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QUADRATIC STARK EFFECT ON ATOMS

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A method is proposed for calculating the polarizabilities of atoms. The method is based on the use of the Green's function of the optical electron in the approximation of the method of the quantum defect. The dynamic polarizabilities of the ground and first-excited states of alkali atoms are calculated in a wide frequency interval, as is the shift of the 5461-Å resonant line of the Hg atom under the influence of radiation from a neodymium laser.

1. INTRODUCTION

THE action of an intense high-frequency field on atoms leads to perturbation of the atomic states. This perturbation, in the general case, is quadratic in terms of the external field, since the atom is a spherically symmetrical system, with the exception of rare cases when the frequency of the external field coincides with the natural atomic frequency. In the latter case, the perturbation is linear in the field—the linear Stark effect.

The calculation of the quadratic Stark effect in alternating external fields reduces to a calculation of the dynamic polarizability $\alpha(\omega)$ of the atom:

$$\Delta E_n^{(2)} = -{}^1/{}_2\alpha_n(\omega)F^2, \tag{1}$$

$\Delta E_n^{(2)}$ is the second-order correction to the energy of the atomic level, F is the amplitude of the external field,

$$\alpha_n(\omega) = \sum_m |\langle n|z|m\rangle|^2\left\{\frac{1}{\omega_{nm}+\omega}+\frac{1}{\omega_{nm}-\omega}\right\}, \tag{2}$$

where n and m are the set of quantum numbers determining the state of the electron in the atom. The atomic system of units is used throughout in this paper.

The summation in (2) is over the complete set of the eigenfunctions of the Hamiltonian of the atom, including the continuous spectrum. It is this circumstance that raises the main difficulty in the theoretical calculation of $\alpha(\omega)$. To overcome this difficulty, a number of methods have been proposed. If we disregard the case of the hydrogen atom, for which $\alpha(\omega)$ was calculated exactly relatively recently[1], the best known is the method connected with the integration of the homogeneous Hartree-Fock equation (see, e.g.,[2]).

This method, however, requires very laborious calculations and is not applicable in practice to calculations of the polarizabilities of the excited states. This circumstance is best emphasized by the fact that, in spite of the importance of knowing $\alpha(\omega)$ in atomic physics, this quantity is presently known only for a small number of atoms, at frequencies not exceeding the first-resonance frequency.

In the present paper we propose a method of calculating the polarizability $\alpha(\omega)$, based on the use of the Green's function of the optical electron in a complex atom. This function, defined by the relation

$$G_E(\mathbf{r},\mathbf{r}') = \sum_m \frac{\psi_m^*(\mathbf{r})\psi_m(\mathbf{r}')}{E-E_m}, \tag{3}$$

was constructed in[3] in the approximation of the quantum-defect method, which is widely used for the calculation of oscillator strengths and ionization widths[4]. It is easily seen that by using (3) it is possible to represent the expression for $\alpha(\omega)$ in the form

$$\alpha_n(\omega) = -\int d\mathbf{r}\,d\mathbf{r}'\psi_n^*(\mathbf{r})z\,\{G_{E_n+\omega}(\mathbf{r},\mathbf{r}') + G_{\;\;n-\omega}(\mathbf{r},\mathbf{r}')\}z'\psi_n(\mathbf{r}'). \tag{4}$$

In Sec. 2 we describe briefly the method of constructing the function $G_E(\mathbf{r}, \mathbf{r}')$. Section 3 contains details of the calculations with this function. In Sec. 4 we use the numerical results for alkali atoms and mercury.

2. GREEN'S FUNCTION OF THE OPTICAL ELECTRON IN THE THEORY OF THE QUANTUM DEFECT

The semi-empirical method of Bates—Damgaard and Burgess—Seaton is well known in atomic physics for the calculation of single-photon electromagnetic transitions and the phase shifts for the scattering of electrons by ions[4]. (We shall henceforth use for brevity the designation QDM—the quantum-defect method.) This method is based on the fact that the matrix elements of the dipole-moment operator receive the main contribution from the regions of large distances from the nucleus, where the effective single-particle potential of the optical electron can be regarded as a Coulomb potential with the residual-ion charge Z. In practice this makes it possible to construct radial wave functions in this region from the solutions of the Schrödinger equation for the Coulomb potential. Besides the Coulomb-like radial dependence of the wave functions, one uses in the QDM essentially the knowledge of the real discrete spectrum of the atom, which makes it possible to construct the wave function of the electron with account taken of the influence exerted on the electron by the atomic residue. We note that although the QDM is based on the single-electron approximation for the wave functions, the use of the experimental spectrum of the atom makes it possible to take effective account of certain collective effects.

Let us construct the Green's function in the QDM approximation.

The single-electron Green's function $G_E(\mathbf{r}, \mathbf{r}')$ satisfies the equation

$$(-{}^1/{}_2\nabla^2 + U(r) - Z/r - E)C_E(\mathbf{r},\mathbf{r}') = -\delta(\mathbf{r}-\mathbf{r}'), \tag{5}$$

where U(r) is the non-Coulomb part of the potential of the atomic residue with asymptotic behavior $r^2U(r) \to 0$ as $r \to 0$ and at $r > r_c$ (r_c is the radius of the core, outside of which the potential can be regarded to be of the Coulomb type). Separating in G_E the angle variables

$$G_E(\mathbf{r},\mathbf{r}')=\sum_{l,m} g_l(E;r,r')Y_{lm}{}^*(\mathbf{r})Y_{lm}(\mathbf{r}'), \tag{6}$$

we obtain for g_l the following equation in the region $r > r_c$:

$$\left\{\frac{1}{2}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)-\frac{l(l+1)}{r^2}\right]+\frac{Z}{r}+E\right\}g_l(E;r,r')=-\frac{\delta(r-r')}{rr'}. \tag{7}$$

The general solution of the inhomogeneous Eq. (7) can be constructed from the fundamental solutions of the corresponding homogeneous equation

$$g_l(E;r,r')=\frac{\nu}{rr'}\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)}M_{\nu,\,l+1/2}\left(\frac{2r_<}{\nu}\right)W_{\nu,\,l+1/2}\left(\frac{2r_>}{\nu}\right) \tag{8}$$
$$+A\frac{\nu}{rr'}W_{\nu,\,l+1/2}\left(\frac{2r}{\nu}\right)W_{\nu,\,l+1/2}\left(\frac{2r'}{\nu}\right),$$

where $\nu = (-2E)^{-1/2}$; $r_>(r_<)$ is the larger (smaller) of the quantities r and r′; M and W are the known Whittaker functions, M being regular at zero, and W regular at infinity[5].

The first term in (8) (the particular solution of the inhomogeneous equation) is the Green's function of the hydrogen atom, and the second term is the solution of the homogeneous equation. Since the Green's function should be regular at infinity, the homogeneous solution containing the functions M should not enter. The constant A can be determined from the condition of matching (8) at $r = r_c$ with the solution of Eq. (5) in the region $r < r_c$. In particular, for hydrogen Eq. (7) is valid everywhere and A = 0.

Since we do not know the Green's function for $r < r_c$, we shall use the QDM to find A. To this end, we consider the asymptotic expression for $g_l(E; r, r')$ as $r, r' \to \infty$ (see, e.g.,[6])

$$g_l(E;r,r')\to\frac{2}{krr'}\exp\left\{i\left[kr_>+\frac{\ln(2kr_>)}{k}-\frac{\pi l}{2}+\sigma_l+\delta_l\right]\right\} \tag{9}$$
$$\times\sin\left[kr_<+\frac{\ln(2kr_<)}{k}-\frac{\pi l}{2}+\sigma_l+\delta_l\right],$$

where $\sigma_l = \arg\Gamma(l + 1 - \nu)$ is the Coulomb phase shift of the scattering, δ_l is the phase shift connected with the deviation of the field from the Coulomb value, and $k = i/\nu$.

Calculating the asymptotic form of (8) and comparing it with (9), we get[3]

$$A=e^{i[2\sigma_l-\pi(l-\nu)]}(e^{2i\delta_l}-1). \tag{10}$$

Formulas (8) and (10) determine the Green's function at $E > 0$, if the phase shifts δ_l are known. For analytic continuation to the region of negative energies, where the phase shifts have no direct physical meaning, we shall use the fundamental QDM relation[7]:

$$\operatorname{ctg}\delta_l(E)\to(1-e^{2\pi i\nu})\left[\operatorname{ctg}\pi\mu_l(E)-\frac{i}{e^{-2\pi i\nu}-1}\right], \tag{11}$$

where $\mu_l(E)$ is the quantum defect, determined for energies corresponding to balanced states by the formula

$$E_{nl}=-\frac{Z^2}{(n-\mu_l(E_{nl}))^2}. \tag{12}$$

Since the potential with the Coulomb asymptotic function has an infinite number of bound states with a condensation point at E = 0, the quantum defect as an analytic function of the energy is determined uniquely by formula (12) in the entire complex E plane.

Taking (11) into account, we obtain the following expression for A in the region $E < 0$:

$$A=\frac{\Gamma(l+1-\nu)}{\Gamma(l+1+\nu)}\frac{\sin\pi(\mu_l(\nu)+l)}{\sin\pi(\mu_l(\nu)+\nu)}. \tag{13}$$

Taking (13) into account, we easily see that the Green's function (8) has poles at the points E determined by (12), and the Coulomb poles in the sum of the two terms of (8) cancel out exactly. The residues at the poles g_l are products of the eigenfunctions R_{nl} in the QDM[3]:

$$R_{nl}(r)=\frac{1}{\nu r}\left[\Gamma(l+1+\nu)\Gamma(\nu-l)\left(1+\frac{\partial\mu_l(\nu)}{\partial\nu}\right)\right]^{-1/2}W_{\nu,\,l+1/2}\left(\frac{2r}{\nu}\right). \tag{14}$$

We shall find it convenient in what follows to represent the function $g_l(E; r, r')$ in the form

$$g_l(E;r,r')=\frac{\nu}{rr'}\Gamma(l+1+\nu)\Gamma(l+1-\nu)\mathfrak{M}_{\nu,\,l}(r_<)\mathfrak{W}_{\nu,\,l}(r_>), \tag{15}$$

where

$$\mathfrak{W}_{\nu,\,l}(r)=\frac{1}{\Gamma(l+1+\nu)}W_{\nu,\,l+1/2}\left(\frac{2r}{\nu}\right),$$
$$\mathfrak{M}_{\nu,\,l}(r)=\frac{1}{(2l+1)!}M_{\nu,\,l+1/2}\left(\frac{2r}{\nu}\right)+\frac{\sin\pi(\mu_l(\nu)+l)}{\sin\pi(\mu_l(\nu)+\nu)}\mathfrak{W}_{\nu,\,l}(r).$$

3. DETAILS OF CALCULATIONS

Using the expression obtained in Sec. 2 for the radial part of the Green's function, as well as in the expansion in terms of the spherical functions (6), we can represent expression (4) for $\alpha(\omega)$ in the form

$$\alpha_{nl}(\omega)=\frac{1}{3(2l+1)}\sum_{i=1,2;\;l'=l\pm1}l_{max}I_{nl'}(\nu_i), \tag{16}$$
$$I_{nl'}(\nu_i)=\frac{\nu_i}{\nu^2}\frac{\Gamma(l+1+\nu)}{\Gamma(\nu-l)}\Gamma(l'+1+\nu_i)\Gamma(l'+1-\nu_i)T_{nl'}(\nu_i),$$

$$T_{nl'}(\nu_i)=\iint_{r_0}^{\infty}rr'\,dr\,dr'\mathfrak{W}_{\nu,\,l}(r)\mathfrak{W}_{\nu,\,l}(r')\mathfrak{M}_{\nu_i,\,l'}(r_<)\mathfrak{W}_{\nu_i,\,l'}(r_>)$$
$$=2\int_{r_0}^{\infty}r\,dr\mathfrak{W}_{\nu,\,l}(r)\mathfrak{W}_{\nu_i,\,l'}(r)\int_{r_0}^{r}r'\,dr'\mathfrak{M}_{\nu_i,\,l'}(r')\mathfrak{W}_{\nu,\,l}(r'), \tag{17}$$
$$l_{max}=\max(l,l'),\quad \nu=(-2E)^{-1/2},\quad \nu_{,2}=(-2E_{nl}\pm2\omega)^{-1/2}.$$

In (16) we have averaged over the magnetic quantum numbers in the nl states. The lower limit r_0 of the integral in (17) eliminates the unphysical divergence of the wave functions at zero.

In the QDM calculation of single-photon transitions the Whittaker function W in (14) is usually calculated by expanding in an asymptotic series:

$$W_{\nu,\,l+1/2}\left(\frac{2r}{\nu}\right)=\left(\frac{2r}{\nu}\right)^{\nu}e^{-r/\nu}\sum_{t=0}^{t_0}b_t(l,\nu)r^{-t}, \tag{18}$$

where

$$b_0=1,\qquad b_t=\frac{\nu}{2t}[l(l+1)-(\nu-t)(\nu-t+1)]b_{t-1}.$$

The parameter t_0 is chosen from the condition that the series be terminated at the minimal term, as is customarily done in the theory of asymptotic series.

The function M in (17) can be easily calculated by

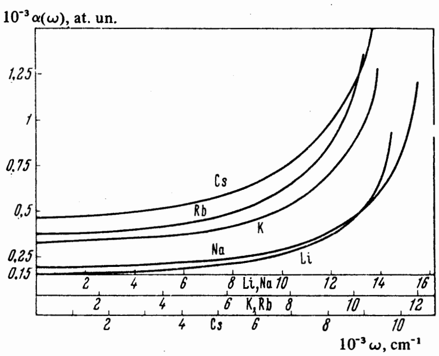

FIG. 1. Polarizabilities of the ground S-states of alkali atoms in the frequency interval up to the first resonance.

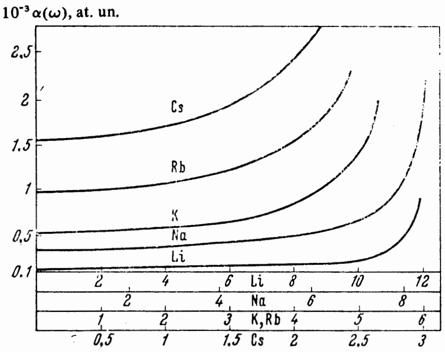

FIG. 4. Polarizabilities of the first excited P-states of alkali atoms in the frequency interval up to the first resonance.

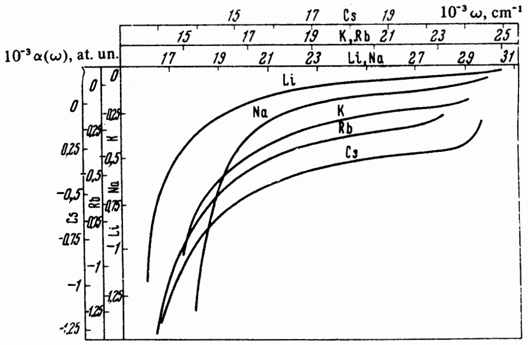

FIG. 2. Polarizabilities of the ground S-states between the first and second resonances.

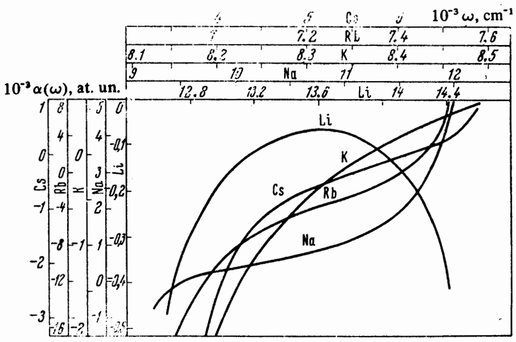

FIG. 5. Polarizabilities of the first excited P-states between the first and second resonances.

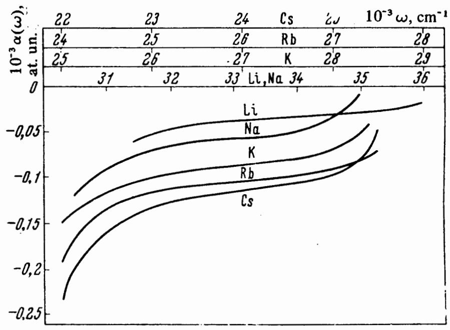

FIG. 3. Polarizabilities of the ground S-states between the second and third resonances.

expansion in a power series:

$$M_{\nu,\, l+\frac{1}{2}}\left(\frac{2r}{\nu}\right)=e^{-r/\nu}\left(\frac{2r}{\nu}\right)^{l+1}\sum_{t=0}^{\infty}a_t(\nu,l)r^t, \tag{19}$$

where

$$a_0=1,\qquad a_t=\frac{2}{\nu t}\,\frac{l+t-\nu}{2l+1+t}\,a_{t-1}.$$

In the calculation of the integral (17), the functions W were calculated both from the asymptotic expansion (18) and by using the convergent expansions in increasing powers of the argument[8]. For the atomic levels and frequencies considered in the present paper, the results differ insignificantly for the two methods of calculating W. In the calculations of the single-photon transitions it is assumed that $r_0 \sim \nu_{\min}/2$, where $\nu_{\min}$ is the minimum value of ν or ν_i in (17). We have chosen the same value for r_0, and the sensitivity of the results to the choice of r_0 turned out to be quite weak.

A very important fact is that the integral (17), in view of the one variable limit in the internal integral, actually turns out to be a single integral if the integration is carried out in equal steps. This causes the time required to calculate the integral (17) to be comparable with the time required to calculate the matrix element of the single-photon transition.

In the calculation of $\alpha(\omega)$ we subtracted from the sum (2) the terms corresponding to the filled shells, making it possible to take into account the Pauli principle[2]. Numerical calculations have shown that the contribution of the filled shells is quite negligible.

4. DISCUSSION OF RESULTS

Concrete calculations of $\alpha(\omega)$ were made for the ground and first-excited levels of Li, Na, K, Rb, and Cs in a wide frequency range. In addition, we calculated the shift of the 5461 Å line of the Hg atom, corresponding to the transition $6^3P_2-7^3S_1$ at the neodymium-laser frequency; this shift was measured experimentally by Platz[9]. Figures 1–6 show the results obtained for the polarizabilities. It is interesting to note the presence of regions of negative dispersion in the P-states.

A comparison with the available theoretical calculation of the dynamic polarization of the ground state of lithium in the frequency interval up to the first resonance[10] shows almost complete agreement with our results.

All that we know for the remaining atoms are the static polarizabilities. Table 1 gives the corresponding

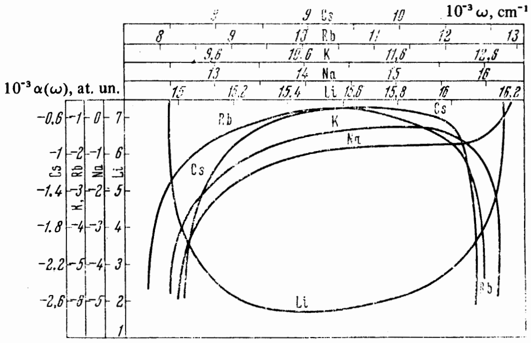

FIG. 6. Polarizabilities of the first excited P-states between the second and third resonances.

Table I

Atom	α_{exp}, Å [11]	α_{theor}, Å, present work
Li	20±3	23,0
Na	24,4±1.7	27.5
K	45,2±3,2	48.7
Rb	48,7±3,4	54
Cs	63.3±4,6	68.8

Table II

Intensity, MW/cm²	ΔE_{exp}, cm^{-1} [9]	ΔE_{theor}, cm^{-1}, present work
30	0.085	0.098
150	0.34	0.49
200	0.44	0.65
400	0.88	1.3

comparisons of our results with the experimental data given by Sternheimer[11].

Table 2 gives a comparison of our results for the shift of the 5461-Å resonance line of the Hg atom at the neodymium-laser frequency, with the experimental data of Platz[9].

We note that in the main the line shift is determined by the shift of the upper 7^3S_1 level of Hg, the polarizability of which is larger by more than one order of magnitude than the polarizability of the lower 6^3P_2 level.

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