manner. We calculate separately the value of these corrections for the pure Coulomb interaction and subtract them from the corrections given in the first two columns of Table I. The values of the contribution made by the interaction between the electrons obtained in this manner are shown in Table II.

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Properties of rotational transitions during collisions between molecules

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Possible rotational relaxation channels in a molecular gas that can be described by selection rules for nonspherical scattering are considered. It is shown that the selection rules for nonspherical scattering can be either exact or approximate. In the former case, the rules are due to some general symmetry properties of the interaction between the molecules; in the latter case, they are due to the dynamics of the particles and, in particular, they depend on the ratio of the moments of inertia of the molecules and on departures from equilibrium in the gas. It is shown that the selection rules obtained in this paper do not differ significantly from the Born-scattering selection rules. Selection rules are obtained for rotational transitions that are forbidden in the case of scattering by an atom, but are possible for scattering by a molecule.

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1. INTRODUCTION

Rotational relaxation in a polyatomic gas, i.e., the redistribution of rotational-level populations as the system tends to the equilibrium state may occur as a result of the complicated character of the nonspherical interaction between the molecules along different channels. The existence of several rotational relaxation channels in polar gases (for example, CH_3CN, CH_3F, C_2H_5CN) is indicated by experiments on the anomalous Senftleben effect.[1,2] Gordiets *et al.* have discussed the possibility of a laser for the microwave band, using the rotational transitions of molecules for which the probabilities of excitation transfer with $\Delta J \neq 0$ and $\Delta K \neq 0$ on collision are different (J and K are the angular momentum and the angular momentum component along an internal axis).

The number of possible relaxation channels, and the relationship between the probabilities of excitation transfer, are determined by the selection rules for transitions between rotational levels during collisions between molecules. These selection rules can be governed by general symmetry principles, for example, time reversal, inversion, and point symmetry of the molecule. Moreover, as will be shown below there may be selection rules governed by the dynamics and interaction of the molecules.

The description of rotational relaxation in the polyatomic case encounters definite difficulties because of the absence of adequate experimental data on the nonspherical scattering of molecules[4,5] and because of the complexity of highly nonequilibrium kinetic problems. Several papers have been published in recent years on the inelastic scattering of polar molecules, investigated by double microwave-microwave[5] and infrared-microwave resonance.[6–9] These methods consist of measuring the change in the absorption of microwave radiation corresponding to a definite transition between rotational levels whose population changes as a result of the application of the pump radiation at the transition frequency between two other levels (rotational or vibrational-rotational), and collisional transitions between pairs of levels. By retuning the frequency of the incident microwave radiation and measuring the absorption in the presence of the pump radiation, it is possible to determine the set of rotational states occupied by the excited molecules after collisions. As a result of such studies, and studies by the method of modulated double microwave resonance,[10,11] it has been possible to establish collisional selection rules for a number of polar molecules.

The selection rules are discussed by Oka[5] in the Born approximation. This discussion makes use of the nonspherical model scattering potential[12] which takes