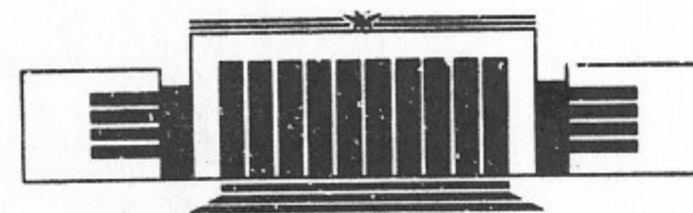ИЯФ

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SCREENING OF COULOMB INTERACTION AND MANY-BODY PERTURBATION THEORY IN ATOMS

Screening of Coulomb Interaction
and Many-Body Perturbation
Theory in Atoms

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ABSTRACT

Taking into account the electron Coulomb interaction
screening considerably improves the convergence of
perturbation theory in residual interaction. The develo-
ped technique allows to take into account screening
diagrams in all orders of perturbation theory. Calcula-
tion of the correlation corrections to the thallium
energy levels is carried out as an example.

The method of calculation based on Relativistic Hartree — Fock
(RHF) equations with taking into account the second order correla-
tion corrections in residual Coulomb interaction provides as a rule
satisfactory accuracy of atomic calculations (e. g. energy levels,
fine and hyperfine structure, electromagnetic transition amplitudes).
But this method usually overestimates the values of correlation cor-
rections (see e. g. Refs [1—5]). Corrections are overestimated even
in the case of V^{N-1} zero approximation (basis set of wave functions
and energies being found in the frozen field of unit charge ion). In
this case correlation corrections are in fact artificially suppressed by
overestimated energy denominators corresponding to the internal
(core) electron excitations. And in a more realistic atomic potential
the factor of overestimation of correlation corrections can reach
1.5—2 (see below).

In this paper the reason of overestimation of correlation correc-
tion is pointed out. The residual Coulomb interaction of electrons
which induces the correlations is strongly screened by core elect-
rons. This is the collective phenomenon similar to the screening of
Coulomb field in plasma. A closer example is the screening of exter-
nal electric field in an atom. According to Schiff theorem homoge-
neous electric field is screened by atomic electrons (at the nucleus
it is screened completely [6], see also [7, 8]). Our numerical calcu-
lations [8] show that the screened electric field changes the sign at
the radius of external electron subshell and oscillates inside the
atom.

Similar picture should occur also for the electric field created by

an external atomic electron. Let the external electron be in the point **R** outside atomic core. The dipole component of its potential is $\sim \mathbf{r} \mathbf{R}/R^3$ and the electron field $\sim \mathbf{R}/R^3 = \text{const}$ inside the atom. According to Schiff theorem this field is to be screened by core electrons. Thus the dipole harmonic is strongly screened. But just this harmonic gives the largest contribution to the correlation corrections.

There are other arguments showing importance of screening effects. Diagrams describing the direct screening effect are presented in Fig. 1. It is easy to verify that all diagrams of this type are proportional to $(N_e)^n$ where N_e is the number of electrons in the
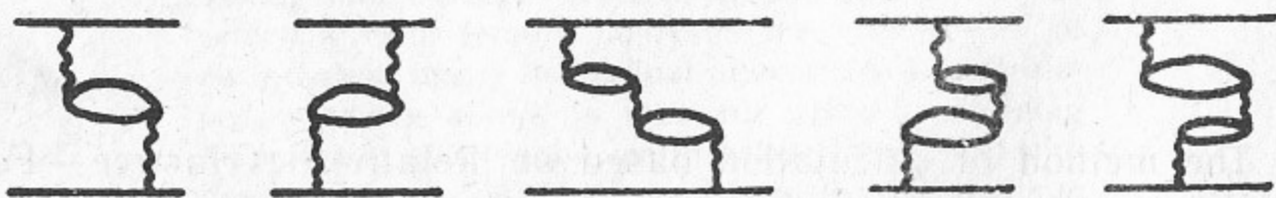

Fig. 1. Direct screening of electron Coulomb interaction.

upper closed subshells which contribute to the correlation correction (numerical calculation shows that effective number $N_e \sim 4$ for Tl), n is the number of loops. All other high order diagrams (including exchange screening diagrams and «ladder» diagrams) do not encrease so strongly with N_e, and their contributions are smaller.

It was pointed out that RPA-chain of diagrams is of great importance in the photoionization processes (see, e. g. Ref. [9]). Here we consider a somewhat similar problem — summation of the chain of diagrams induced by Coulomb interaction. However, there are distinctions between these problems.

Let us now turn to the calculation of correlation corrections taking into account the screening effects. We will specify our calculation to the energy (ionization potential) of the lowest thallium state — $6p_{1/2}$. Previously similar calculations with two different zero approximations but without consideration of screening were carried out by us [4]. In the first case we used relativistic Hartree — Fock state basis calculated in the frozen field of Tl$^+$ ion (potential V^{N-1}). All the subshells of this ion are closed. In the second case we used the potential $V_P = V^N - (1-P) V_0 (1-P)$, where V_0 is zero multipolarity direct potential, created by the external $6p_{1/2}$-electron, $V^N = V^{N-1} + V_0$ is the atomic potential acting on core electrons, P is the projection operator to core electron orbitals, $P = \sum_{n \leqslant N-1} |n\rangle \langle n|$.

Both potentials allow to obtain complete orthogonal basis sets and calculate correlation corrections by means of perturbation theory (see diagrams on Fig. 2). The advantage of the first method is its
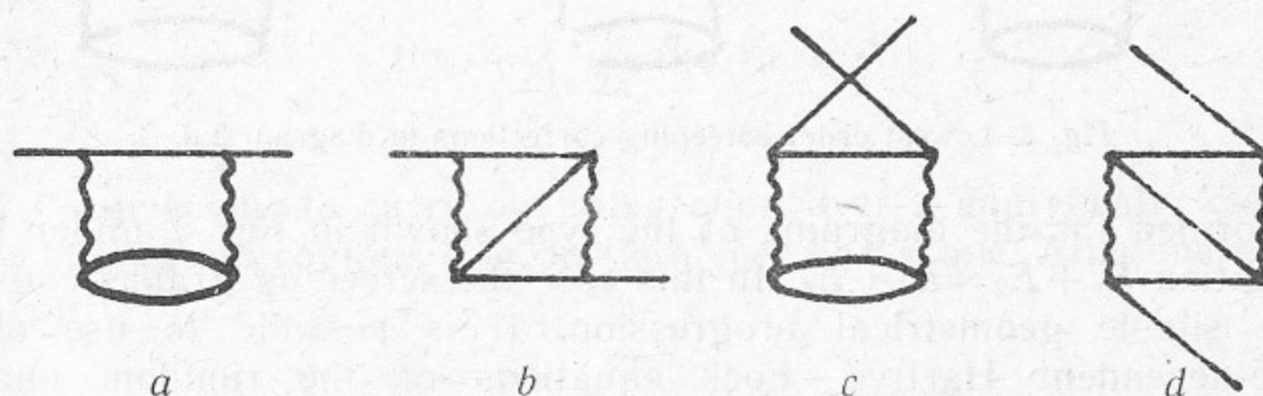

Fig. 2. Correlation corrections to electron energy.

simplicity. And the V^{N-1} potential is a reasonable approximation for the potential acting on the external electron. However, a drawback of this method is that the core electrons move in the ion potential, i. e. without $6p_{1/2}$-field. Consequently, V^{N-1} method strongly overestimates energy intervals between occupied core states and free states. For example, the minimal $6s - 6p$ interval differs from the correct one by large Coulomb integral $F_0(6s, 6p)$. As a result the calculated interval exceeds the experimental one by a factor of two.

The V_P potential is chosen to be free of this drawback. Core electrons interact with the potential V^N, the external electron — with the potential $V^{N-1} - PV_0 \approx V^{N-1}$. However the calculation technique is more cumbersome here[*]. As for results, the zero approximation with V_P potential proved to be better than V^{N-1} potential whereas the energies with correlation corrections were worse. As we understand it now the overestimated energy denominators in the V^{N-1} method imitated the suppression related to the screening of residual Coulomb interaction.

Formally taking into account the screening graphs in the lowest (third) order of perturbation theory (see examples in Fig. 3) we get correction of opposite sign and almost the same absolute value as the corresponding second order diagram (see diagram 2,a for this example). In such case one has to sum the whole chain of screening diagrams. In the standard Schrödinger perturbation theory with many-body energy denominators such summation can be easily

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[*] Subtraction graphs with potential $(1-P) V_0 (1-P)$ appear in the perturbation theory in the exact and Hartree — Fock Hamiltonian difference $H - H_{HF}$.

Fig. 3. Lowest order screening corrections to diagram 2,a.

performed for the diagrams of the type shown in Fig. 1 under the condition $E_1 + E_2 = E_3 + E_4$. In this case the screening graphs constitute simple geometrical progression. It is possible to use also time-dependent Hartree — Fock equations or the ramdom phase approximation here. In the case of loop summation in the correlation correction (see examples in Fig. 3), there is no simple geometrical progression here due to overlapping of energy denominators of different loops (intermediate states with large number of excited electrons appear if loops overlap, see e. g. second and third graph on Fig. 3) [*]. The summation problem is exactly solved by the Feynman diagram technique. This technique involves single-particle denominators but an additional integration over frequencies is necessary in each loop (see, e. g. Ref. [10]). Feynman Green's function is of the form

Fig. 4. Polarization operator.

$$\hat{G}(\varepsilon) = \sum_{\gamma} \frac{|\gamma\rangle\langle\gamma|}{\varepsilon - \varepsilon_\gamma + i\delta} + \sum_{n} \frac{|n\rangle\langle n|}{\varepsilon - \varepsilon_n - i\delta}, \qquad \delta \to 0. \tag{1}$$

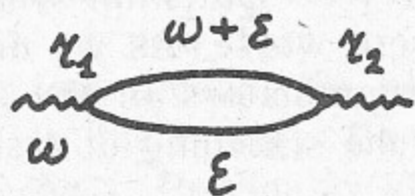Here $|n\rangle$ is an occupied core electron state, $|\gamma\rangle$ is the state outside the core. The simplest way of the Green's function calculation is the summation over the discrete and continuous spectrum. However, in practice a higher numerical accuracy is provided by another method. As it is known the radial Green's function G_0 for the equation without nonlocal exchange interaction can be expressed in terms of solutions χ_0 and χ_∞ of Schrödinger or Dirac equations that are regular at

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[*] Approximate summation can also be done here if the virtual excitation energy of the external electron $\omega = E - E_\gamma$ is much less than the core electron excitation energy. This is the case for alkaline atoms. The sum of the second and the third graph on Fig. 3 is approximately equal to the first graph here. There is also way of summation related to the introduction of pair correlation functions (see, e. g. Ref. [12]).

$r \to 0$ and $r \to \infty$ correspondingly: $G_0(r_1, r_2) \infty \chi_0(r_<) \chi_\infty(r_>)$, $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$. Exchange interaction V_{ex} is taken into account by solving a matrix equation $\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V}_{ex} \hat{G}$. Polarization operator (Fig. 4) is

$$\hat{\Pi}(\omega) = \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \hat{G}(\omega + \varepsilon) \hat{G}(\varepsilon). \tag{2}$$

It is convenient to carry out integration over ε analytically closing the integration contour e. g. in the upper half-plane. After the integration:

$$\hat{\Pi} = \sum_{n,\gamma} \frac{2i(\varepsilon_n - \varepsilon_\gamma)}{(\varepsilon_n - \varepsilon_\gamma)^2 - \omega^2} \psi_n^+(r_1) \psi_\gamma(r_1) \psi_\gamma^+(r_2) \psi_n(r_2) =$$

$$= i \sum_{n} \psi_n(r_1) [\hat{G}(\varepsilon_n + \omega) + \hat{G}(\varepsilon_n - \omega)] \psi_n(r_2). \tag{3}$$

In the Feynman technique the second order energy correction is given by two graphs shown in Fig. 5. In this order it is easy to perform analytical integration over ω using the formulae (1), (3).
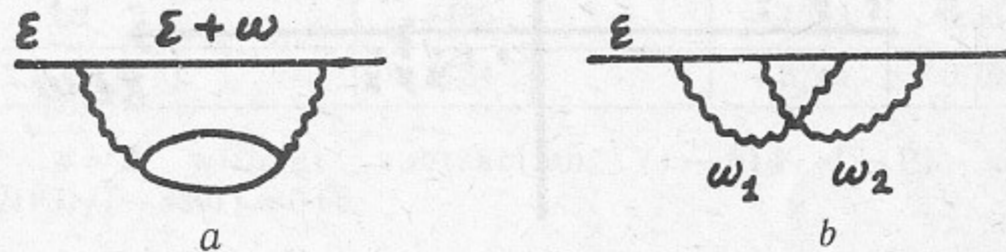

Fig. 5. Correlation corrections to energy in Feynman diagram technique.

After the integration the graph 5,a transforms to 2,a and 2,c Note, that the graph 2,a originates from the sum over the free states $|\gamma\rangle$ in eq. (1) and 2,c — over occupied states $|n\rangle$. Similarly the graphs 2,b and 2,d originate from 5,b.

In order to sum all the screening diagram chain one should perform the summation before integration over ω. In a practical calculation polarization operator $\hat{\Pi}$ is a matrix in a discrete coordinate space: $\hat{\Pi}(\omega) \to \Pi_{r_1 r_2}^k(\omega)$. Here k is the multipolarity of a Coulomb quantum. The Coulomb interaction operator is $\hat{Q} \to Q_{r_1 r_2}^k = \frac{r_<^k}{r_>^{k+1}}$. Multipole expansion is carried out both in Coulomb interaction and polarization operator, i. e. the angular variables are separated. It is convenient to include the integration measure $dr_1 \, dr_2$ into Coulomb

$$\pi(\omega) = \text{⬜} = \text{◯} + \text{◯◯} + \dots$$

Fig. 6. Screening diagram chain for effective polarization operator $\pi(\omega)$.

matrix. In the V_P method it is necessary to take into account subtraction diagrams with potential $(1-P)V_0(1-P)$.

It is easy now to find all the sum of screening diagrams on Fig. 6:

$$\hat{\pi}(\omega) = \hat{\Pi}(\omega)\,[\,1 + i\hat{Q}\,\hat{\Pi}(\omega)\,]^{-1}. \qquad (4)$$

Integration over ω is carried out numerically. It is convenient to rotate on 90° integration contour from real axis to the complex ω plane parallel to imaginary axis. For example, integration contour for diagram 5,a is presented on Fig. 7.
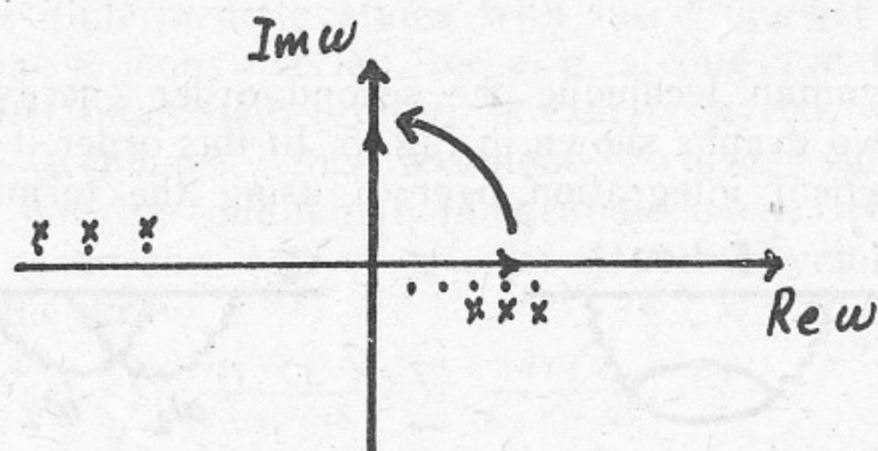

Fig. 7. 90°-rotation of integration contour over ω in diagram 5,d. Points denote Green's functions poles, Grosses denote polarization operator poles.

Results of correlation correction calculations for $6p_{1/2}$ energy level are presented in the Table 1 (basis orbital set is obtained in V_P-potential). Contributions of different multipoles are listed for the 2,a and 2,c diagrams. As it was expected the strongest screening effect appears for $k=1$. Screening factor is 0.4—0.5 here. For further applications we introduce the average screening factor $\hat{f}_k$ for Coulomb integral: $\hat{f}_k = $ (screened correction/nonscreened correction)$^{1/2}$. E. g., for $k=1$ $\hat{f}_k \approx 0.7$. For $k=0$ there is strong cancellation between Coulomb electron-electron interaction and subtraction contribution of $(1-P)V_0(1-P)$. Therefore we use the values of correlation corrections without subtraction for $\hat{f}_k$ calculation. One can use these factors to take into account screening effects approxi-

Table 1

Screening of Correlation Corrections (Fig. 2,a, 2,b, 2,c, 2,d) to Energy of $6p_{1/2}$-Electron. Basis Set of Orbitals is Obtained in V_P Potential. Units are cm^{-1}.

Graph	k	a	b	c	d
2,a	0	−2	246	137	0.66*)
	1	−9751	2079	−4822	0.49
	2	−3428	−2668	−2826	0.82
	3	−1466	−1248	−1284	0.88
	4, 5, 6	−742	−711	−712	0.96
	$\sum_k$	−15389	−2302	−9507	0.62
2,c	0	558	120	324	0.58
	1	10004	−4595	4285	0.43
	2	120	100	104	0.87
	3	275	220	230	0.84
	4	13	12	12	0.92
	$\sum_k$	10970	−4143	4955	0.45
2,b		3170		2090	0,66
2,d		−3485		−1253	0.36
2,a,b,c,d			−4734	−3745	0.79

*) For $k=0$ without subtraction $(1-P)V_0(1-P)$ contribution $(\hat{f}_k)^2 = (-2193)/(-3301) \approx 0.66$.

k is multipolarity of Coulomb interaction; a—correlation corrections without screening; b—with screening in two-loops approximation (see, e. g. diagram 2,a+diagrams 3); c—with exact screening; d—average Coulomb integral screening factor squared: $(\hat{f}_k)^2 = $ (screened correction/unscreened correction).

Table 2

Energy Levels $6p_{1/2}$, $6p_{3/2}$ (Ionization Potentials) in Thallium. Units are cm^{-1}.

	a	b	c	d
$6p_{1/2}$	46296	51030	50011	49264
$6p_{1/2}$	38677		42204	41471

a—zero approximation—Relativistic Hartree—Fock (RHF) calculation in V_P potential; b—RHF+second order correlation corrections; c—RHF+screened correlations; d—experiment [11].

mately in calculations of correlation corrections to other physical values (hyperfine structure, electromagnetic amplitudes, parity violation effects etc). Of course, it is possible to introduce radial dependent empirical screening functions.

Comparison of calculated and experimental energies is presented in the Table 2. It is seen that consideration of screening effect essentially improve the accuracy of calculations.

Our preliminary (slightly more rough) calculations have shown that accuracy $\sim 1\%$ results also for $7s$, $6d$ levels and $6p$ fine structure interval.

In conclusion we would like to pay attention to another phenomenon where screening of Coulomb interaction is essential. This is the electron coupling in superconductors. Consider for example hole
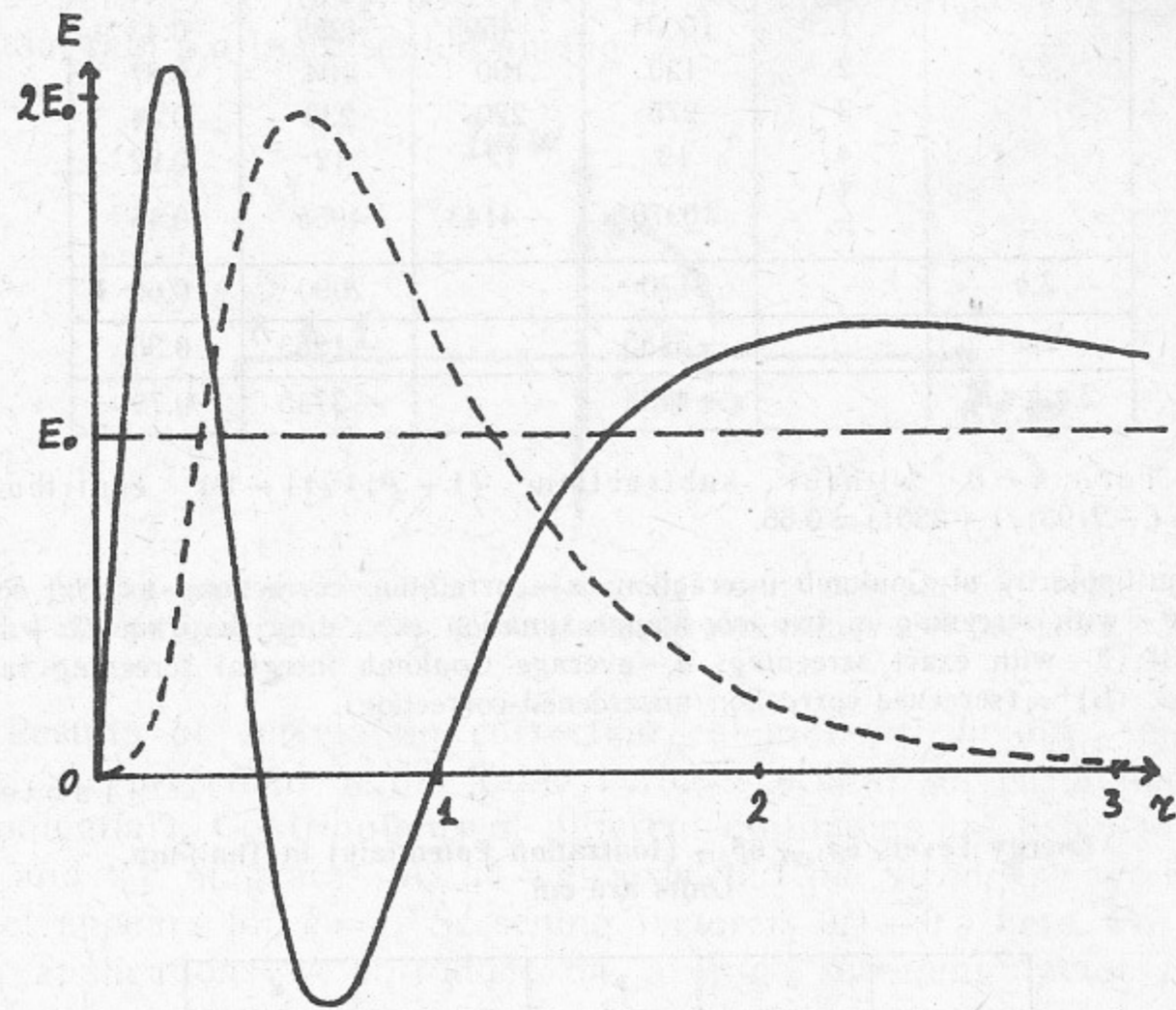

Fig. 8. Plot of electric field $E_t = E_0 + E_e$, in Cu^+ on the z-axis (solid curve). E_e is the electron field induced by external field $E_0 = E_{0z}$. The dotted curve is the radial probability density of 3,d-electron. The distance is shown in atomic units.

conductive zone originated from the deep $3d$ copper electrons which strongly interact with ions (a situation similar to high temperature

superconductors). In the strong (electron-ion) coupling approximation there are two contributions to electron-electron interaction. Firstly, both electrons can be at the same atom. We calculate the largest zero multipolarity Coulomb integral $F_0(3d, 3d)$. Its unscreened value is 210000 cm^{-1}. Single-loop screening reduces F_0 to the value 115000 cm^{-1}. And after summation of screening diagrams we obtain 147000 cm^{-1}. We see that the screening effect is large but it does not change the sign of electron-electron interaction.

Of course, we estimate here only high energy excitation contribution. There are also low-lying electron levels which depend on superconductor (e. g. splitted hybrid $3d(Cu)$ or $2p(O)$ ion levels). Their contribution to screening can be very essential.

Secondly, electrons can be at the different atoms. As we have noted screened external electric field changes the sign on the radius of outer electron shell. Graph of screened field on z-axis ($E = E_z$) for Cu^+ is presented in Fig. 8. There is also radial probability density for $3d$-electron in this Figure ($W(r) = |\chi(r)|^2$, $\psi(r) = Y_{2m}(\theta, \varphi)\chi(r)/r$). It is interesting that the maximum of probability is in the area of inverse field. We can consider it as a hint that interaction of electrons situated at different atoms is strongly suppressed or even changes the sign due to atomic screening effect. And finally atomic screening effect could essentially influence usual phonon pairing mechanism due to screening of ion lattice deformation field.

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и многочастичная теория возмущения в атомах**