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CORRELATION POTENTIAL METHOD FOR CALCULATION OF ENERGY LEVELS, HYPERFINE STRUCTURE AND E1-TRANSITION AMPLITUDES IN ATOMS WITH ONE UNPAIRED ELECTRON

ABSTRACT

Energy levels, fine and hyperfine structure as well as E1-transition amplitudes in thallium and gold are calculated. Application of relativistic Hartree—Fock equations with taking into account electron shells polarization and correlation corrections to wave function, as a rule, provides a few per cent accuracy. This is an order of magnitude better than accuracy of simple Hartree—Fock calculations. The estimation of structural radiation is carried out.

I. INTRODUCTION

Hartree—Fock (HF) method does not provide high accuracy of calculations in heavy atoms. For example, in Li the accuracy of ionization potential HF calculation is 1% while in Cs it is 10%, and the accuracy of fine structure HF calculation in $6p$-state of Cs is 30% (see, e. g., Ref. [1]). HF calculations of matrix elements of operators also lead to large errors.

Consideration of only electron shell polarization by external field (random phase approximation or Time-Dependent Hartree—Fock (TDHF) method) is not sufficient. For example, accuracy of relativistic Hartree—Fock (RHF) calculation of hyperfine structure (HFS) is 38%, taking into account of electron core polarization decreases error to 26%. Accuracy is drastically improved if we take into account both polarization and second order correlation corrections (inaccuracy $\lesssim 2\%$, [2, 3]). The similar situation takes place in Fr [2] and ion Ra$^+$ [4].

Alkaline atoms have an external electron which overlaps very little with the electrons of compact core. This property permits to use perturbation theory in residual interaction of external electron with core for calculation of correlation corrections.

In the present work methods of polarization and correlation corrections calculation developed in Refs [1—3] are applied for calculations in thallium and gold. These atoms, similar to alkaline atoms, have one unpaired electron. However, this electron is close to internal electrons. At first sight this means that perturbation theory in interaction of external electron with core electrons is not ap-

plicable here since the interaction is not small. However we will see that perturbation theory results have high accuracy in Tl and Au. This fact can be easily understood: the potential of external electron is nearly constant in the core region and practically does not change the wave functions of the core electrons. By other words, the non-diagonal matrix elements of external electron potential are small.

Calculation of correlation corrections can be essentially simplified if one takes into account only the dominating correlation diagrams rather than all second order diagrams. It is convenient to do by introducing so-called correlation potential into the equation for single-particle orbital. Correlation potential is a non-local operator calculated by means of perturbation theory. It's average value identically coincides with the correlation correction to energy. For comparison of two methods we have carried out calculations of Tl hyperfine structure. In the first calculation we took into account all the second order correlation corrections in residual interaction. In the second calculation we took into account the dominating diagrams only by means of correlation potential method. These diagrams correspond to renormalization of one-electron wave function. It is seen from comparison with experiment that both methods have inaccuracy of the same order of magnitude. The methods similar to our correlation potential method were used to calculate light alkaline atoms HFS [5] and scattering phases (see Ref. [6] and references therein).

Correlation potential method provides high accuracy in electromagnetic transition calculations too. Our calculations in Cs [3] and present calculations in Tl and Au show that the disagreement in E1-amplitudes between calculation and experiment is about a few per cent.

Except the dominating correlation corrections which are the renormalization of external electron wave function, we consider second order renormalization of electromagnetic vertex (structural radiation). In the present paper we obtain the approximate formula for structural radiation. The situation here resembles low-energy theorem for bremsstrahlung (Low theorem).

Recently preprint [7] appeared where energy levels, HFS and E1-amplitudes were calculated by RHF method with polarization taken into account. Correlation corrections were not considered. Results of Ref. [7] agree with our corresponding values for Cs, Tl and Au.

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2. CORRELATION CORRECTION TO ENERGY. CORRELATION POTENTIAL

To use perturbation theory, the exact Hamiltonian of an atom is devided into two parts: the first part is a sum of the single-particle Hamiltonians allowing an exact numerical solution, and the second part represents the residual interaction.

$$H = \sum_{i=1}^{N} H_0(\vec{r}_i) + U, \tag{1}$$

$$H_0 = \vec{\alpha}\vec{p} + (\beta - 1)m - \frac{Ze^2}{r} + V^{N-1}, \tag{2}$$

$$U = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{N} V^{N-1}(\vec{r}_i). \tag{3}$$

Here $\vec{\alpha}$ and β are Dirac matrices, Z is the nuclear charge and N is the number of electrons, $V^{N-1} = V_{dir} + V_{exch}$ is the sum of direct and non-local exchange potentials created by $(N-1)$ core electrons. Core orbitals are calculated without taking into account interaction with external electron. The main advantage of such method is the following: H_0 generates complete orthogonal set of single-particle orbitals, both for core electrons and for the external electron.

Correlation correction to the ionization energy of external electron is calculated by means of perturbation theory in residual interaction U. First order correction is zero. Second order correction is determined by four diagrams shown in Fig. 1 ($|\alpha\rangle$ is the state of external electron; $|n\rangle$, $|m\rangle$ are the core states; $|\beta\rangle$, $|\gamma\rangle$ are the states outside core; for detailes see Ref. [1]). Note that contribution of
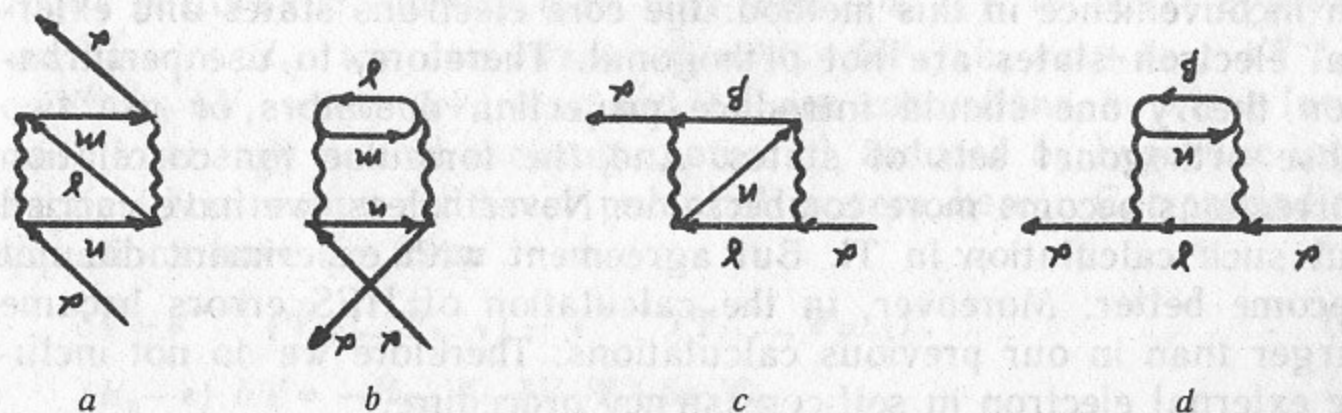

Fig. 1.

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diagrams 1,a and 1,b at $\gamma = \alpha$ corresponds to rearrangement of core in the average field of the external electron.

Results of energy levels calculation are presented in Table 1. Fine structure intervals can be found as difference of corresponding energies. Comparison with experiment shows that the accuracy of calculation with correlation corrections is 0.1—0.7% for high levels and 3—4% for lower p-levels, error of fine structure intervals $\sim 2\%$ for p-levels and 7% for $6d$-level.

Table 1

Energy Levels (Ionization Potentials) in Thallium and Gold
(in units cm^{-1})

	State	RHF	RHF+ +correlations	Experiment [16]	Brueckner orbitals
Tl	$6p_{1/2}$	43909	50654	49264	50542
	$6p_{3/2}$	36670	42704	41471	42780
	$7s$	21100	22952	22786	23100
	$7p_{1/2}$	14282	15203	15104	15086
	$7p_{3/2}$	13359	14227	14103	14129
	$6d_{3/2}$	12218	13130	13146	13310
	$6d_{5/2}$	12167	13042	13064	13205
Au	$6s$	60136	74286	74410	74840
	$6p_{1/2}$	29353	35484	37051	36363
	$6p_{3/2}$	26679	31339	33236	32067

In Tl and Au the average field of external electron is not small. Therefore desire to take this field into account in zero approximation arises, i. e. to carry out self-consistency procedure for core orbitals including interaction with external electron [8, 9]. There is an inconvenience in this method: the core electrons states and external electron states are not orthogonal. Therefore, to use perturbation theory one should introduce projection operators or use two close orthogonal sets of states. And the formulae for correlation corrections become more combersome. Nevertheless, we have carried out such calculation in Tl. But agreement with experiment did not become better. Moreover, in the calculation of HFS errors became larger than in our previous calculations. Therefore we do not include external electron in self-consistency procedure.

For further applications we consider another way of correlation correction calculation. Let us add to V^{N-1} in eq. (2) a non-local

correlation potential $\hat{\Sigma}$ chosen so that its average value for the state of external electron coincides with correlation correction to energy.

$$\delta E_\alpha = \langle \alpha | \hat{\Sigma} | \alpha \rangle,$$

$$\hat{\Sigma} \, \Psi_\alpha = \int \Sigma \, (\vec{r}_1, \vec{r}_2, E_\alpha) \, \Psi_\alpha \, (\vec{r}_2) \, d^3 r_2. \tag{4}$$

It is easy to write the correlation potential explicitly. For example, a part of the mass operator $\Sigma \, (\vec{r}_1, \vec{r}_2, E_\alpha)$ corresponding to Fig. 1,a, is of the form:

$$\Sigma^{(a)} \, (\vec{r}_1, \vec{r}_2, E) =$$

$$= e^4 \sum_{n,\beta,\gamma} \iint d^3 r_3 \, d^3 r_4 \frac{\Psi_n^{+*} (\vec{r}_3) \, r_{13}^{-1} \, \Psi_\gamma (\vec{r}_1) \, \Psi_\gamma^+ (\vec{r}_2) \, \Psi_\beta (\vec{r}_3) \, \Psi_\beta^+ (\vec{r}_4) \, r_{24}^{-1} \, \Psi_n (\vec{r}_4)}{E + E_n - E_\gamma - E_\beta}. \tag{5}$$

Detailed description of $\hat{\Sigma}$ calculation can be found in Ref. [3].

Solving the equation for single-particle orbital in potential $V = V_{dir} + V_{exch} + \hat{\Sigma}$ we get external electron energy with correlation correction. Difference from direct perturbation theory calculation here is $\sim (\Sigma)^2$ and is small. Note that the single-particle states, found in such a way, practically coincide with Brueckner orbitals (see e. g. Ref. [5]) and despite some distinction in definition we will call the orbitals in the potential $V^{N-1} + \hat{\Sigma}$ the Bbueckner orbitals.

3. HYPERFINE STRUCTURE (HFS).
ENHANCEMENT OF CORRELATION POTENTIAL CONTRIBUTION
TO CORRELATION CORRECTION

It is convenient to include hyperfine interaction H_{hf} in single-particle orbitals rather than take it into account by means of many-body perturbation theory (see, e. g. Refs [5, 2]). In linear approximation in H_{hf} we can write $\tilde{\Psi}_n = \Psi_n + \delta \Psi_n$, $\tilde{\varepsilon}_n = \varepsilon_n + \delta \varepsilon_n$, $\tilde{V}^{N-1} = V^{N-1} + \delta V$, where $\delta \Psi_n$, $\delta \varepsilon_n$ and δV are corrections to wave function, to energy and to exchange potential, induced by hyperfine interaction (correction to direct potential is zero here). Corresponding equations have the form

$$\delta V = V^{N-1} \, (\tilde{\Psi}_1, ..., \tilde{\Psi}_{N-1}) - V^{N-1} \, (\Psi_1, ..., \Psi_{N-1}), \tag{6}$$

$$(H_0 - \varepsilon) \, \delta \Psi = -H_{hf} \cdot \Psi - \delta V \cdot \Psi + \delta \varepsilon \cdot \Psi, \tag{7}$$

$$\delta \varepsilon = \langle \Psi | H_{hf} | \Psi \rangle + \langle \Psi | \delta V | \Psi \rangle. \tag{8}$$

These equations should be solved self-consistently for all core electrons (without external electron). Corrections $\delta\Psi$ and $\delta\varepsilon$ for external electron should be found at frozen core. External electron correction $\delta\varepsilon$ determines atomic hyperfine structure. Term $\langle\Psi|\delta V|\Psi\rangle$ in eq. (8) for $\delta\varepsilon$ corresponds to core polarization contribution to HFS. In many-body perturbation theory this method corresponds to summation of diagram series in Fig. 2.

Fig. 2.

Correlation corrections to HFS are calculated in the same way as corrections to energy. It is necessary to select terms linear in H_{hf} from formulae for second order correlation corrections expressed through $\tilde\Psi$, $\tilde\varepsilon$. Detailes of calculations can be found in Ref. [2]. Results of calculation for Tl HFS are presented in Table 2.

Table 2

Hyperfine Structure Constants in ^{205}Tl
(in units 10^{-3} cm^{-1})

	RHF, $\langle\Psi\|H_{hf}\|\Psi\rangle$	RHF+ +polarization, $\langle\Psi\|H_{hf}+\delta V\|\Psi\rangle$	RHF+ +polarization+ +correlations	Experiment [17—21]	Brueckner orbitals+polarization, $\langle\Psi_{Br}\|H_{hf}+\delta V\|\Psi_{Br}\rangle$
$6p_{1/2}$	580	707	694	710.853	726
$6p_{3/2}$	43	—64	24	8.8407	—64
$7s$	252	347	415	417	416
$7p_{1/2}$	65	66	68	71(2)	69
$7p_{3/2}$	6.2	3.9	13.3	10.3(2)	6.5

Direct calculations in second order in residual interaction are quite cumbersome. There is an essentially more simple method of approximate correlation correction calculation based on correlation potential (4) [3]. We find the orbital of external electron Ψ in «Brueckner» potential $V = V_{dir} + V_{exch} + \hat\Sigma$ rather than in HF potential $V = V_{dir} + V_{exch}$. And then we calculate $\delta\varepsilon$ (8) using «Brueckner» function Ψ found in this way. In many-body perturbation theory based on HF basis set this method corresponds to taking into account

the diagrams shown in Fig. 3 (renormalization of external electron wave function) and neglecting the second order diagrams for renor-
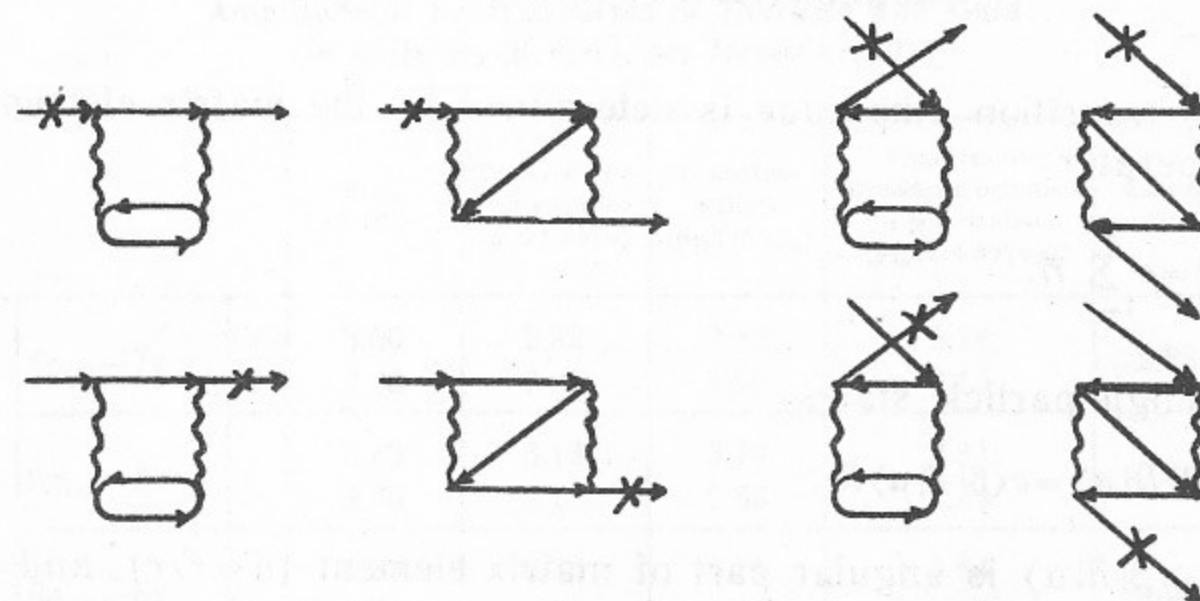

Fig. 3.

malization of vertex (several diagrams of this type are presented in Fig. 4). In the Ref. [3] it is shown by means of numerical calcula-
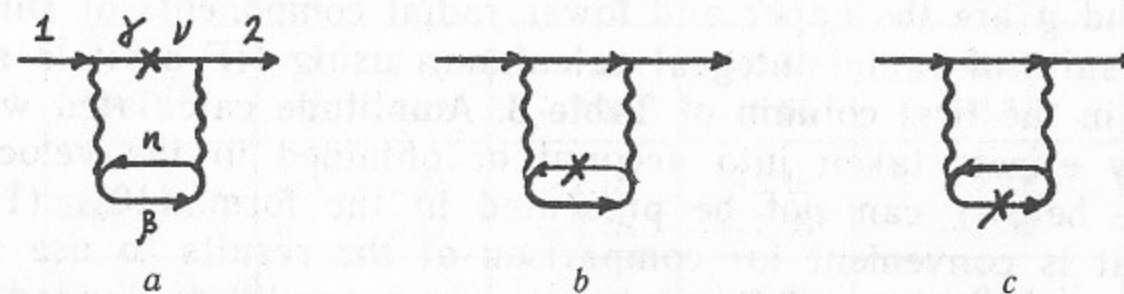

Fig. 4.

tion that this approximation works well in the alkaline atoms and theoretical arguments clarifying this fact are presented.

Results of thallium HFS calculations based on correlation potential method are presented in Table 2. Comparison with experiment shows that accuracy is practically the same as in exact calculations in second order of perturbation theory. It is 1—3% for s- and $p_{1/2}$-levels. For $p_{3/2}$-levels accuracy is low due to very strong compensation between Hartree—Fock value $\langle 6p_{3/2}|H_{hf}|6p_{3/2}\rangle$, core polarization $\langle 6p_{3/2}|\delta V|6p_{3/2}\rangle$ and correlation correction.

4. E1-TRANSITION AMPLITUDES. CORRELATION POTENTIAL METHOD

E1-transition amplitude is determined by the matrix element of the operator

$$\vec{D} = e \sum_{i=1}^{N} \vec{r}_i. \tag{9}$$

For single-particle states

$$\langle \beta | \vec{D} | \alpha \rangle = e \langle \beta | \vec{n} | \alpha \rangle R. \tag{10}$$

Here $\langle \beta | \vec{n} | \alpha \rangle$ is angular part of matrix element ($\vec{n} = \vec{r}/r$), and R is radial integral

$$R = \int_0^{\infty} (f_\beta f_\alpha + g_\beta g_\alpha) \, r \, dr \tag{11}$$

where f and g are the upper and lower radial components of Dirac spinor. Results of radial integral calculation using HF orbitals are presented in the first column of Table 3. Amplitude calculated with many-body effects taken into account or obtained in the velocity form (see below) can not be presented in the form (10), (11). However it is convenient for comparison of the results to use the radial integral which we define formally as an amplitude divided by angular matrix element $\langle \beta | \vec{n} | \alpha \rangle$. One can extract the experimental value of radial integral R_{exp} from oscillator strength using standard formulae (see Ref. [10]).

Polarization effects are taken into account by using TDHF equations. Let us remind how to modify HF equations in the presence of time-depended perturbation

$$H_{int} = (\hat{f} e^{-i\omega t} + \hat{f}^+ e^{i\omega t}). \tag{12}$$

Total atomic TDHF function is Slatter determinant constructed from single-particle orbitals

$$\tilde{\Psi}_k e^{-i\varepsilon_k t} = (\Psi_k + X_k e^{-i\omega t} + Y_k e^{i\omega t}) e^{-i\varepsilon_k t}. \tag{13}$$

Equations for corrections X_k, Y_k induced by perturbation H_{int} can be

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Amplitude of E1-Transitions in Thallium and Gold
(in units $ea_B \langle \beta | \vec{n} | \alpha \rangle$, see formula (10))

			RHF, $\langle \beta | D | \alpha \rangle$	TDHF = RHF + + polarization, $\langle \beta | D + \delta V | \alpha \rangle$	Brueckner orbitals: $\langle \beta_{Br} | D | \alpha_{Br} \rangle$	Final results: Brueckner oritals + + polarization, $\langle \beta_{Br} | D + \delta V | \alpha_{Br} \rangle$	Experiment [22, 23]
Tl	$6p_{1/2} - 7s$	l	2.50	2.32	2.32	2.14	2.23(6)
		v	2.00	2.32	1.90	2.15	
	$6p_{3/2} - 7s$	l	3.43	3.13	3.10	2.81	2.83(6)
		v	2.75	3.13	2.55	2.84	
	$6p_{1/2} - 8s$	l	0.80	0.75	0.71	0.64	0.67(3)
		v	0.61	0.75	0.56	0.65	
	$6p_{3/2} - 8s$	l	0.86	0.70	0.77	0.63	—
		v	0.64	0.70	0.61	0.65	
	$7p_{1/2} - 7s$	l	−8.14	−7.86	−7.52	−7.20	−7.27(7)
		v	−7.72	−7.86	−7.07	−7.13	
	$7p_{3/2} - 7s$	l	−7.65	−7.45	−7.08	−6.85	−6.84(7)
		v	−7.22	−7.45	−6.66	−6.79	
	$6p_{1/2} - 6d_{3/2}$	l	−2.35	−2.15	−2.40	−2.18	−1.99(8)
		v	−2.17	−2.15	−2.28	−2.32	
	$6p_{3/2} - 6d_{3/2}$	l	−3.16	−2.94	−3.08	−2.84	−2.64(13)
		v	−2.96	−2.94	−2.94	−3.00	
Au	$6s - 6p_{1/2}$	l	−3.33	−2.72	−3.07	−2.31	−2.24(12)
		v	−3.27	−2.72	−2.94	−2.24	
	$6s - 6p_{3/2}$	l	−3.21	−2.65	−2.96	−2.23	−2.22(8)
		v	−3.16	−2.65	−2.83	−2.15	

obtained from variational equation

$$\delta \langle \tilde{\Phi} | H + H_{int} - i \frac{\partial}{\partial t} | \tilde{\Phi} \rangle = 0 \tag{14}$$

by variation of X_k and Y_k

$$(H_0 - \varepsilon_i - \omega) X_i = -(\hat{f} + \delta \hat{V}) \Psi_i,$$
$$(H_0 - \varepsilon_i + \omega) Y_i = -(\hat{f}^+ + \delta \hat{V}^+) \Psi_i, \tag{15}$$

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$$\delta \hat{V} \Psi = \sum_{k=1}^{N-1} \int \frac{d^3 r_2}{|r_1 - r_2|} \{[Y_{\vec{k}}^+(2) \Psi_k(2) + \Psi_{\vec{k}}^+(2) X_k(2)] \Psi(1) -$$

$$-[Y_{\vec{k}}^+(2) \Psi_k(1) + \Psi_{\vec{k}}^+(2) X_k(1)] \Psi(2)\}.$$

Similar to stationary case we solve eqs (15) self-consistently only for $N-1$ core electrons (V^{N-1} approximation). Wave function of external electron can then be found in frozen core field. This method allows one to find complete orthonormal set of orbitals with quasi-energy ε_k.

Expression for external electron transition amplitude $M_{\beta\alpha}$ from state $|\alpha\rangle$ to state $|\beta\rangle$ induced by the field (12), can be found by comparison of solution (13) of eqs (15) with conventional time-dependent perturbation theory

$$\tilde{\Psi}_k = \Psi_\alpha + \frac{M_{\beta\alpha}}{E_\alpha - E_\beta + \omega} \Psi_\beta e^{-i\omega t}. \tag{16}$$

We keep here only the resonant term ($\omega \approx E_\beta - E_\alpha$). On the other hand, as follows from eq. (15)

$$\langle \Psi_\beta | \tilde{\Psi}_\alpha \rangle \simeq \langle \Psi_\beta | X_\alpha e^{-i\omega t} \rangle = \frac{\langle \Psi_\beta | \hat{f} + \delta\hat{V} | \Psi_\alpha \rangle}{E_\alpha - E_\beta + \omega} e^{-i\omega t}. \tag{17}$$

Comparing (17) and (16) we find

$$M_{\beta\alpha} = \langle \Psi_\beta | \hat{f} + \delta\hat{V} | \Psi_\alpha \rangle. \tag{18}$$

Contribution of $\delta\hat{V}$ here corresponds to direct and exchange electron core polarization (compare with formula (8) for $\delta\varepsilon$). Formula (18) corresponds to well known random phase approximation (see, e. g. Ref. [11]).

The Hamiltonian of electron interaction with electric field of electromagnetic wave

$$E = E_0 \cdot (e^{-i\omega t} + e^{i\omega t}) \tag{19}$$

depends on the choice of scalar φ and vector-potential $\vec{A}$ gauge. Conventional «length» form of interaction corresponds to the choice

$$\varphi = -2\vec{E}_0 \vec{r} \cos(\omega t - \vec{k}\vec{r}),$$

$$\vec{A} = -\frac{2(\vec{E}_0 \vec{r}) \vec{k}}{\omega} \cos(\omega t - \vec{k}\vec{r}) \approx 0, \tag{20}$$

$$H_{int}^l \simeq -e\vec{r}\vec{E}(t), \quad \hat{f}_l = -e\vec{r}\vec{E}_0,$$

where $\vec{k}$ is a wave vector. We neglect here corrections $\sim kr$ and magnetic interaction. Another standard «velocity» form corresponds to

$$\varphi = 0, \quad \vec{A} = -\frac{2\vec{E}_0}{\omega} \sin(\omega t - \vec{k}\vec{r}),$$

$$H_{int}^{(v)} \simeq -\frac{2e\vec{a}\vec{E}_0}{\omega} \sin \omega t, \quad \hat{f}_v = ie \frac{\vec{a}\vec{E}_0}{\omega}. \tag{21}$$

The gauge (21) can be obtained from (21) by means of gauge transformation

$$\varphi \to \varphi + \frac{\partial}{\partial t} \theta, \quad \vec{A} \to \vec{A} - \vec{\nabla}\theta,$$

$$\theta = \frac{2\vec{E}_0 \vec{r}}{\omega} \sin(\omega t - \vec{k}\vec{r}). \tag{22}$$

It is known that in TDHF calculations amplitude is gauge invariant (see e. g. Refs [11, 25]). It is easy to verify. Gauge transformation of wave function

$$\tilde{\Phi} \to \tilde{\Phi}' = \tilde{\Phi} \exp\left(i \sum_k \theta(r_k)\right) \tag{23}$$

leaves TDHF wave function $\tilde{\Phi}'$ one-determinant. Therefore, if $\tilde{\Phi}$ is the solution of equation (14) in one gauge the transformed function $\tilde{\Phi}'$ is the solution of the equation with gauge transformed H' (it is easy to verify by direct substitution of the transformation (22), (23) to equation (14)). The common phase in wave function (23) does not influence the transition amplitudes and the field of electrons.

The relation between solutions X, Y in l-form and v-form can be found from equations (23), (22) in linear approximation (see e. g. Ref. [12])

$$X_v = X_l + \frac{e\vec{r}\vec{E}_0}{\omega} \Psi,$$

$$Y_v = Y_l - \frac{e\vec{r}\vec{E}_0}{\omega} \Psi. \tag{24}$$

These expressions are valid both for core electrons and for external electron. Gauge invariance of the amplitudes immediately follows

from (24). According to (17) the amplitude is residue of $\langle \Psi | X_\alpha \rangle$ at Hartree—Fock frequency $\omega = E_\beta - E_\alpha$, but gauge term in (24) has no pole.

Note that gauge invariance of amplitude in TDHF takes place also when any additional single-particle interaction is included (e. g. weak interaction, Refs [13, 12]) and in many-photon transitions [13].

Therefore, coincidence of l- and v-forms in TDHF is identical and is the test of numerical calculation accuracy only.

Other test of accuracy and self-consistency of TDHF-equations is the value of electric field at the nucleus. As known, static electric field at nucleus is shielded completely by electrons (Schift theorem [14]). We have shown [15] that this theorem is valid in TDHF at $\omega = 0$. Therefore, static field at the nucleus must be

$$\vec{E}_t(0) = \vec{E}_0 + \langle \vec{E}_e(0) \rangle = \vec{E}_0 \frac{Z_i}{Z} \qquad (25)$$

where Z_i is the ion charge, E_0 is the external field, E_e is induced electron field. For example, in Tl^+ ion $E_t(0) = E_0/81$. Optical transition frequency is small with respect to core electron excitation energy, and $E_t(0)$ here is close to (25) (see also Ref. [26]). For example, at the frequency of $6p-7s$ transition the difference from static case is $-4 \cdot 10^{-3} E_0$ only. A plot of $E_t(r)$ was presented in the same Ref. [15]. It is interesting that «shielded» field E_t can be considerably larger than E_0 and has nontrivial radial dependence. Asymptotic value (25) is reached near the nucleus only.

Results of TDHF calculations with core polarization taken into account are presented in Table 3.

To refine the calculations it is necessary to take into account correlation corrections. As we have mentioned in the section 3 the contribution of dominating diagrams presented in Fig. 3 can be easily taken into account by means of Brueckner orbitals for external electron. It is enough to use them in formula (18). Note that core polarization δV can be calculated at Hartree—Fock frequency ω. Contribution of frequency shift in polarization due to correlations has a higher (third) order in residual interaction. But the shift of frequency in operator f_v (21) in v-form should be taken into account because it is the correction of the second order.

Final results of calculation by the polarization potential method are presented in the fourth column in Table 3. In this case there is

no exact theorem about coincidence of l- and v-forms. And the difference between them is the test of physical approximation. It is seen from Table 3 that coincidence of l- and v-forms and agreement with experiment are quite satisfactory. The exception are $6p-6d$ transitions where the difference of v-form calculation with experiment reaches 15%. This difference becomes smaller if we taken into account structural radiation which is not very small in v-form (see following section 5).

5. STRUCTURAL RADIATION AND LOW-ENERGY THEOREM

Introduction of correlation potential allows us to take into account dominating correlation corrections (Fig. 3), where interaction with electromagnetic field is included into external line. In linear approximation in correlation potential their contribution to the amplitudes of the transition $1 \rightarrow 2$ ($E_2 > E_1$) has the form

$$M_3 = \langle Y_2 | \hat{\Sigma} (E_1) | \Psi_1 \rangle + \langle \Psi_2 | \hat{\Sigma} (E_2) | X_1 \rangle \qquad (26)$$

with conditions

$$\langle Y_2 | \Psi_1 \rangle = \langle \Psi_2 | X_1 \rangle = 0. \qquad (27)$$

These conditions follow from perturbation theory. Correction to function Ψ_i

$$\Psi_i' = \sum_{n \neq i} \frac{|n\rangle \langle n| \hat{\Sigma} |i\rangle}{E_i - E_n}$$

is orthogonal to Ψ_i. Conditions (27) allows one to find unique solution for equations (15) for X_1 and Y_2 inspite of the fact that there is the resonance in them ($\omega = E_2 - E_1$).

In v-form calculation the term corresponding to the frequency shift due to correlations in the operator f_v (21) should be added

$$\Delta (\langle 2| f_v | 1 \rangle) = \langle 2| ie\vec{a}\vec{E}_0 | 1 \rangle \left(\frac{1}{\omega + \Delta\omega} - \frac{1}{\omega} \right) =$$

$$= -\frac{\Delta\omega}{\omega} \langle 2| \frac{ie\vec{a}\vec{E}_0}{\omega} | 1 \rangle = -\frac{\Delta\omega}{\omega} \langle 2| -e\vec{r}\vec{E}_0 | 1 \rangle.$$

Corresponding contribution to the amplitude is equal to

$$M_{\Delta\omega} = -\frac{\Delta\omega}{\omega}\langle 2|e\vec{r}|1\rangle, \tag{28}$$

$$\Delta\omega = \langle 2|\hat{\Sigma}|2\rangle - \langle 1|\hat{\Sigma}|1\rangle.$$

The polarization in formula (28) is the third order correction and it is out of our accuracy of calculation. But as follows from gauge transformation of X, Y (24) and condition (27), gauge invariant result should contain contribution (28) with unshielded operator $e\vec{r}$.

Correlation corrections (26), (28) discussed above are equivalent in linear approximation in $\hat{\Sigma}$ to addition of correlation potential in equation for external electron orbitals. However, natural question arises how to estimate remaining diagrams (see, e. g. Fig. 4). By analogy with bremsstrahlung problem this contribution will be called structural radiation.

It is easy to show that the relative contribution of structural radiation is proportional to small factor $\Delta E_e/\Delta E_c$, where ΔE_e is a distance between energy levels of external electron ($\Delta E_e \sim \omega$), ΔE_c is an average core electron excitation energy in the sum (5). Indeed, electromagnetic vertex in diagrams in Fig. 3 changes a state of external electron, and denominator is $E_a - E_\gamma \sim \Delta E_e$. If the vertex is placed into internal line (Fig. 4), the many-body perturbation theory denominator corresponds to core electron excitation energy ΔE_c.

Thus, contribution of diagrams in Fig. 3 is $\Delta E_c/\Delta E_e$ times larger that of Fig. 4. Numerical calculation shows that $\Delta E_c \sim 2\,\mathrm{Ry}$, $\Delta E_e \sim 0.2-0.3\,\mathrm{Ry}$, i. e. structural radiation suppression factor $\sim \Delta E_e/\Delta E_c \sim 1/10$.

Using the parameter $\Delta E_e/\Delta E_c$ one can estimate structural radiation more accurately.

The largest contribution is probably given by the structural radiation diagram shown in Fig. 4,a. Indeed, this diagram determines long-range asymptotics of electromagnetic vertex correction. Similarly asymptotics in mass operator is determined by the dominating diagram shown in Fig. 1,a (see, e. g. Ref. [3]).

$$\sum_{r_1,r_2\to\infty}(\vec{r}_1,\vec{r}_2) \approx \Sigma_{1,a}(\vec{r}_1,\vec{r}_2) \approx -\frac{e^2\alpha}{2r_1^4}\,\delta(\vec{r}_1-\vec{r}_2),$$

$$\alpha = -2e^2 \sum_{\substack{n\ \mathrm{occupied}\\ \gamma\ \mathrm{unoccupied}}} \frac{\langle n|r_z|\gamma\rangle\langle\gamma|r_z|n\rangle}{E_n-E_\gamma}. \tag{29}$$

Here α is core polarizability. Estimation of diagram 4,a contribution is similar to derivation of formula (29). Structural radiation amplitude is

$$\bar{M}_{str} \simeq \langle 2|\hat{\bar{\Gamma}}(\mathrm{Fig.}\ 4,a)|1\rangle,$$

$$\vec{\Gamma}_{4,a}(\vec{r}_1,\vec{r}_2,E_1,E_2) =$$

$$= \sum_{\substack{n\\ \beta,\gamma,\nu}} \frac{\langle n|\frac{e^2}{r_{24}}|\beta\rangle|\gamma\rangle\langle\nu|\vec{D}|\gamma\rangle\langle\gamma|\langle\beta|\frac{e^2}{r_{13}}|n\rangle}{(E_1+E_n-E_\gamma-E_\beta)(E_2+E_n-E_\nu-E_\beta)}. \tag{30}$$

Since external electron energy E_γ or E_ν is small in comparison with core electron energy E_n, we can approximately substitute E_γ by E_ν in formula (30) and use completeness condition $\sum_\gamma|\gamma\rangle\langle\gamma| = \delta(\vec{r}-\vec{r}')$.

Thus we find at $E_2 - E_1 = \omega \sim \Delta E_e \ll \Delta E_c$

$$\hat{\Gamma} \approx -\vec{D}\frac{\partial\hat{\Sigma}}{\partial E}. \tag{31}$$

Analogously substitution E_ν by E_γ leads to

$$\hat{\Gamma} = -\frac{\partial\hat{\Sigma}}{\partial E}\vec{D}. \tag{32}$$

At large distances r_1, r_2 $\hat{\Sigma}$ is local (see (29)) and expression (31) coincides with (32) identically

$$\Gamma_{4,a}(\vec{r}_1,\vec{r}_2\to\infty) \approx \frac{e^3\alpha'\vec{r}}{2r^4}\,\delta(\vec{r}_1-\vec{r}_2),$$

$$\alpha' = 2e^2 \sum_{n,\gamma} \frac{\langle n|r_z|\gamma\rangle\langle\gamma|r_z|n\rangle}{(E_n-E_\gamma)^2}. \tag{33}$$

This formula (cutted off at core radius) is suitable for rough estimation of structural radiation. However in numerical calculations we use exact non-local expression for $\hat{\Sigma}$. In this case formula (31) does not coincide with (32). This fact can be used for estimation of accuracy of transformation from (30) to (31), (32). The point is that first corrections to formulae (31) and (32) in $(E_\nu-E_\gamma)/\Delta E_c$ expansion have opposite sings. Difference between calculations using formulae (31) and (32) constitutes $10-40\%$. The result can

be refined as follows

$$\vec{\Gamma} = -\frac{1}{2}\left[\bar{D}\frac{\partial\Sigma}{\partial E} + \frac{\partial\Sigma}{\partial E}\bar{D}\right].$$ (34)

In this case first corrections in $(E_v - E_\gamma)/\Delta E_c$ compensate one another.

All the remaining diagrams of structural radiation compensate each other and give small contribution to the asymptotics of $\vec{\Gamma}(\vec{r})$. For example, contribution $\infty \vec{r}/r^4$ of diagram 4,b compensates corresponding contribution of 4,c, and their asymptotics is $\vec{r}/r^6$. As a result, matrix element between the states of external electron is small.

The method described above is not applicable for estimation of structural radiation in v-form. Here the states with large energy difference $E_\gamma - E_v$ give essential contributions in the sum (30), and it is impossible to use completeness condition. However, the magnitude of structural radiation in v-form can be easily expressed through its value in l-form using gauge transformation of wave function (24). The result is

$$M_{str}^{(v)} = M_{str}^{(l)} + \frac{e}{\omega}\langle 2|\hat{\Sigma}(E_2)\vec{r} - \vec{r}\hat{\Sigma}(E_1)|1\rangle \approx$$

$$\approx \frac{e}{\omega}\langle 2|[\hat{\Sigma}(\bar{E}),\vec{r}]|1\rangle.$$ (35)

We take into account that $E_2 - E_1 = \omega$, $\bar{E} = (E_1 + E_2)/2$ and

$$\hat{\Sigma}\left(E \pm \frac{\omega}{2}\right) \simeq \hat{\Sigma}(E) \pm \frac{\partial\hat{\Sigma}}{\partial E}\frac{\omega}{2}.$$

In the second order of perturbation theory in residual interaction there is one more contribution to the amplitude related to the change of the normalization of wave functions Ψ_1 and Ψ_2 due to configuration mixing. It is easily transformed to the form

$$M_{norm} = \frac{1}{2}\langle 2|\bar{D}|1\rangle\left[\langle 2|\frac{\partial\hat{\Sigma}}{\partial E}|2\rangle + \langle 1|\frac{\partial\hat{\Sigma}}{\partial E}|1\rangle\right].$$ (36)

Total correlation second order correction is determined by formulae (26), (30), (34), (36) in l-form and (26), (28), (30), (35), (36) in v-form. Using the wave functions transformation (24) it is easy to verify that total correction is gauge invariant.

Results of E1-amplitude calculation in Tl by TDHF method, correlation corrections and total transition amplitudes are presented in Table 4. It is seen that contributions of structural radiation and normalization in l-form are small and compensate each other. Thus the result in l-form practically coincides (with accuracy of order of small corrections $\sim\Sigma^2$) with simple calculation by correlation potential method (see Table 3). In v-form structural radiation is larger because of the term proportional to $1/\omega$ (see formula (35)).

Table 4

Perturbation Theory Calculation of E1-Amplitudes in Thallium
(in units $ea_B\langle\beta|\bar{n}|\alpha\rangle$, see formula (10))

		TDHF	Mass operator (correlation potential) contribution, (26)	Frequency shift in v-form operator, (28)	Structural radiation (34), (35)	Normalization of states (36)	Final results, TDHF+ +correlations	Experiment [22, 23]
$6p_{1/2}-7s$	l	2.32	−0.22	—	0.02	−0.03	2.09	2.23(6)
	v	2.32	0.27	−0.53	0.06	−0.03	2.09	
$6p_{3/2}-7s$	l	3.13	−0.40	—	0.03	−0.04	2.72	2.83(6)
	v	3.13	0.48	−0.92	0.07	−0.04	2.72	
$6p_{1/2}-8s$	l	0.75	−0.10	—	0.01	−0.01	0.65	0.67(3)
	v	0.75	0.03	−0.15	0.03	−0.01	0.65	
$6p_{3/2}-8s$	l	0.70	−0.05	—	0.01	−0.01	0.65	—
	v	0.70	0.11	−0.18	0.03	−0.01	0.65	
$6p_{1/2}-6d_{3/2}$	l	−2.15	0.06	—	−0.03	0.03	−2.09	−1.99(8)
	v	−2.15	−0.46	0.43	0.06	0.03	−2.09	
$6p_{3/2}-6d_{3/2}$	l	−2.94	0.21	—	−0.04	0.04	−2.73	−2.64(13)
	v	−2.94	−0.55	0.66	0.06	0.04	−2.73	

Note that formula (35) has some analogy with a well-known Low theorem about the $\omega\to 0$ limit for bremsstrahlung amplitude in scattering (see, e. g. Ref. [24]). Similarly to discrete spectrum case the largest contribution here is also given by radiation from external line (diagrams shown in Fig. 3) due to small denominator ($\sim 1/\omega$) in the intermediate state of external electron. According to Low theorem contribution of the following order in ω, including structural radiation, is found from gauge invariance requirement.

Similarly it can be done for discrete spectrum transitions. Dominating term in v-form structural radiation (35) $\frac{e}{\omega}\langle 2|[\Sigma,\vec{r}]|1\rangle$ also can be found here from requirement of amplitude gauge invariance. In l-form calculation, structural radiation is $\sim\omega$ times smaller (compare (35) and (34)) and can not be obtained from gauge invariance requirement. This fact can be clarified as follows. Dominating diagrams (Fig. 3) besides the enhancement $\sim 1/\omega$ due to small denominator, can have additional enhancement factor which is large matrix element of operator r between high excited states (limit $\omega\to 0$ corresponds to a highly excited atom). Comparison with v-form calculation shows that this enhancement is $\sim 1/\omega$ also ($\langle 2|\vec{r}|1\rangle = -\frac{i}{\omega}\langle 2|\vec{p}|1\rangle$). But structural radiation $\langle 2|\vec{r}\frac{\partial\Sigma}{\partial E}|1\rangle$ has no such enhancement.

6. CONCLUSION

In the present work we discuss the following method of atomic calculations. Wave functions of closed subshells are found by relativistic Hartree—Fock method without interaction with external electron. Hartree—Fock Hamiltonian generates complete set of orbitals including external electron states. First order correction in residual Coulomb interaction to the ionization energies of external electron is zero in this case. Second order corrections are found by means of perturbation theory.

Polarization corrections to matrix element of interaction operator (e. g., hyperfine interaction or electric dipole interaction with radiation) are found by solving Hartree—Fock equation in external field (time-dependent Hartree—Fock method). Second order correlation corrections can be found by two ways. First method is many-body perturbation theory, and it is very cumbersome. Second approximate way is the correlation potential method. Orbitals of external electron used in matrix element calculation should be replaced by Brueckner orbitals found with correlation potential taken into account. Correlation potential is calculated by means of perturbation theory. This method is essentially simpler and corresponds to taking into account dominating diagrams (correlation corrections to wave function) only.

Thallium and gold are probably most complicated atoms with one external electron. To test physical approximation we have calculated by two methods the energy levels, fine and hyperfine structure and several E1-amplitudes. Earlier we carried out some similar calculations for cesium, francium an ion Ra$^+$ [1—4]. In all the cases when there is no strong compensation of different contributions to calculated value, the accuracy of calculations is some per cent in both methods.

Thus, simultaneous consideration of electron core polarization and correlation corrections to external electron wave function allows one to obtain an order of magnitude better accuracy than simple Hartree—Fock calculation.

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Correlation Potential Method
for Calculation of Energy Levels,
Hyperfine Structure and E1-Transition Amplitudes
in Atoms with One Unpaired Electron[*]

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Применение метода корреляционного потенциала для расчетов уровней энергии, сверхтонкой структуры и амплитуд E1-переходов в атомах с одним неспаренным электроном