Perturbation Theory for QED Calculations of High-Z Few-electron Atoms

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1 Introduction

Experimental investigations of heavy few-electron ions (see, e.g., [1]) have triggered a great interest to accurate quantum electrodynamic (QED) calculations of these systems. At present, such calculations are feasible only by perturbation theory in two small parameters α and $1/Z$, where $\alpha \approx 1/137$ is the fine structure constant and Z is the nuclear charge number. For heavy few-electron ions, the parameters α and $1/Z$ characterize the QED and interelectronic-interaction corrections, respectively. To derive formal expressions for these corrections in a systematic way one needs to employ special methods. One of such methods was first developed by Gell-Mann and Low [2] and Sucher [3]. This method is based on introducing an adiabatically damped factor, $\exp(-\lambda|t|)$, in the interaction Hamiltonian and expressing the energy shift in terms of so-called adiabatic S_λ matrix elements. The Gell-Mann–Low–Sucher formula for the energy shift of a single level gained wide spreading in the literature related to high-Z few-electron atoms [4–9]. This is mainly due to a simple formulation of the method. However, practical calculations showed that the presence of the adiabatic factor strongly complicates derivations of formal expressions for the energy shift in second and higher orders

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of the perturbation theory. In addition, this method requires special investigation of the renormalization procedure since the adibatic S_λ-matrix suffers from ultraviolet divergences. This is due to the fact that the adiabatically damped factor, $\exp(-\lambda|t|)$, is non-covariant and, therefore, the ultraviolet divergences can not be removed from S_λ if $\lambda \neq 0$. For the case of a single level, this problem can be disregarded since, from the physical point of view, one may expect the divergenes to cancel each other in the expression for the energy shift. However, this is not the case if one considers degenerate levels. We can not expect that the standard renormalization procedure makes the secular operator finite in the ultraviolet limit [5, 6]. Similar difficulties occur in the evolution operator method developed in [10–14]. Some modifications of these methods gaining on their extention to quasidegenerate states were recently considered in [15, 16]. We note also that at present there is no formalism based on the Gell-Mann–Low–Sucher or the evolution operator method which would be suitable for calculation of the transition or scattering amplitudes.

In this paper we consider another method to construct the perturbation theory for high-Z few-electron systems. This method, which was developed in [17–21] and described in details in [22], provides a solution of all the problems appearing in the other formalisms indicated above. In particular, it is equally suitable for calculations energy levels of single, degenerate, and quasidegenerate states as well as for calculations of the transition and scattering amplitudes. It was successfully employed in many practical calculations (see, e.g., [22–30] and references therein). Since one of the key elements of the method consists in using two-time Green functions, in what follows we will call it the two-time Green function (TTGF) method.

It should be noted that there are also some other methods employing Green functions. In particular, in [6, 31, 32] two-time Green functions were used to construct quasipotential equations for high-Z few-electron systems. This corresponds to the perturbation theory in the Brillouin-Wigner form. In contrast to that, the method considered here yields the perturbation theory in the Rayleigh-Schrödinger form, which is much more convenient for calculations of high-Z few-electron atoms.

Below we formulate the basic principles of the TTGF method. The relativistic unit system ($\hbar = c = 1$) and the Heaviside charge unit ($\alpha = \frac{e^2}{4\pi}, e < 0$) are used in the paper.

2 Energy Levels

In high-Z few-electron atoms the number of electrons, denoted by N, is much smaller than the nuclear charge number Z. For this reason, the interaction of the electrons with each other and with the quantized electromagnetic field is much smaller (by factors $1/Z$ and α, respectively) than the interaction of the electrons with the Coulomb field of the nucleus. Therefore, we can assume

that in zeroth approximation the electrons interact only with the Coulomb field of the nucleus and obey the Dirac equation

$$(-\mathrm{i}\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}+\beta m+V_{\mathrm{C}}(\mathbf{x}))\psi_n(\mathbf{x})=\varepsilon_n\psi_n(\mathbf{x})\,. \tag{1}$$

The interaction of the electrons with each other and with the quantized electromagnetic field is accounted for by perturbation theory. In this way we obtain quantum electrodynamics in the Furry picture. We note that we could start also with the Dirac equation with an effective potential $V_{\mathrm{eff}}(\mathbf{x})$ (e.g., a local version of the Hartree-Fock potential) which approximately accounts for the interelectronic interaction. Then the interaction with the potential $\delta V(\mathbf{x}) = V_{\mathrm{C}}(\mathbf{x}) - V_{\mathrm{eff}}(\mathbf{x})$ must be accounted for by perturbation theory. However, for simplicity, in what follows we will consider that in zeroth approximation the electrons interact only with the Coulomb field of the nucleus.

We will consider the perturbation theory with the standard QED vacuum. The transition to the formalism in which closed shells are regarded as belonging to the vacuum can be performed in a usual manner (see, e.g., [22]).

Before to introduce the two-time Green function and formulate the perturbation theory, we consider standard equations for the $2N$-time Green function in quantum electrodynamics.

2.1 $2N$-Time Green Function

In principle, the complete information about the energy levels of an N-electron atom can be derived from the Green function defined as

$$G(x'_1,\dots x'_N;x_1,\dots x_N)=\langle 0|T\psi(x'_1)\cdots\psi(x'_N)\overline{\psi}(x_N)\cdots\overline{\psi}(x_1)|0\rangle\ , \tag{2}$$

where $\psi(x)$ is the electron-positron field operator in the Heisenberg representation, $\overline{\psi}(x)=\psi^\dagger\gamma^0$, and T is the time-ordered product operator. It can be shown (see, e.g., [33,34]) that in the interaction representation the Green function is given by

$$\begin{aligned}
&G(x'_1,\dots x'_N;x_1,\dots x_N)\\
&=\frac{\langle 0|T\psi_{\mathrm{in}}(x'_1)\cdots\psi_{\mathrm{in}}(x'_N)\overline{\psi}_{\mathrm{in}}(x_N)\cdots\overline{\psi}_{\mathrm{in}}(x_1)\exp\{-\mathrm{i}\int\mathrm{d}^4z\,\mathcal{H}_I(z)\}|0\rangle}{\langle 0|T\exp\{-\mathrm{i}\int\mathrm{d}^4z\,\mathcal{H}_I(z)\}|0\rangle}\\
&=\Big\{\sum_{m=0}^{\infty}\frac{(-\mathrm{i})^m}{m!}\int\mathrm{d}^4y_1\cdots\mathrm{d}^4y_m\,\langle 0|T\psi_{\mathrm{in}}(x'_1)\cdots\psi_{\mathrm{in}}(x'_N)\\
&\quad\times\overline{\psi}_{\mathrm{in}}(x_N)\cdots\overline{\psi}_{\mathrm{in}}(x_1)\mathcal{H}_I(y_1)\cdots\mathcal{H}_I(y_m)|0\rangle\Big\}\\
&\quad\times\Big\{\sum_{l=0}^{\infty}\frac{(-\mathrm{i})^l}{l!}\int\mathrm{d}^4z_1\cdots\mathrm{d}^4z_l\,\langle 0|T\mathcal{H}_I(z_1)\cdots\mathcal{H}_I(z_l)|0\rangle\Big\}^{-1}
\end{aligned} \tag{3}$$

where

$$\mathcal{H}_I(x) = \frac{e}{2}\,[\overline{\psi}_{\rm in}(x)\gamma_\mu, \psi_{\rm in}(x)]A^\mu_{in}(x) - \frac{\delta m}{2}\,[\overline{\psi}_{\rm in}(x), \psi_{\rm in}(x)] \tag{4}$$

is the interaction Hamiltonian. The commutators in (4) refer to operators only. The first term in (4) describes the interaction of the electron-positron field with the quantized electromagnetic field and the second one is the mass renormalization counterterm. It is assumed that the interaction of the electrons with the Coulomb field of the nucleus is included in the unperturbed Hamiltonian, i.e. the Furry picture is used.

The Green function G is constructed by perturbation theory according to (3) with the aid of the Wick theorem (see, e.g., [33]). The individual terms of the perturbation series are conveniently represented by so-called Feynman diagrams. Some of these diagrams contain ultraviolet divergences and, therefore, must be regularized. It can be shown that in calculation of any physical quantity the divergent parts either cancel each other or incorporate into the renormalized (physical) values of the electron charge and mass. Alternatively, from the very beginning one can formulate the theory in terms of the renormalized field operators, the renormalized electron charge, and the renormalized Green functions. It results in appearing additional counterterms in the Feynman rules. Both schemes can easily be adopted within the approach considered here.

The spectral representation for G shows that it contains the complete information about the energy levels of the atomic system. However, it is a hard task to extract this information directly from G because it depends on $2(N-1)$ relative times. It is much more convenient to employ the two-time Green function

$$\widetilde{G}(t',t) \equiv G(t'_1 = t'_2 = \cdots t'_N \equiv t'; t_1 = t_2 = \cdots t_N \equiv t)\;, \tag{5}$$

which also contains the complete information about the energy levels.

2.2 Two-Time Green Function and Its Analytical Properties

Let us introduce the Fourier transform of the two-time Green function by

$$\begin{aligned}
&\mathcal{G}(E; \mathbf{x}'_1, \ldots \mathbf{x}'_N; \mathbf{x}_1, \ldots \mathbf{x}_N)\delta(E - E') \\
&= \frac{1}{2\pi{\rm i}}\frac{1}{N!}\int_{-\infty}^{\infty} {\rm d}x^0 {\rm d}x'^0\ \exp\left({\rm i}E'x'^0 - {\rm i}Ex^0\right) \\
&\quad \times \langle 0|T\psi(x'^0, \mathbf{x}'_1)\cdots\psi(x'^0, \mathbf{x}'_N)\overline{\psi}(x^0, \mathbf{x}_N)\cdots\overline{\psi}(x^0, \mathbf{x}_1)|0\rangle\;,
\end{aligned} \tag{6}$$

where, as in (2), the Heisenberg representation for the electron-positron field operators is used. Defined by (6) for real E, the Green function $\mathcal{G}$ can be continued analytically to the complex E plane. Analytical properties of this type of Green functions in the complex E plane were studied in various fields of physics (see, e.g., [35–38]). To consider these properties we derive

the spectral representation for $\mathcal{G}$. Using the time-shift transformation rule for the Heisenberg operators

$$\psi(x^0,\mathbf{x}) = \exp\left(\mathrm{i}Hx^0\right)\psi(0,\mathbf{x})\exp\left(-\mathrm{i}Hx^0\right) \tag{7}$$

and the equations

$$H|n\rangle = E_n|n\rangle\ , \qquad\qquad \sum_n |n\rangle\langle n| = I\ , \tag{8}$$

where H is the Hamiltonian of the system in the Heisenberg representation, we find

$$\begin{aligned}
&\mathcal{G}(E;\mathbf{x}'_1,\ldots,\mathbf{x}'_N;\mathbf{x}_1,\ldots,\mathbf{x}_N)\delta(E-E')\\
&= \frac{1}{2\pi\mathrm{i}}\frac{1}{N!}\int_{-\infty}^{\infty}\mathrm{d}x^0\mathrm{d}x'^0\,\exp\left(\mathrm{i}E'x'^0-\mathrm{i}Ex^0\right)\\
&\quad\times\Big\{\theta(x'^0-x^0)\sum_n\exp\left[\mathrm{i}(E_0-E_n)(x'^0-x^0)\right]\langle 0|\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N)|n\rangle\\
&\quad\times\langle n|\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1)|0\rangle + (-1)^{N^2}\theta(x^0-x'^0)\\
&\quad\times\sum_n\exp\left[\mathrm{i}(E_0-E_n)(x^0-x'^0)\right]\langle 0|\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1)|n\rangle\\
&\quad\times\langle n|\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N)|0\rangle\Big\}\ .
\end{aligned} \tag{9}$$

Assuming, for simplicity, $E_0 = 0$ (it corresponds to choosing the vacuum energy as the origin of reference) and taking into account that

$$\begin{aligned}
&\int_{-\infty}^{\infty}\mathrm{d}x^0\mathrm{d}x'^0\,\theta(x'^0-x^0)\exp\left[-\mathrm{i}E_n(x'^0-x^0)\right]\exp\left[\mathrm{i}(E'x'^0-Ex^0)\right]\\
&\qquad = 2\pi\delta(E'-E)\frac{\mathrm{i}}{E-E_n+\mathrm{i}0}\ ,
\end{aligned} \tag{10}$$

$$\begin{aligned}
&\int_{-\infty}^{\infty}\mathrm{d}x^0\mathrm{d}x'^0\,\theta(x^0-x'^0)\exp\left[-\mathrm{i}E_n(x^0-x'^0)\right]\exp\left[\mathrm{i}(E'x'^0-Ex^0)\right]\\
&\qquad = -2\pi\delta(E'-E)\frac{\mathrm{i}}{E+E_n-\mathrm{i}0}\ ,
\end{aligned} \tag{11}$$

we obtain

$$\mathcal{G}(E) = \sum_n\frac{\Phi_n\overline{\Phi}_n}{E-E_n+i0} - (-1)^N\sum_n\frac{\Xi_n\overline{\Xi}_n}{E+E_n-i0}\ , \tag{12}$$

where the variables $\mathbf{x}'_1,\ldots,\mathbf{x}'_N,\mathbf{x}_1,\ldots,\mathbf{x}_N$ are implicit and

$$\Phi_n(\mathbf{x}_1,\ldots\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\langle 0|\psi(0,\mathbf{x}_1)\cdots\psi(0,\mathbf{x}_N)|n\rangle\ , \tag{13}$$

$$\Xi_n(\mathbf{x}_1,\ldots\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\langle n|\psi(0,\mathbf{x}_1)\cdots\psi(0,\mathbf{x}_N)|0\rangle\ . \tag{14}$$

In (12) the summation runs over all bound and continuum states of the system of the interacting fields. Let us introduce the functions

$$A(E;\mathbf{x}'_1,\ldots,\mathbf{x}'_N;\mathbf{x}_1,\ldots,\mathbf{x}_N) = \sum_n \delta(E-E_n) \times\Phi_n(\mathbf{x}'_1,\ldots,\mathbf{x}'_N)\overline{\Phi}_n(\mathbf{x}_1,\ldots,\mathbf{x}_N)\ , \quad (15)$$

$$B(E;\mathbf{x}'_1,\ldots,\mathbf{x}'_N;\mathbf{x}_1,\ldots,\mathbf{x}_N) = \sum_n \delta(E-E_n) \times\Xi_n(\mathbf{x}'_1,\ldots,\mathbf{x}'_N)\overline{\Xi}_n(\mathbf{x}_1,\ldots,\mathbf{x}_N)\ . \quad (16)$$

These functions satisfy the conditions

$$\int_{-\infty}^{\infty} \mathrm{d}E\ A(E;\mathbf{x}'_1,\ldots,\mathbf{x}'_N;\mathbf{x}_1,\ldots,\mathbf{x}_N) = \frac{1}{N!}\langle 0|\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N) \times\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1)|0\rangle\ , \quad (17)$$

$$\int_{-\infty}^{\infty} \mathrm{d}E\ B(E;\mathbf{x}'_1,\ldots,\mathbf{x}'_N;\mathbf{x}_1,\ldots,\mathbf{x}_N) = \frac{1}{N!}\langle 0|\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1) \times\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N)|0\rangle\ . \quad (18)$$

In terms of these functions, (12) has the form

$$\mathcal{G}(E) = \int_0^{\infty} \mathrm{d}E'\ \frac{A(E')}{E-E'+\mathrm{i}0} - (-1)^N \int_0^{\infty} \mathrm{d}E'\ \frac{B(E')}{E+E'-\mathrm{i}0}\ , \quad (19)$$

where we have omitted the variables $\mathbf{x}_1,\ldots,\mathbf{x}_N,\mathbf{x}'_1,\ldots,\mathbf{x}'_N$ and have taken into account that $A(E')=B(E')=0$ for $E'<0$ since $E_n\geq 0$. In fact, due to charge conservation, only states with an electric charge of eN contribute to A in the sum over n in the right-hand side of (15) and only states with an electric charge of $-eN$ contribute to B in the sum over n in the right-hand side of (16). This can easily be shown by using the following commutation relations

$$[Q,\psi(x)] = -e\psi(x)\ , \qquad [Q,\overline{\psi}(x)] = e\overline{\psi}(x)\ , \quad (20)$$

where Q is the charge operator in the Heisenberg representation. Therefore, (19) can be written as

$$\mathcal{G}(E) = \int_{E^{(+)}_{\mathrm{min}}}^{\infty} \mathrm{d}E'\ \frac{A(E')}{E-E'+\mathrm{i}0} - (-1)^N \int_{E^{(-)}_{\mathrm{min}}}^{\infty} \mathrm{d}E'\ \frac{B(E')}{E+E'-\mathrm{i}0}\ , \quad (21)$$

where $E^{(+)}_{\mathrm{min}}$ is the minimal energy of states with electric charge eN and $E^{(-)}_{\mathrm{min}}$ is the minimal energy of states with electric charge $-eN$. So far we considered $\mathcal{G}(E)$ for real E. Equation (21) shows that the Green function $\mathcal{G}(E)$ is the sum of Cauchy-type integrals. Using the fact that the integrals $\displaystyle\int_{E^{(+)}_{\mathrm{min}}}^{\infty} \mathrm{d}E\ A(E)$

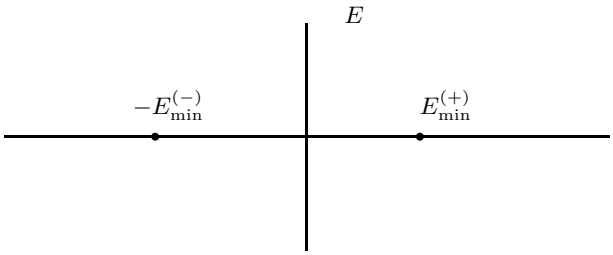

Fig. 1. Singularities of the two-time Green function in the complex E plane

and $\int_{E^{(-)}_{\rm min}}^{\infty} {\rm d}E\, B(E)$ converge (see (17), (18)), one can show with the help of standard mathematical methods that the equation

$$\mathcal{G}(E) = \int_{E^{(+)}_{\rm min}}^{\infty} {\rm d}E'\, \frac{A(E')}{E-E'} - (-1)^N \int_{E^{(-)}_{\rm min}}^{\infty} {\rm d}E'\, \frac{B(E')}{E+E'} \tag{22}$$

defines an analytical function of E in the complex E plane with the cuts $(-\infty, -E^{(-)}_{\rm min}]$ and $[E^{(+)}_{\rm min}, \infty)$ (see Fig. 1). This equation provides the analytical continuation of the Green function to the complex E plane. According to (21), to get the Green function for real E we have to approach the right-hand cut from the upper half-plane and the left-hand cut from the lower half-plane.

In what follows we will be interested in bound states of the system. According to (12)–(22), the bound states correspond to the poles of the function $\mathcal{G}(E)$ on the right-hand real semiaxis. If the interaction between the electron-positron field and the electromagnetic field is switched off, the poles corresponding to bound states are isolated. Switching on the interaction between the fields transforms the isolated poles into branch points. This is caused by the fact that due to zero photon mass the bound states are no longer isolated points of the spectrum. Disregarding the instability of excited states, the singularities of the Green function $\mathcal{G}(E)$ are shown in Fig. 2. The poles corresponding to the bound states lie on the upper boundary of the cut starting

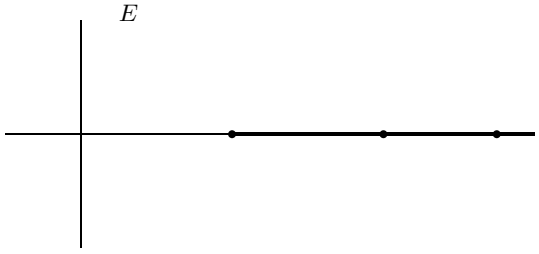

Fig. 2. Singularities of the two-time Green function in the bound-state region, disregarding the instability of excited states

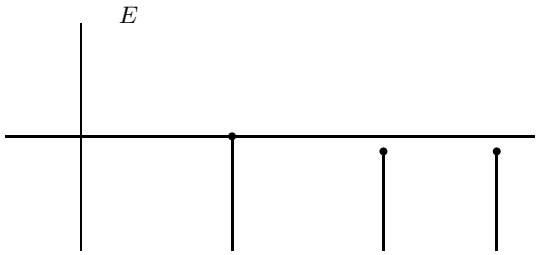

Fig. 3. Singularities of the two-time Green function in the bound-state region if the cuts are turned down, to the second sheet of the Riemann surface. The instability of excited states is taken into account

from the pole corresponding to the ground state. It is natural to assume that $\mathcal{G}(E)$ can be continued analytically under the cut, to the second sheet of the Riemann surface. As a result of this continuation the singularities of $\mathcal{G}(E)$ can be turned down. In fact due to instability of excited states the energies of these states have small imaginary components and, therefore, the related poles lie slightly below the right-hand real semiaxis (Fig. 3). However, in calculations of the energy levels and the transition and scattering amplitudes of non-resonance processes we can neglect the instability of excited states and, therefore, assume that the poles lie on the real axis. The imaginary parts of the energies must be taken into account if one considers resonance scattering processes.

To formulate the perturbation theory for calculations of the energy levels and the transition and scattering amplitudes we will need to isolate the poles corresponding to the bound states from the related cuts. It can be done by introducing a non-zero photon mass μ which is generally assumed to be larger than the energy shift (or the energy splitting) of the level (levels) under consideration and much smaller than the distance to other levels. The singularities of $\mathcal{G}(E)$ with non-zero photon mass, including one- and two-photon spectra, are shown in Fig. 4. As one can see from this figure, introducing the photon mass makes the poles corresponding to the bound states to be isolated.

In every finite order of perturbation theory the singularities of the Green function $\mathcal{G}(E)$ in the complex E-plane are defined by the unperturbed Hamiltonian. It can be shown (see [22] and references therein) that to n-th order of perturbation theory the Green function has poles of all orders till $n+1$ at the unperturbed positions of the bound state energies.

2.3 Energy Shift of a Single Level

In this section we derive the energy shift $\Delta E_a = E_a - E_a^{(0)}$ of a single isolated level a of an N-electron atom due to the perturbative interaction. The unperturbed energy $E_a^{(0)}$ is equal to the sum of the one-electron Dirac-Coulomb

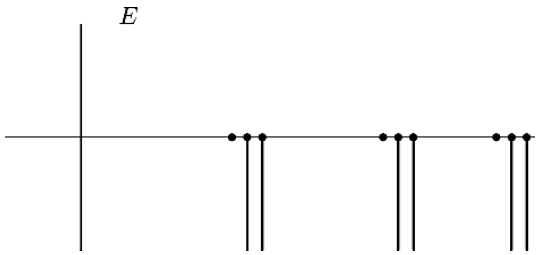

Fig. 4. Singularities of the two-time Green function in the bound state region for a non-zero photon mass, including one- and two-photon spectra, if the cuts are turned down, to the second sheet of the Riemann surface. The instability of excited states is disregarded

energies

$$E_a^{(0)} = \varepsilon_{a_1} + \cdots + \varepsilon_{a_N} \ , \tag{23}$$

which are defined by the Dirac equation (1). In the simplest case the unperturbed wave function $u_a(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is a one-determinant function

$$u_a(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{Pa_1}(\mathbf{x}_1) \cdots \psi_{Pa_N}(\mathbf{x}_N) \ , \tag{24}$$

where ψ_n are the one-electron Dirac wave functions defined by (1) and P is the permutation operator. In the general case the unperturbed wave function is a linear combination of the one-determinant functions

$$u_a(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \sum_b C_a^b \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{Pb_1}(\mathbf{x}_1) \cdots \psi_{Pb_N}(\mathbf{x}_N) \ . \tag{25}$$

We introduce the Green function $g_{aa}(E)$ by

$$\begin{aligned} g_{aa}(E) &= \langle u_a | \mathcal{G}(E) \gamma_1^0 \cdots \gamma_N^0 | u_a \rangle \\ &\equiv \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \mathrm{d}\mathbf{x}'_1 \cdots \mathrm{d}\mathbf{x}'_N \ u_a^\dagger(\mathbf{x}'_1, \ldots, \mathbf{x}'_N) \\ &\quad \times \mathcal{G}(E, \mathbf{x}'_1, \ldots, \mathbf{x}'_N; \mathbf{x}_1, \ldots, \mathbf{x}_N) \gamma_1^0 \cdots \gamma_N^0 u_a(\mathbf{x}_1, \ldots, \mathbf{x}_N) \ . \end{aligned} \tag{26}$$

From the spectral representation for $\mathcal{G}(E)$ (see (12)–(22)) we have

$$g_{aa}(E) = \frac{A_a}{E - E_a} + \text{terms that are regular at } E \sim E_a \ , \tag{27}$$

where

$$\begin{aligned} A_a = \frac{1}{N!} \int \mathrm{d}\mathbf{x}_1 \cdots \mathrm{d}\mathbf{x}_N \mathrm{d}\mathbf{x}'_1 \cdots \mathrm{d}\mathbf{x}'_N \ u_a^\dagger(\mathbf{x}'_1, \ldots, \mathbf{x}'_N) \langle 0 | \psi(0, \mathbf{x}'_1) \cdots \psi(0, \mathbf{x}'_N) | a \rangle \\ \times \langle a | \psi^\dagger(0, \mathbf{x}_N) \cdots \psi^\dagger(0, \mathbf{x}_1) | 0 \rangle u_a(\mathbf{x}_1, \ldots, \mathbf{x}_N) \ . \end{aligned} \tag{28}$$

Fig. 5. The contour Γ surrounds the pole corresponding to the level under consideration and keeps outside all other singularities. For simplicity, only one- and two-photon spectra are displayed

We assume here that a non-zero photon mass μ is introduced to isolate the pole corresponding to the bound state a from the related cut. We consider that the photon mass is larger than the energy shift under consideration and much smaller than the distance to other levels. To generate the perturbation series for E_a it is convenient to use a contour integral formalism developed first in operator theory by Szökefalvi-Nagy and Kato [39–42]. Choosing a contour Γ in the complex E plane in a way that it surrounds the pole corresponding to the level a and keeps outside all other singularities (see Fig. 5), we have

$$\frac{1}{2\pi\mathrm{i}}\oint_\Gamma \mathrm{d}E\; E g_{aa}(E) = E_a A_a \;, \tag{29}$$

$$\frac{1}{2\pi\mathrm{i}}\oint_\Gamma \mathrm{d}E\; g_{aa}(E) = A_a \;. \tag{30}$$

Here we have assumed that the contour Γ is oriented anticlockwise. Dividing (29) by (30), we obtain

$$E_a = \frac{\dfrac{1}{2\pi\mathrm{i}}\oint_\Gamma \mathrm{d}E\; E g_{aa}(E)}{\dfrac{1}{2\pi\mathrm{i}}\oint_\Gamma \mathrm{d}E\; g_{aa}(E)} \tag{31}$$

It is convenient to transform (31) to a form that directly yields the energy shift $\Delta E_a = E_a - E_a^{(0)}$. To zeroth order, substituting the operators

$$\psi_{\mathrm{in}}(0,\mathbf{x}) = \sum_{\varepsilon_n>0} b_n\psi_n(\mathbf{x}) + \sum_{\varepsilon_n<0} d_n^\dagger\psi_n(\mathbf{x}) \;, \tag{32}$$

$$\overline{\psi}_{\mathrm{in}}(0,\mathbf{x}) = \sum_{\varepsilon_n>0} b_n^\dagger\overline{\psi}_n(\mathbf{x}) + \sum_{\varepsilon_n<0} d_n\overline{\psi}_n(\mathbf{x}) \tag{33}$$

into (13) and (14) instead of $\psi(0,\mathbf{x})$ and $\overline{\psi}(0,\mathbf{x})$, respectively, and considering the states $|n\rangle$ in (13) and (14) as unperturbed states in the Fock space, from (12)–(14) and (26) we find

$$g_{aa}^{(0)} = \frac{1}{E - E_a^{(0)}} \,. \tag{34}$$

Denoting $\Delta g_{aa} = g_{aa} - g_{aa}^{(0)}$, from (31) we obtain the desired formula [17]

$$\Delta E_a = \frac{\dfrac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; (E - E_a^{(0)}) \Delta g_{aa}(E)}{1 + \dfrac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; \Delta g_{aa}(E)} \,. \tag{35}$$

The Green function $\Delta g_{aa}(E)$ is constructed by perturbation theory

$$\Delta g_{aa}(E) = \Delta g_{aa}^{(1)}(E) + \Delta g_{aa}^{(2)}(E) + \cdots \,, \tag{36}$$

where the superscript denotes the order in a small parameter (for instance, α). If we represent the energy shift as a series

$$\Delta E_a = \Delta E_a^{(1)} + \Delta E_a^{(2)} + \cdots \,, \tag{37}$$

formula (35) yields

$$\Delta E_a^{(1)} = \frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; \Delta E \, \Delta g_{aa}^{(1)}(E) \,, \tag{38}$$

$$\Delta E_a^{(2)} = \frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; \Delta E \, \Delta g_{aa}^{(2)}(E) - \left(\frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; \Delta E \, \Delta g_{aa}^{(1)}(E) \right) \left(\frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; \Delta g_{aa}^{(1)}(E) \right) \,, \tag{39}$$

where $\Delta E \equiv E - E_a^{(0)}$.

Deriving (31) and (35) we have assumed that a non-zero photon mass μ is introduced. This allows taking all the cuts outside the contour Γ as well as regularizing the infrared singularities of individual contributions. As was noted in the previous subsection, the singularities of the two-time Green function in the complex E plane are defined by the unperturbed Hamiltonian if it is constructed by perturbation theory. In particular, it means that in n-th order of perturbation theory $g_{aa}(E)$ has poles of all orders till $n+1$ at the position of the unperturbed energy level under consideration. Therefore, in calculations by perturbation theory it is sufficient to consider the photon mass as a very small parameter which provides a separation of the pole from the related cut. At the end of the calculations after taking into account a whole gauge invariant set of Feynman diagrams we can put $\mu \to 0$. The possibility of taking the limit $\mu \to 0$ follows, in particular, from the fact that the contour Γ can be shrunk continuosly to the point $E = E_a^{(0)}$ (see Fig. 5).

Generally speaking, the energy shift of an excited level derived by formula (35) contains an imaginary component which is caused by its instability. This component determines the width of the spectral line in the Lorentz approximation.

2.4 Perturbation Theory for Degenerate and Quasidegenerate Levels

We are interested in the atomic levels with energies $E_1, \ldots, E_s$ arising from unperturbed degenerate or quasidegenerate levels with energies $E_1^{(0)}, \ldots, E_s^{(0)}$. As usual, we assume that the energy shifts of the levels under consideration or their splitting caused by the interaction are much smaller than the distance to other levels. The unperturbed eigenstates form an s-dimensional subspace Ω. We denote the projector on Ω by

$$P^{(0)} = \sum_{k=1}^{s} P_k^{(0)} = \sum_{k=1}^{s} u_k u_k^\dagger \,, \tag{40}$$

where $\{u_k\}_{k=1}^s$ are the unperturbed wave functions which, in a general case, are linear combinations of one-determinant functions (see (25)). We project the Green function $\mathcal{G}(E)$ on the subspace Ω

$$g(E) = P^{(0)} \mathcal{G}(E) \gamma_1^0 \ldots \gamma_N^0 P^{(0)} \,, \tag{41}$$

where, as in (26), the integration over the electron coordinates is implicit. As in the case of a single level, to isolate the poles of $g(E)$ corresponding to the bound states under consideration, we introduce a non-zero photon mass μ. We assume that the photon mass μ is larger than the energy distance between the levels under consideration and much smaller than the distance to other levels. In this case we can choose a contour Γ in the complex E plane in a way that it surrounds all the poles corresponding to the considered states $(E_1, \ldots E_s)$ and keeps outside all other singularities, including the cuts starting from the lower-lying bound states (see Fig. 6). In addition, if we neglect the instability of the states under consideration, the spectral representation (see (12)–(22)) gives

$$g(E) = \sum_{k=1}^{s} \frac{\varphi_k \varphi_k^\dagger}{E - E_k} + \text{ terms that are regular inside of } \Gamma \,, \tag{42}$$

where

$$\varphi_k = P^{(0)} \Phi_k \,, \qquad \varphi_k^\dagger = \Phi_k^\dagger P^{(0)} \,. \tag{43}$$

As in the case of a single level, in zeroth approximation one easily finds

$$g^{(0)}(E) = \sum_{k=1}^{s} \frac{P_k^{(0)}}{E - E_k^{(0)}} \,. \tag{44}$$

We introduce the operators K and P by

$$K \equiv \frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; E g(E) \,, \tag{45}$$

$$P \equiv \frac{1}{2\pi \mathrm{i}} \oint_\Gamma \mathrm{d}E \; g(E) \,. \tag{46}$$

Fig. 6. The contour Γ surrounds the poles corresponding to the quasidegenerate levels under consideration and keeps outside all other singularities. For simplicity, only one-photon spectra are displayed

Using (42), we obtain

$$K = \sum_{i=1}^{s} E_i \varphi_i \varphi_i^\dagger \,, \tag{47}$$

$$P = \sum_{i=1}^{s} \varphi_i \varphi_i^\dagger \,. \tag{48}$$

We note here that, generally speaking, the operator P is not a projector (in particular, $P^2 \neq P$). If the perturbation goes to zero, the vectors $\{\varphi_i\}_{i=1}^s$ approach the correct linearly independent combinations of the vectors $\{u_i\}_{i=1}^s$. Therefore, it is natural to assume that the vectors $\{\varphi_i\}_{i=1}^s$ are also linearly independent. It follows that one can find such vectors $\{v_i\}_{i=1}^s$ that

$$\varphi_i^\dagger v_k = \delta_{ik} \,. \tag{49}$$

Indeed, let

$$\varphi_i = \sum_{j=1}^{s} a_{ij} u_j \,, \qquad v_k = \sum_{l=1}^{s} x_{kl} u_l \,. \tag{50}$$

The biorthogonality condition (49) gives

$$\sum_{j=1}^{s} a_{ij} x_{kj} = \delta_{ik} \,. \tag{51}$$

Since the determinant of the matrix $\{a_{ij}\}$ is nonvanishing due to the linear independence of $\{\varphi_i\}_{i=1}^s$, the system (51) has a unique solution for any fixed $k = 1, \ldots, s$. From (47)–(49) we have

$$P v_k = \sum_{i=1}^{s} \varphi_i \varphi_i^\dagger v_k = \varphi_k \,, \tag{52}$$

$$K v_k = \sum_{i=1}^{s} E_i \varphi_i \varphi_i^\dagger v_k = E_k \varphi_k \,. \tag{53}$$

Hence we obtain the equation for v_k, E_k [17]

$$Kv_k = E_k P v_k \ . \tag{54}$$

According to (49) the vectors v_k are normalized by the condition

$$v_{k'}^\dagger P v_k = \delta_{k'k} \ . \tag{55}$$

The solvability of (54) yields an equation for the atomic energy levels

$$\det\left(K - EP\right) = 0 \ . \tag{56}$$

The generalized eigenvalue problem (54) with the normalization condition (55) can be transformed by the substitution $\psi_k = P^{\frac{1}{2}} v_k$ to the ordinary eigenvalue problem ("Schrödinger-like equation") [21]

$$H\psi_k = E_k \psi_k \tag{57}$$

with the ordinary normalization condition

$$\psi_k^\dagger \psi_{k'} = \delta_{kk'} \ , \tag{58}$$

where $H \equiv P^{-\frac{1}{2}}(K)P^{-\frac{1}{2}}$.

The energy levels are determined from the equation

$$\det(H - E) = 0 \ . \tag{59}$$

Generally speaking, the energies determined by this equation contain imaginary components which are due to the instability of excited states. In the case when the imaginary components are much smaller than the energy distance between the levels (or the levels have different quantum numbers), they define the widths of the spectral lines in the Lorentz approximation. In the opposite case, when the imaginary components are comparable with the energy distance between the levels which have the same quantum numbers, the spectral line shape depends on the process of the formation of the states under consideration even in the resonance approximation (see [22,24] for details). If the instability of excited states can be disregarded, we assume $H \equiv (H + H^\dagger)/2$ in (57), (59).

The operators K and P are constructed by formulas (45) and (46) using perturbation theory

$$K = K^{(0)} + K^{(1)} + K^{(2)} + \cdots \ , \tag{60}$$

$$P = P^{(0)} + P^{(1)} + P^{(2)} + \cdots \ , \tag{61}$$

where the superscript denotes the order in a small parameter. The operator H is

$$H = H^{(0)} + H^{(1)} + H^{(2)} + \cdots \ , \tag{62}$$

where

$$H^{(0)} = K^{(0)} \,, \tag{63}$$

$$H^{(1)} = K^{(1)} - \frac{1}{2}P^{(1)}K^{(0)} - \frac{1}{2}K^{(0)}P^{(1)} \,, \tag{64}$$

$$\begin{aligned} H^{(2)} = {} & K^{(2)} - \frac{1}{2}P^{(2)}K^{(0)} - \frac{1}{2}K^{(0)}P^{(2)} \\ & -\frac{1}{2}P^{(1)}K^{(1)} - \frac{1}{2}K^{(1)}P^{(1)} \\ & +\frac{3}{8}P^{(1)}P^{(1)}K^{(0)} + \frac{3}{8}K^{(0)}P^{(1)}P^{(1)} \\ & +\frac{1}{4}P^{(1)}K^{(0)}P^{(1)} \,. \end{aligned} \tag{65}$$

It is evident that in zeroth order

$$K^{(0)}_{ik} = E^{(0)}_i \delta_{ik} \,, \tag{66}$$

$$P^{(0)}_{ik} = \delta_{ik} \,, \tag{67}$$

$$H^{(0)}_{ik} = E^{(0)}_i \delta_{ik} \,. \tag{68}$$

To derive (54)–(57) we have introduced a non-zero photon mass μ which was assumed to be larger than the energy distance between the levels under consideration and much smaller than the distance to other levels. At the end of the calculations after taking into account a whole gauge invariant set of Feynman diagrams, we can put $\mu \to 0$. The possibility of taking this limit in the case of quasidegenerate states follows from the fact that the cuts can be drawn to the related poles by a deformation of the contour Γ as shown in Fig. 7.

3 Transition Probabilities

Let us consider the transition of an atom from an initial state a to a final state b with the emission of a photon with momentum $\mathbf{k}_f$ and polarization $\boldsymbol{\epsilon}_f$. The transition probability is given as

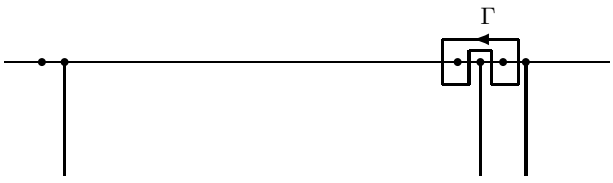

Fig. 7. A deformation of the contour Γ that allows drawing the cuts to the related poles in the case of quasidegenerate states when $\mu \to 0$. For simplicity, only one-photon spectra are displayed

$$dW = 2\pi|\tau_{\gamma_f,b;a}|^2\delta(E_b + k_f^0 - E_a)\mathrm{d}\mathbf{k}_f \ , \tag{69}$$

where $\tau_{\gamma_f,b;a}$ is the transition amplitude which is connected with the S-matrix element by

$$S_{\gamma_f,b;a} = 2\pi\mathrm{i}\tau_{\gamma_f,b;a}\delta(\varepsilon_b + k_f^0 - \varepsilon_a) \tag{70}$$

and $k_f^0 \equiv |\mathbf{k}_f|$. According to the standard reduction technique (see, e.g., [33,34]), the transition amplitude is

$$S_{\gamma_f,b;a} = -\mathrm{i}Z_3^{-\frac{1}{2}} \int \mathrm{d}^4y \ \frac{\epsilon_f^{\nu *} \exp{(\mathrm{i}k_f \cdot y)}}{\sqrt{2k_f^0(2\pi)^3}} \langle b|j_\nu(y)|a\rangle \ . \tag{71}$$

Here $j_\nu(y)$ is the electron-positron current operator in the Heisenberg representation, $|a\rangle$ and $|b\rangle$ are the vectors of the initial and final states in the Heisenberg representation, Z_3 is a renormalization constant, $a \cdot b \equiv a_\nu b^\nu$, $\epsilon_f = (0, \boldsymbol{\epsilon}_f)$, and $k_f = (k_f^0, \mathbf{k}_f)$. Employing the equation

$$j^\nu(y) = \exp{(\mathrm{i}Hy^0)} j^\nu(0,\mathbf{y}) \exp{(-\mathrm{i}Hy^0)} \ , \tag{72}$$

we obtain

$$\begin{aligned} S_{\gamma_f,b;a} &= -\mathrm{i}Z_3^{-\frac{1}{2}} \int \mathrm{d}^4y \ \exp{[\mathrm{i}(E_b + k_f^0 - E_a)y^0]} A_f^{\nu *}(\mathbf{y}) \langle b|j_\nu(0,\mathbf{y})|a\rangle \\ &= -2\pi\mathrm{i}Z_3^{-\frac{1}{2}} \delta(E_b + k_f^0 - E_a) \int \mathrm{d}\mathbf{y} \ A_f^{\nu *}(\mathbf{y}) \langle b|j_\nu(0,\mathbf{y})|a\rangle \ , \end{aligned} \tag{73}$$

where

$$A_f^\nu(\mathbf{x}) = \frac{\epsilon_f^\nu \exp{(\mathrm{i}\mathbf{k}_f \cdot \mathbf{x})}}{\sqrt{2k_f^0(2\pi)^3}} \tag{74}$$

is the wave function of the emitted photon. Since $|a\rangle$ and $|b\rangle$ are bound states, (73) as well as the standard reduction technique [33, 34] cannot be used for a direct evaluation of the amplitude. The desired calculation formula can be derived within the TTGF formalism [18–20].

To formulate the method for a general case, we assume that in zeroth approximation the state a belongs to an s_a-dimensional subspace of unperturbed degenerate states Ω_a and the state b belongs to an s_b-dimensional subspace of unperturbed degenerate states Ω_b. We denote the projectors onto these subspaces by $P_a^{(0)}$ and $P_b^{(0)}$, respectively. We denote the exact states originating from Ω_a by $|n_a\rangle$ and the exact states originating from Ω_b by $|n_b\rangle$. We also assume that on an intermediate stage of the calculations a non-zero photon mass μ is introduced. It is considered to be larger than the energy splitting of the initial and final states under consideration and much smaller than the distance to other levels.

We introduce

$$\begin{aligned}
&\mathcal{G}_{\gamma_f}(E',E;\mathbf{x}'_1,\dots\mathbf{x}'_N;\mathbf{x}_1,\dots\mathbf{x}_N)\delta(E'+k^0-E)\\
&=\frac{1}{2\pi\mathrm{i}}\frac{1}{2\pi}\frac{1}{N!}\int_{-\infty}^{\infty}\mathrm{d}x^0\mathrm{d}x'^0\int\mathrm{d}^4y\ \exp\left(\mathrm{i}E'x'^0-\mathrm{i}Ex^0\right)\exp\left(\mathrm{i}k^0y^0\right)\\
&\quad\times A_f^{\nu *}(\mathbf{y})\langle 0|T\psi(x'^0,\mathbf{x}'_1)\cdots\psi(x'^0,\mathbf{x}'_N)\\
&\quad\times j_\nu(y)\overline{\psi}(x^0,\mathbf{x}_N)\cdots\overline{\psi}(x^0,\mathbf{x}_1)|0\rangle\ ,
\end{aligned}\tag{75}$$

where, as in the previous section, $\psi(x)$ is the electron-positron field operator in the Heisenberg representation. Let us investigate the singularities of $\mathcal{G}_{\gamma_f}$ in the region $E'\sim E_b^{(0)}$ and $E\sim E_a^{(0)}$. Using the transformation rules

$$\begin{aligned}
\psi(x^0,\mathbf{x})&=\exp\left(\mathrm{i}Hy^0\right)\psi(x^0-y^0,\mathbf{x})\exp\left(-\mathrm{i}Hy^0\right)\ ,\\
j(y^0,\mathbf{y})&=\exp\left(\mathrm{i}Hy^0\right)j(0,\mathbf{y})\exp\left(-\mathrm{i}Hy^0\right)\ ,
\end{aligned}\tag{76}$$

we obtain

$$\begin{aligned}
&\mathcal{G}_{\gamma_f}(E',E;\mathbf{x}'_1,\dots\mathbf{x}'_N;\mathbf{x}_1,\dots\mathbf{x}_N)\delta(E'+k^0-E)\\
&=\frac{1}{2\pi\mathrm{i}}\frac{1}{2\pi}\frac{1}{N!}\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{d}t'\int\mathrm{d}^4y\ \exp\left(\mathrm{i}E't'-\mathrm{i}Et\right)\exp\left[\mathrm{i}(E'+k^0-E)y^0\right]\\
&\quad\times A_f^{\nu *}(\mathbf{y})\langle 0|T\psi(t',\mathbf{x}'_1)\cdots\psi(t',\mathbf{x}'_N)\\
&\quad\times j_\nu(0,\mathbf{y})\overline{\psi}(t,\mathbf{x}_N)\cdots\overline{\psi}(t,\mathbf{x}_1)|0\rangle\\
&=\frac{1}{2\pi\mathrm{i}}\delta(E'+k^0-E)\frac{1}{N!}\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{d}t'\int\mathrm{d}\mathbf{y}\ \exp\left(\mathrm{i}E't'-\mathrm{i}Et\right)\\
&\quad\times A_f^{\nu *}(\mathbf{y})\langle 0|T\psi(t',\mathbf{x}'_1)\cdots\psi(t',\mathbf{x}'_N)\\
&\quad\times j_\nu(0,\mathbf{y})\overline{\psi}(t,\mathbf{x}_N)\cdots\overline{\psi}(t,\mathbf{x}_1)|0\rangle\ .
\end{aligned}\tag{77}$$

Using again the time-shift transformation rules, we obtain

$$\begin{aligned}
&\mathcal{G}_{\gamma_f}(E',E;\mathbf{x}'_1,\dots\mathbf{x}'_N;\mathbf{x}_1,\dots\mathbf{x}_N)\\
&=\frac{1}{2\pi\mathrm{i}}\frac{1}{N!}\int_{-\infty}^{\infty}\mathrm{d}t\mathrm{d}t'\int\mathrm{d}\mathbf{y}\ \exp\left(\mathrm{i}E't'-\mathrm{i}Et\right)\sum_{n_1,n_2}A_f^{\nu *}(\mathbf{y})\\
&\quad\times\exp\left(-\mathrm{i}E_{n_1}t'\right)\exp\left(\mathrm{i}E_{n_2}t\right)\theta(t')\theta(-t)\langle 0|T\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N)|n_1\rangle\\
&\quad\times\langle n_1|j_\nu(0,\mathbf{y})|n_2\rangle\langle n_2|\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1)|0\rangle+\cdots\ .
\end{aligned}\tag{78}$$

Here we have assumed $E_0=0$, as in the previous section. Taking into account the identities

$$\begin{aligned}
\int_0^{\infty}\mathrm{d}t\ \exp\left[\mathrm{i}(E'-E_{n_1})t\right]&=\frac{\mathrm{i}}{E'-E_{n_1}+\mathrm{i}0}\ ,\\
\int_{-\infty}^{0}\mathrm{d}t\ \exp\left[\mathrm{i}(-E+E_{n_2})t\right]&=\frac{\mathrm{i}}{E-E_{n_2}+\mathrm{i}0}\ ,
\end{aligned}\tag{79}$$

we find

$$\begin{aligned}
&\mathcal{G}_{\gamma_f}(E',E;\mathbf{x}'_1,\dots\mathbf{x}'_N;\mathbf{x}_1,\dots\mathbf{x}_N)\\
&=\frac{\mathrm{i}}{2\pi}\frac{1}{N!}\sum_{n_1,n_2}\int \mathrm{d}\mathbf{y}\; A^{\nu *}_f(\mathbf{y})\frac{1}{E'-E_{n_1}+\mathrm{i}0}\frac{1}{E-E_{n_2}+\mathrm{i}0}\\
&\quad\times\langle 0|T\psi(0,\mathbf{x}'_1)\cdots\psi(0,\mathbf{x}'_N)|n_1\rangle\langle n_1|j_\nu(0,\mathbf{y})|n_2\rangle\\
&\quad\times\langle n_2|\overline{\psi}(0,\mathbf{x}_N)\cdots\overline{\psi}(0,\mathbf{x}_1)|0\rangle+\cdots\,. \qquad (80)
\end{aligned}$$

We are interested in the analytical properties of $\mathcal{G}_{\gamma_f}$ as a function of the two complex variables E' and E in the region $E'\sim E^{(0)}_b$, $E\sim E^{(0)}_a$. These properties can be studied using the double spectral representation of this type of Green function (see [22, 38]). As it follows from the spectral representation, the terms which are omitted in (80) are regular functions of E' or E if $E'\sim E^{(0)}_b$ and $E\sim E^{(0)}_a$, and, for a non-zero photon mass μ, the Green function $\mathcal{G}_{\gamma_f}(E',E)$ has isolated poles in the variables E' and E at the points $E'=E_{n_b}$ and $E=E_{n_a}$, respectively. Let us now introduce a Green function $g_{\gamma_f,b;a}(E',E)$ by

$$g_{\gamma_f,b;a}(E',E)=P^{(0)}_b\mathcal{G}_{\gamma_f}(E',E)\gamma^0_1\cdots\gamma^0_N P^{(0)}_a\;, \qquad (81)$$

where, as in (26), the integration over the electron coordinates is implicit. It can be written as

$$\begin{aligned}
g_{\gamma_f,b;a}(E',E)&=\frac{\mathrm{i}}{2\pi}\sum_{n_a=1}^{s_a}\sum_{n_b=1}^{s_b}\frac{1}{E'-E_{n_b}}\frac{1}{E-E_{n_a}}\\
&\quad\times\varphi_{n_b}\int \mathrm{d}\mathbf{y}\; A^{\nu *}_f(\mathbf{y})\langle n_b|j_\nu(0,\mathbf{y})|n_a\rangle\varphi^\dagger_{n_a}\\
&\quad+\text{ terms that are regular functions of } E' \text{ or } E \text{ if } E'\sim E^{(0)}_b\\
&\qquad\text{and } E\sim E^{(0)}_a\;, \qquad (82)
\end{aligned}$$

where the vectors φ_k are defined by (43). Let the contours Γ_a and Γ_b surround the poles corresponding to the initial and final levels, respectively, and keep outside other singularities of $g_{\gamma_f,b;a}(E',E)$ including the cuts starting from the lower-lying bound states. Comparing (82) with (73) and taking into account the biorthogonality condition (49), we obtain the desired formula [18]

$$S_{\gamma_f,b;a}=Z_3^{-1/2}\delta(E_b+k^0_f-E_a)\oint_{\Gamma_b}\mathrm{d}E'\oint_{\Gamma_a}\mathrm{d}E\; v^\dagger_b g_{\gamma_f,b;a}(E',E)v_a\;, \qquad (83)$$

where by a we imply one of the initial states and by b one of the final states under consideration. The vectors v_k are determined from (54)–(55).

In the case of a single initial state (a) and a single final state (b), the vectors v_a and v_b simply become normalization factors. So, for the initial state,

$$v_a^* P_a v_a = v_a^* \frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_a} \mathrm{d}E \; g_{aa}(E) v_a = 1 \tag{84}$$

and, therefore,

$$|v_a|^2 = \Big[\frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_a} \mathrm{d}E \; g_{aa}(E)\Big]^{-1} . \tag{85}$$

Choosing

$$v_a = \Big[\frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_a} \mathrm{d}E \; g_{aa}(E)\Big]^{-1/2} , \; v_b = \Big[\frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_b} \mathrm{d}E \; g_{bb}(E)\Big]^{-1/2} , \tag{86}$$

we obtain

$$\begin{aligned} S_{\gamma_f,b;a} = Z_3^{-1/2} \delta(E_b + k_f^0 - E_a) \oint_{\Gamma_b} \mathrm{d}E' \; \oint_{\Gamma_a} \mathrm{d}E \; g_{\gamma_f,b;a}(E', E) \\ \times \Big[\frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_b} \mathrm{d}E \; g_{bb}(E)\Big]^{-1/2} \Big[\frac{1}{2\pi \mathrm{i}} \oint_{\Gamma_a} \mathrm{d}E \; g_{aa}(E)\Big]^{-1/2} . \end{aligned} \tag{87}$$

The Green function $g_{\gamma_f,b;a}$ is constructed by perturbation theory after the transition in (75) to the interaction representation and using the Wick theorem [22].

4 Conclusion

We have formulated the perturbation theory for calculations of the energy levels and the transitions probabilities in high-Z few-electron atoms. The TTGF method can also be used for calculations of scattering processes. The corresponding formulas for the photon scattering by an atom and for the radiative recombination of an electron with an atom are presented in [22]. Application of the method to resonance scattering processes yields a systematic theory for the spectral line shape. For a detailed consideration of these processes within the TTGF method we refer to [22].

References

1. H.F. Beyer, H.-J. Kluge, V.P. Shevelko: *X-ray Radiation of Highly Charged Ions* (Springer, Berlin 1997)
2. M. Gell-Mann, F. Low: Phys. Rev. **84**, 350 (1951)
3. J. Sucher: Phys. Rev. **107**, 1448 (1957)
4. L.N. Labzowsky: Zh. Eksp. Teor. Fiz. **59**, 168 (1970) [Sov. Phys. JETP **32**, 94 (1970)]
5. M.A. Braun, A.D. Gurchumelia: Teor. Mat. Fiz. **45**, 199 (1980) [Theor. Math. Phys. **45**, N2 (1980)]

6. M.A. Braun, A.D. Gurchumelia, U.I. Safronova: *Relativistic Atom Theory* (Nauka, Moscow 1984)
7. L. Labzowsky, G. Klimchitskaya, Yu. Dmitriev: *Relativistic Effects in Spectra of Atomic Systems* (IOP Publishing, Bristol 1993)
8. P.J. Mohr, G. Plunien, G. Soff: Phys. Rep. **293**, 227 (1998)
9. J. Sapirstein: Rev. Mod. Phys. **70**, 55 (1998)
10. J. Hubbard: Proc. Roy. Soc. A **240**, 539 (1957)
11. S.S. Schweber: *An Introduction to Relativistic Quantum Field Theory* (Harper & Row, New York 1961)
12. A.N. Vasil'ev, A.L. Kitanin: Teor. Mat. Fiz. **24**, 219 (1975) [Theor. Math. Phys. **24**, N2 (1975)]
13. S.A. Zapryagaev, N.L. Manakov, V.G. Pal'chikov: *Theory of One- and Two-Electron Multicharged Ions* (Energoatomizdat, Moscow 1985)
14. J. Sapirstein: Phys. Scr. **36**, 801 (1987)
15. Yu.Yu. Dmitriev, T.A. Fedorova: Phys. Lett. A **245**, 555 (1998)
16. I. Lindgren, S. Salomonson, B. Åsén: Phys. Rep. **389**, 161 (2004)
17. V.M. Shabaev: The quantum-electrodynamical perturbation theory in the Raylegh-Schrödinger form for the calculation of the energy levels of atomic systems. In: *Many-particles Effects in Atoms*, ed by U.I. Safronova (AN SSSR, Nauchnyi Sovet po Spektroskopii, Moscow 1988) pp 15–23
18. V.M. Shabaev: The quantum-electrodynamical perturbation theory in the Raylegh-Schrödinger form for the calculation of the transition probabilities and the cross-sections of various processes. In: *Many-particles Effects in Atoms*, ed by U.I. Safronova (AN SSSR, Nauchnyi Sovet po Spektroskopii, Moscow 1988) pp 24–33
19. V.M. Shabaev: Izv. Vuz. Fiz. **33**, 43 (1990) [Sov. Phys. Journ. **33**, 660 (1990)]
20. V.M. Shabaev: Teor. Mat. Fiz. **82**, 83 (1990) [Theor. Math. Phys. **82**, 57 (1990)]
21. V.M. Shabaev: J. Phys. A **24**, 5665 (1991)
22. V.M. Shabaev: Phys. Rep. **356**, 119 (2002)
23. V.M. Shabaev, I.G. Fokeeva: Phys. Rev. A **49**, 4489 (1994)
24. V.M. Shabaev: Phys. Rev. A **50**, 4521 (1994)
25. V.A. Yerokhin, A.N. Artemyev, T. Beier et al: Phys. Rev. A **60**, 3522 (1999)
26. A.N. Artemyev, T. Beier, G. Plunien et al: Phys. Rev. A **62**, 022116 (2000)
27. V.M. Shabaev, V.A. Yerokhin, T. Beier et al: Phys. Rev. A **61**, 052112 (2000)
28. E.-O. Le Bigot, P. Indelicato, V.M. Shabaev: Phys. Rev. A **63**, 040501(R) (2001)
29. V.M. Shabaev: Phys. Rev. A **64**, 052104 (2001)
30. P. Indelicato, V.M. Shabaev, A.V. Volotka: Phys. Rev. A **69**, 062506 (2004)
31. M.A. Braun: Teor. Mat. Fiz. **72**, 394 (1987) [Theor. Math. Phys. **72**, 958 (1987)]
32. V.M. Shabaev: Teor. Mat. Fiz. **63**, 394 (1985) [Theor. Math. Phys. **63**, 588 (1985)]
33. C. Itzykson, J.-B. Zuber: *Quantum Field Theory* (McGraw-Hill, New York 1980)
34. J.D. Bjorken, D. Drell: *Relativistic Quantum Fields* (McGraw-Hill, New York 1965)
35. V.L. Bonch-Bruevich, S.V. Tyablikov: *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam 1962)
36. A.B. Migdal: *Theory of Finite Fermi Systems and Properties of Atomic Nuclei* (Nauka, Moscow 1983)

37. A.A. Logunov, A.N. Tavkhelidze: Nuovo Cim. **29**, 380 (1963)
38. R.N. Faustov: Teor. Mat. Fiz. **3**, 240 (1970) [Theor. Math. Phys. **3**, N2 (1970)]
39. B. Sz-Nagy: Comm. Math. Helv. **19**, 347 (1946/47)
40. T. Kato: Progr. Theor. Phys. **4**, 514 (1949)
41. T. Kato: *Perturbation Theory for Linear Operators* (Springer, Berlin 1966)
42. M. Reed, B. Simon: *Methods of Modern Mathematical Physics*, vol. 4 (Academic Press, New York 1978)