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SHIELDING OF AN EXTERNAL ELECTRIC FIELD IN ATOMS

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ABSTRACT

It is shown that the Hartree—Fock method provides the exact fulfilment of the Shiff theorem (external electric field shielding at the nucleus). The numerical calculation of the electric field in Tl^+ ion was carried out. The shielded field $\vec{E}_{tot}=\vec{E}_0+\vec{E}_e$ (E_0 is the external field, E_e is the induced field of electrons) has the non-trivial radial dependence inside the atom.

In calculation of the atomic polarizabilities and of the oscillator strengths the problem of an electric field inside the atom arises. It is well known that at the nucleus of the neutral atom the static electric field is shielded completely (the Schiff theorem [1]). One can easy understand this theorem. The homogeneous electric field does not accelerate the neutral atom. Therefore the field acting on atom's nucleus is equal to zero. However if one uses the approximate atomic wave functions the Schiff theorem generally speaking could be violated.

In the present paper we show that the Hartree—Fock wave functions, self-consistent in the external electric field reproduce the shielding of field at the nucleus. For an illustration we have carried out the numerical calculation of electric field in Tl^+ ion. The radial dependence of the field turned out to be very complicated. Let us denote by $\vec{E}_0$ the external field and by $\vec{E}_e$ induced field of electrons. The total field $\vec{E}_t=\vec{E}_0+\vec{E}_e$ few times changes the sign inside the atom. The most interesting point is that E_t can exceed the external field E_0.

Let us remind how to calculate the field at the nucleus using the exact atomic wave function. The Hamiltonian of an atom in the external electric field E_0 has the form

$$H_E=\sum_{k=1}^{N}\vec{\alpha}_k\vec{p}_k+\beta_k m-\frac{Ze^2}{r_k}+\sum_{i<k}\frac{e^2}{r_{ik}}+|e|\vec{E}_0\vec{r}_k\,. \qquad (1)$$

Here $\vec{\alpha}$, β are the Dirac matrices, Z is a nucleus charge, N is a

number of the electrons, $-|e|$ is the electron charge. The Breit interaction can be neglected even in heavy atom (see e. g. ref. [2]).

Commutator of the total momentum of the electrons $\vec{P}=\sum_{k=1}^{N}\vec{p}_k$ with the Hamiltonian is given by

$$\frac{i}{|e|}[\vec{P},H_E]=\sum_{k=1}^{N}\left(-Z|e|\vec{\nabla}_k\frac{1}{r_k}+E_0\right)=Z\vec{E}_e+N\vec{E}_0. \tag{2}$$

Here $\vec{E}_e=-|e|\sum\vec{\nabla}_k\frac{1}{r_k}$ is the field of the electrons at $r=0$. For the eigenstate Φ of the Hamiltonian H_E we have

$$0=\langle\Phi\left|\frac{i}{|e|}[\vec{P},H_E]\right|\Phi\rangle=Z\langle\vec{E}_e\rangle+N\vec{E}_0. \tag{3}$$

Thus, the total electric field at the nucleus

$$E_t(0)=\vec{E}_0+\langle\vec{E}_e\rangle=\vec{E}_0\left(1-\frac{N}{Z}\right)=\vec{E}_0\frac{Z_i}{Z}, \tag{4}$$

where $Z_i=Z-N$ is the charge of an ion. In the neutral atom the field at the nucleus vanishes.

Let us calculate now the field at the origin in the Hartree—Fock approximation. We stress that we mean the Hartree—Fock approximation in the external field. The wave functions $|\mathrm{HF}\rangle$ are the eigenstates of the Hamiltonian

$$H_{\mathrm{HF}}=\sum_{k=1}^{N}(H_0(r_k)+|e|\vec{E}_0\vec{r}_k), \tag{5}$$

where $H_0=\vec{\alpha}\vec{p}+\beta m-\frac{Ze^2}{r}+V$, $V=V_{direct}+V_{exch}$ is the sum of the direct and exchange self-consistent potentials of the electrons. Thus, we have

$$0=\langle\mathrm{HF}|\,[P,H_{\mathrm{HF}}]\,|\mathrm{HF}\rangle=\langle\mathrm{HF}|\,[P,H_E]\,|\mathrm{HF}\rangle+\langle\mathrm{HF}|\,[P,U]\,|\mathrm{HF}\rangle. \tag{7}$$

Here U is the residual Coulomb interaction

$$U=H_E-H_{\mathrm{HF}}=\sum_{i<k}\frac{1}{r_{ik}}-\sum_k V(r_k). \tag{8}$$

It easy to show, that the term $\langle[P,U]\rangle$ in eq. (7) vanishes. Using the complete set of the eigenstates $|n\rangle$ of the Hamiltonian H_{HF} we can decompose it in such a way

$$\langle\mathrm{HF}|\,[\vec{P},U]\,|\mathrm{HF}\rangle=\sum_n(\langle\mathrm{HF}|\vec{P}|n\rangle\langle n|U|\mathrm{HF}\rangle-\langle\mathrm{HF}|U|n\rangle\langle n|\vec{P}|\mathrm{HF}\rangle). \tag{9}$$

Momentum $\vec{P}$ is a one particle operator. Therefore it has the matrix elements only to the states with excitation of the one electron. At the same time the matrix elements of the residual Coulomb interaction U to such states are equal to zero (see e. g. ref. [2]). Thus matrix element (9) is equal to zero and so we see from eqs (2), (7) that Hartree—Fock approximation reproduces the exact formula (4) for the electric field at the origin.

We calculate now in the Hartree—Fock approximation the electric field at the arbitrary distance from the nucleus. We mean the induced field (the part of field which is proportional to external one). One can expand Hartree—Fock equation $(H_0+|e|\vec{E}_0\vec{r}-\varepsilon_k)\tilde{\psi}_k=0$ in the linear approximation in external field.

$$\tilde{\psi}_k=\psi_k+\delta\psi_k,$$
$$H_0\psi_k=\varepsilon_k\psi_k, \tag{10}$$
$$(H_0-\varepsilon_k)\,\delta\psi_k=-|e|\vec{E}_0\vec{r}\psi_k-\delta V\psi_k, \tag{11}$$
$$\delta V=V(\tilde{\psi}_1,\tilde{\psi}_2,\ldots,\tilde{\psi}_N)-V(\psi_1,\psi_2,\ldots,\psi_N). \tag{12}$$

Here $\tilde{\psi}_k$ is the solution of Hartree—Fock equation in the field, ψ_k is the solution without field, $\delta\psi_k$ and $\delta V=\delta V_{direct}+\delta V_{exch}$ are the corrections to the wave function and potential induced by the field. The equations (11)—(12) should be solved in self-consistent way for all the atomic electrons. For numerical calculations it is convenient to expand the correction $\delta\psi$ in the states with definite angular momentum. If function ψ_k has the total angular momentum j and orbital angular momentum l then three components in correction $\delta\psi$ arise. First component has $j'=j$, $l'=l\pm1$, for the second and third $j'=j\pm1$, $l'=l\pm1$, (for $j=1/2$ there are only two corrections). Thus in Tl^+ the total number of the radial Dirac equations for the corrections is 56. For example, in Al^+ the self-consistent solution of the eqs (11), (12) does not cause any problem. However in Tl^+ this is rather long computation because of large number of corrections.

Let us suppose that we carry out iterations in solving eqs (11), (12) in such a way. At n-th iteration $\delta V^{(n)}$ is fixed and we define $\delta\psi^{(n)}\equiv\delta\psi$, where $\delta\psi$ is solution of eq. (11) at $\delta V=\delta V^{(n)}$. At next ite-

ration we put $\delta V^{(n+1)}=V(\psi+\delta\psi^{(n)})-V(\psi)$ in accordance with eq. (12) and so on. In this case the n-th iteration corresponds to n-th order of perturbation theory in the basis of HF states without field. The electric field at the origin as a function of n is shown at Fig. 1. It is seen that one needs to take into account the configuration mixing in ~20th order of perturbation theory even to get the correct order of magnitude of the field ($E(0)\sim E_0/Z$). It needs ~30—35 iterations to get the accuracy ~20% in $E(0)$.

We can accelerate essentially the convergence procedure by standard way introducing the «weight»: $\delta\psi^{(n)}=\frac{1}{2}(\delta\psi+\delta\psi^{(n+1)})$. The field at $r=0$ for such procedure is shown at Fig. 1 as well.

The plot of the field $\vec{E}_t(r)=\vec{E}_0+\langle\vec{E}_e\rangle$ on the z axis in the Tl^+ is shown at Fig. 2. The axis z is directed along the external field $\vec{E}_0$. Contrary to the well known case of Debye shielding the field profile is rather complicated. Most surprising is the deep $E_t\approx-3E_0$ at the radius of 1s-electron orbit ($r\sim a_B/Z$). Nevertheless at the $r\ll a_B/Z$ the field approaches the asimptotical value $E_t=E_0/Z$.

The above discussion concerns the static field. In the time-dependent field $\vec{E}=\vec{E}_0\cos\omega t$ there is no exact shielding at the nucleus. However difference from static case is small for small frequency. Field is the even function of frequency. Therefore $\delta E(r)\sim\frac{\omega^2}{\omega_n^2}E(r,\omega=0)$ where ω_n is the minimal excitation energy of electrons. Only near the resonance $\delta E\sim\frac{\omega^2}{\omega^2-\omega_n^2}E\gg E$.

We have carried out calculation of the electric field in Tl^+ using the time-dependent Hartree—Fock method. The plot of field on z-axis for frequency $\omega=0.207$ Ry/$\hbar$ is presented at Fig. 2. This frequency corresponds to $6p_{1/2}\to 7s$ transition of the external electron in Tl*). For Tl^+ minimal excitation energy is $\omega_n=E_{6p}-E_{6s}$, so $\omega^2/\omega_n^2\sim 1/10$. In accordance with the estimate deviation of «time-dependent E» curve at Fig. 2 from static one is of the order of 10%.

There is another exact theorem which is valid in frameworks of time-dependent Hartree—Fock method, namely the gauge invariance of the transition amplitudes (see e. g. refs [3, 4]). One can easy to check this statement. Gauge transformation of electromagnetic potentials

*) We want to stress that this is not experimental $6p_{1/2}-7s$ energy interval, but interval calculated in frozen core approximation [2].

$$\varphi'=\varphi+\frac{\partial\theta}{\partial t},\qquad \vec{A}'=\vec{A}-\vec{\nabla}\theta \tag{13}$$

leaves the Hartree—Fock wave function $\tilde{\Phi}$ be one-determinant:

$$\tilde{\Phi}'=\tilde{\Phi}\exp\{ie\sum_{k=1}^{N}\theta(r_k,t)\}. \tag{14}$$

Therefore if $\tilde{\Phi}$ is the solution of Hartree—Fock equation in one gauge $\delta\langle\tilde{\Phi}\left(i\frac{\partial}{\partial t}-H\right)\tilde{\Phi}\rangle=0$ the transformed function $\tilde{\Phi}'$ is the solution of the transformed equation $\delta\langle\tilde{\Phi}'\left(i\frac{\partial}{\partial t}-H'\right)\tilde{\Phi}'\rangle=0$. The common phase in eq. (14) does not influence the transition amplitudes and field of electrons.

Due to the gauge invariance the transition amplitudes calculated in velocity and length form should be identical. For the linearly polarized plane electromagnetic wave ($E=E_0\cos(\omega t-\vec{k}\vec{r})$) gauge corresponding to velocity form looks as follows

$$\varphi=0,\qquad \vec{A}=-\frac{\vec{E}_0}{\omega}\sin(\omega t-\vec{k}\vec{r}),$$

$$H_{int}^{(v)}\approx\frac{|e|\vec{a}\vec{E}_0}{\omega}\sin\omega t. \tag{15}$$

In length form

$$\varphi=-\vec{E}_0\vec{r}\cos(\omega t-\vec{k}\vec{r}),\qquad \vec{A}=-\frac{(\vec{E}_0\vec{r})\vec{k}}{\omega}\cos(\omega t-\vec{k}\vec{r})\approx 0,$$

$$H_{int}\approx|e|\vec{E}_0\vec{r}\cos\omega t.$$

We neglect the corrections $\sim kr$. The gauge (15) can be obtained from (16) by transformation (13) with

$$\theta=\frac{\vec{E}_0\vec{r}}{\omega}\sin(\omega t-\vec{k}\vec{r}).$$

To control the accuracy we have calculated E1-amplitudes for transitions of an external electron in Tl. The amplitudes in l and v-form coincide with an accuracy $\sim 10^{-3}$. Of course this disagreement is not defect of Hartree—Fock, but pure numerical unaccuracy. For example, for mentioned above $6p_{1/2}\to 7s$ transition the ratio of cal-

culated amplitude to experimental one is 1.04 ± 0.03. We present the experimental error. So good agreement is accidental because of theoretical uncertainty which is due to correlation correction. We remind the reader that in the present paper only Hartree—Fock (or time-dependent HF) calculations are considered. The correlation corrections can be taken into account by the method used in ref. [6]. The results of such calculation of E1-amplitudes in Tl would be presented in following paper .

Let us note that equality of amplitudes in l and v-form follows from eqs (13)—(16) not only for one-photon transition, but for many-photon transition as well.

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REFERENCES

1. *L.I. Schiff*. Phys. Rev. 132 (1963) 2194.
2. *V.A. Dzuba, V.V. Flambaum and O.P. Sushkov*. J. Phys. B16 (1983) 715.
3. *M.Ya. Amusia, N.A. Cherepkov*. Case studies in atomic physics 5 (1975) 4
4. *A.-M. Martensson—Pendrill*. J. de Physique 46 (1985) 1949.
5. *A. Gallager, A. Lurio*. Phys. Rev. A136 (1964) 87.
6. *V.A. Dzuba, V.V. Flambaum, P.G. Silvestrov and O.P. Sushkov*. Phys. B18 (1985) 597.

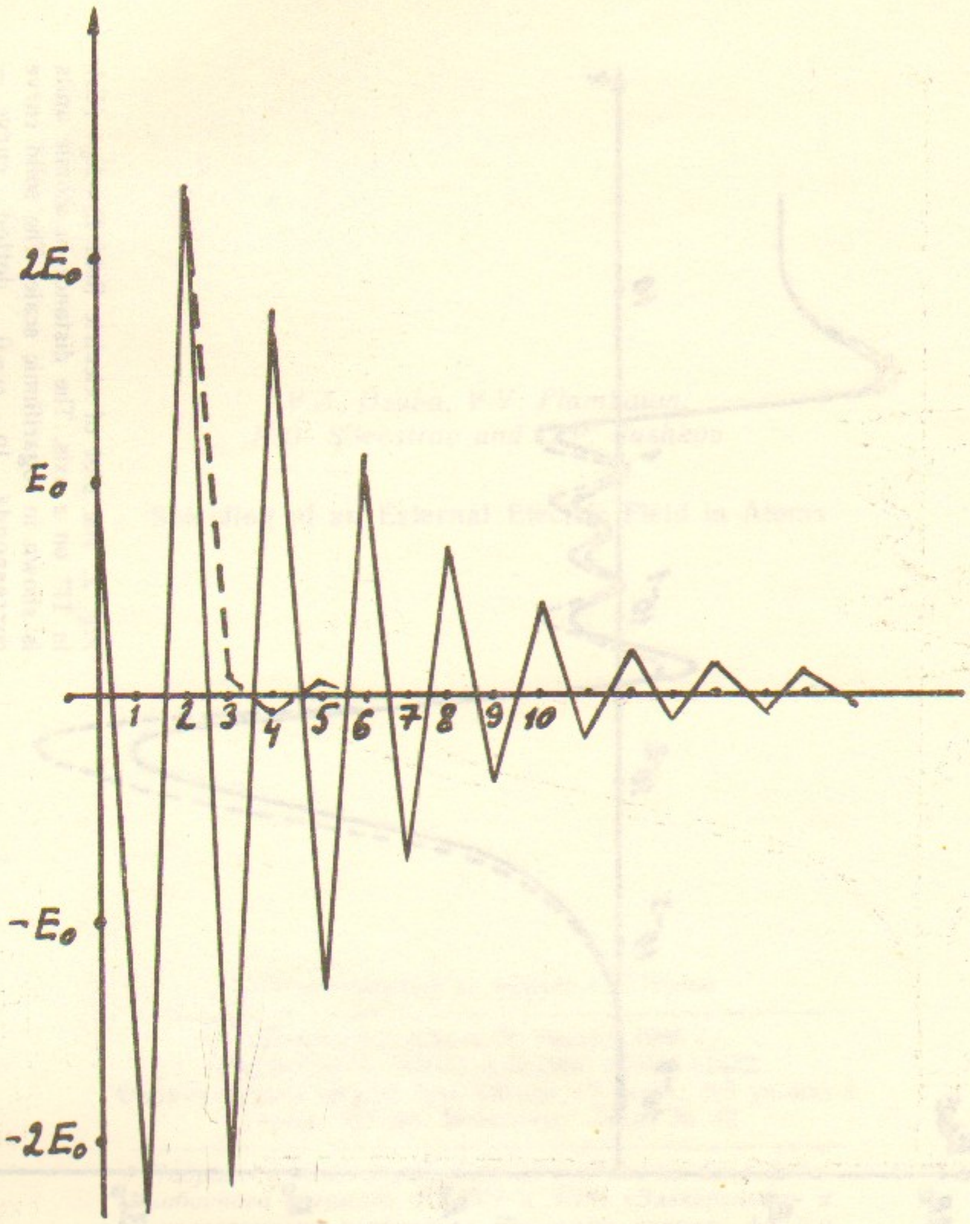

Fig. 1. The electric field at the origin in Tl^+ as a function of a number of iteration. The solid curve corresponds to the calculation without weighting («perturbation theory»), the dotted curve—with the weighting $(\delta\psi^{(n)} = \frac{1}{2}(\delta\psi + \delta\psi^{(n-1)}))$.

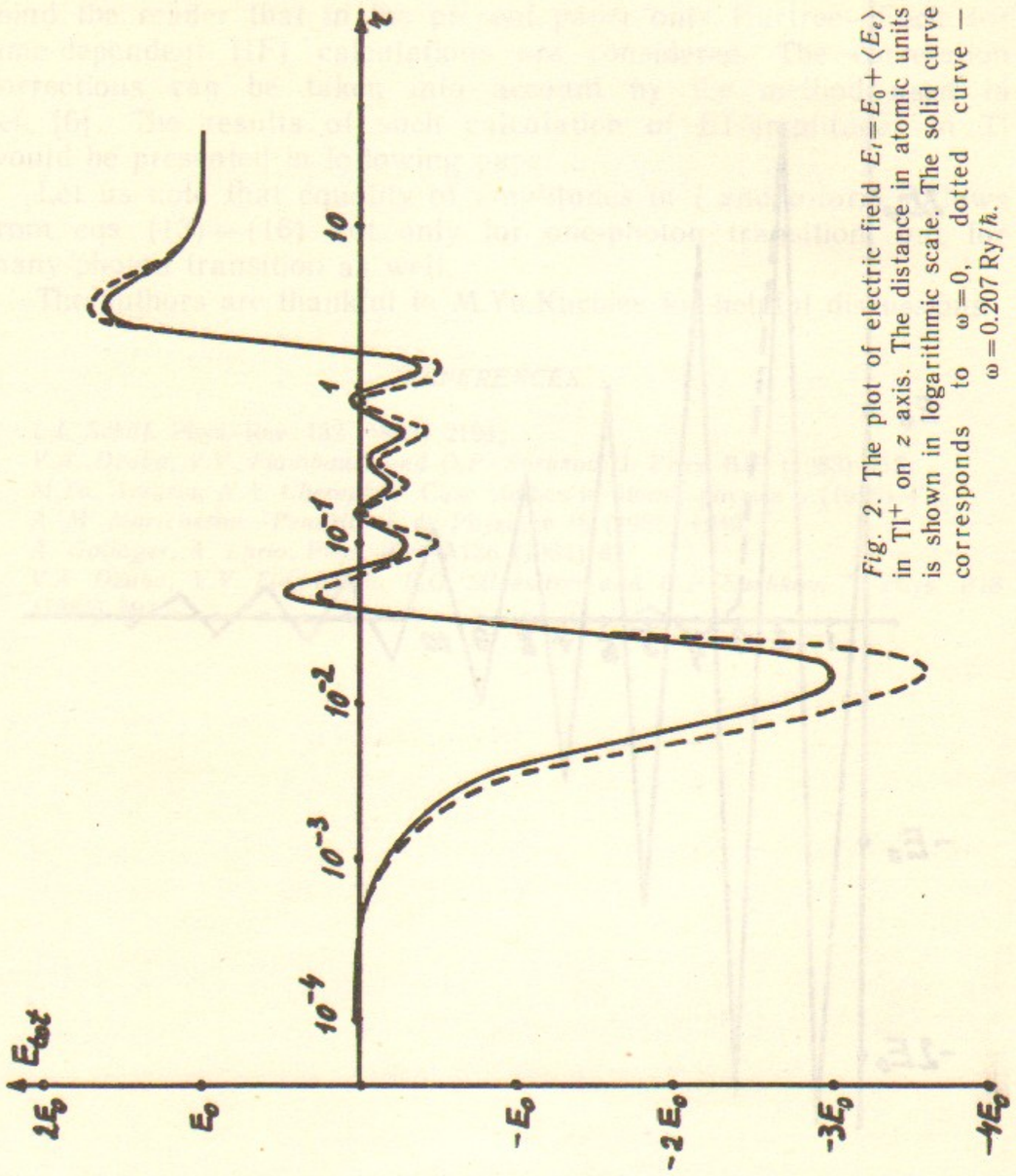

Fig. 2. The plot of electric field $E_t = E_0 + \langle E_e \rangle$ in Tl^+ on z axis. The distance in atomic units is shown in logarithmic scale. The solid curve corresponds to $\omega = 0$, dotted curve — $\omega = 0.207$ Ry/$\hbar$.

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