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Method of the reduced-added Green function in the calculation of atomic polarizabilities

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The Green function in the quantum defect theory provides an exact account for high-excited and continuum electronic states. We modify it by taking into account the ground and low-excited states using their wave functions calculated *ab initio*. As an application, we present a simple and efficient semianalytical method for the calculation of atomic electric frequency-dependent scalar dipole polarizability, for both real and imaginary frequencies. The polarizabilities calculated for some atoms (Li, Na, K, Be, Mg, Ca, Si, P, S, O, Al, Ge, C, N, F, He, Ne, Ar, Kr, and Xe) are compared with existing methods of computational quantum chemistry and with experiments; good accuracy of the proposed method is demonstrated.

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I. INTRODUCTION

The polarizabilities of atoms and molecules, which determine their interactions with other particles and external electric fields due to the induced electric-dipole moment, are responsible for numerous effects in optics and spectroscopy. For instance, in dc fields the quadratic Stark effect [1] is determined by the static polarizability. Numerous effects caused by the linear response of atoms and molecules to ac fields, such as optical refractivity and Rayleigh and Raman scattering [2,3], are determined by the dynamic polarizability $\alpha(\omega)$ where ω is the frequency of the optical field. The van der Waals interactions of atoms are expressed in terms of $\alpha(\mathrm{i}\omega)$ of each atom by the Casimir-Polder formula [4]. For molecules, the dynamical polarizability (together with its asymmetry) determines a number of effects in strong ac fields. For example, the dynamical quadratic Stark effect leads to a change of the equilibrium geometry of a molecule [5] as well as to molecular alignment [6–8].

So the calculation of static and frequency-dependent polarizabilities is important for the analysis of different problems in atomic and molecular physics. Though the static polarizability of the simplest hydrogen atom was calculated in parabolic coordinates as early as in 1926 [9], calculations of the dynamical polarizability are more complex since they include summation over high-excited discrete and continuum states. In a one-electron approximation this difficulty was overcome by solving the inhomogeneous Schrödinger equation or by the use of the Coulomb Green function (GF).

For the hydrogen atom, in Ref. [10] a Laplace transformation was used to solve the inhomogeneous Schrödinger equation analytically. The frequency-dependent polarizability of the ground state of the hydrogen atom was calculated by this method in Ref. [11]. For other atoms the application of direct numerical integration of the inhomogeneous Schrödinger equation to the calculation of dipole and quadrupole static polarizability and shielding factors was reviewed by Dalgarno [12].

Some years later, analytic expressions for the frequency-dependent polarizability of the hydrogen atom was obtained in Ref. [13] using the Coulomb GF in momentum representation [14] and in the Refs. [15] using the coordinate representation [16]. Relativistic effects in the frequency-dependent polarizability of the hydrogen atom were taken into account in Ref. [17]. Various aspects of the use of the Coulomb GF in multiphoton calculations were reviewed in Ref. [18]. More recent analytic results for the dynamical polarizabilities of hydrogenic states with arbitrary quantum numbers are given in Ref. [19].

The polarizability of atoms other than hydrogen can be evaluated taking into account the transitions of a single "optical" electron in a Coulomb-like potential of the atomic core. The non-Coulomb effects of the core charge distribution can be accounted for by quantum defect theory (QDT) [20,68] or by model potential [21]. The GF formalism in the QDT framework (QDGF) was elaborated on for atoms in Ref. [22]. Its application to the calculation of the dynamical polarizabilities of ground and low-excited states of alkali-metal atoms showed good accordance with experiment [23]. Similar results were obtained using the model potential approach [24] (see also [25] and references therein).

The above formalism can be generalized to simplest molecular systems. For instance, the QDGF was developed for molecular H_2^+ ions [26] using spheroidal functions and for polar Rydberg molecules [27,28] using dipole-Coulomb angular wave functions, which provide an exact account for the dipole moment of the molecular core [29].

Despite their analyticity and computational economy [30], QDT methods have scarcely been used in the calculation of the polarizability even for the simplest molecules and atoms. Due to their one-electronic nature, they have not managed to provide an accuracy comparable with the accuracy of many-electron methods used in modern computational chemistry (an exception is high-excited Rydberg states [31]; for those, the computational chemistry methods are extremely expensive). These methods demonstrate good accuracy for simple systems (for example, a direct sum-over-states approach for alkali-metal atoms [32] and random phase approximation for closed-shell systems [33]). Various computational methods for atomic and molecular polarizabilities are well reviewed in numerous sources (see, for instance, [34,35]).

The aim of the present work is to modify the GF method to provide an effective account for the many-electron effects

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and thus to enable simple calculations of atomic and molecular polarizabilities (and other multiphoton process probabilities) for arbitrary (including the excited) electronic states with an accuracy comparable with that achieved in theoretical chemistry.

However, with the present rapid development of computer hardware, the computational requirements of some high-precision methods become now less problematic, so calculational simplicity is not the main aim of the present work. In fact, using the advantages of QDT (such as physical clarity, exact correspondence between the calculated and the experimental resonances, exact account of the highly excited and continuum states) we propose further development of the single-channel QDT for multiphoton processes in complex atoms with essentially non-one-electron spectrum structure.

Many-electron effects are most significant for the ground and for some low-excited states, and simple (one-electron) models are therefore least satisfactory for these states. So the main idea of the proposed method is to use an *ab initio* description for these states through the corresponding oscillator strengths instead of the oscillator strengths appearing in the one-electron expression for the polarizability. As for the high-excited and continuum states (which require the most computational resources in the *ab initio* calculations), their addition to the polarizability is calculated using the simple one-electron models, which, however, take into account the many-electron structure of the ground-state wave function. In other words, some low-excited states (their total number is thereinafter denoted as N) in the GF eigenstate expansion are numerically substituted by the states calculated using *ab initio* methods, and we refer to this substitution as a reduce-adding procedure. Note that the reduced Coulomb GF (without adding the *ab initio* terms), which is needed for stationary perturbation calculations, was found in Ref. [36].

A brief outline of this work is as follows. In Sec. II we develop the general QDGF formalism. Based on an analysis of the inhomogeneous Whittaker equation in Sec. II A we derive expressions for the QDGF for positive (Sec. II B) and negative (Sec. II D) energies. The derivation uses a general relationship between the quantum defect and scattering phases which is proved in the Sec. II C. In the same subsection we introduce some analytic QD-related functions of complex energy; these functions were not required for simple (e.g. alkali-like) atoms but they are important for atoms with complex spectra and comprise the mathematical basis of the proposed method. Section II E introduces the reduced-added GF used for the calculations. The results of the calculation of the dipole scalar polarizability for Li, Na, K, Be, Mg, Ca, Si, P, S, O, Al, Ge, C, N, F, He, Ne, Ar, Kr, and Xe are presented and discussed in Sec. III. Their comparison with the available experimental data and *ab initio* calculations demonstrates the efficiency of the proposed method.

Atomic units are used throughout the work.

II. GREEN FUNCTION IN QUANTUM DEFECT THEORY

One of the key principles of the QDT usage in atomic physics is that the largest contribution to the dipole transition matrix elements is given by distances far from the atomic core where the effective one-electron potential of the optical electron can be considered to have a Coulomb shape with a residual ion charge Z. In practice, it allows one to approximate the optical electron wave function using solutions of the Schrödinger equation for the Coulomb potential. Knowledge of the experimental atomic spectrum enables an account of the atomic core influence on the optical electron and, effectively, for some collective effects.

The first QDT applications to atomic processes were calculations of the bound-bound [37] and bound-free [38] transition matrix elements as well as calculations of the scattering phases [39]. The problems discussed in the present work are related to further development of the one-channel QDT for atomic calculations. One of such development is concerned with construction of the GF formalism in the QDT framework (QDGF) [22]. Its generalization to noninteger angular momentum values, which arise in polar molecule theory [29], is given in Ref. [27,28].

The QDGF developed in Ref. [22] proved to be useful in calculations of multiphoton process probabilities in alkaline atoms [23], whose even ground states can be described by QDT with satisfactory accuracy. However, application of QDT for atoms with more than one electron in the outer shell requires some improvement of the mathematical technique. The same problem is relevant for the one-electron QDGF as well, and the solution is given in this section.

A. General formalism

The one-electron GF $G(E,\mathbf{r},\mathbf{r}')$ corresponding to the virtual electron energy E satisfies the equation

$$\left\{\frac{1}{2}\nabla^2 - U(r) + \frac{Z}{r} + E\right\} G(E,\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'), \qquad (1)$$

where $U(r)$ is the non-Coulomb part of the atomic potential. For distances larger than the core radius r_c the potential is considered to have a Coulomb shape: $U(r>r_c)=0$.

Separating the radial and angular variables in

$$G(E,\boldsymbol{r},\boldsymbol{r}') = \sum_{lm} g_l(E,r,r') Y_{lm}(\boldsymbol{r}) Y^*_{lm}(\boldsymbol{r}'), \qquad (2)$$

we obtain the equation for the radial QDGF $g_l(E,r,r')$:

$$\left\{\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{l(l+1)}{2r^2} - U(r) + \frac{Z}{r} + E\right\} g_l(E,r,r') = \frac{1}{rr'}\delta(r-r'). \qquad (3)$$

The general solution of the inhomogeneous equation (3) in the $r>r_c$ domain may be constructed as a combination of fundamental solutions of the corresponding homogeneous equation:

$$g_l(E,r,r') = g_l^C(E,r,r') + A\frac{\nu}{Zrr'} W_{\nu,l+1/2}\left(\frac{2Zr}{\nu}\right) W_{\nu,l+1/2}\left(\frac{2Zr'}{\nu}\right), \qquad (4)$$

$$g_l^C(E,r,r') = \frac{\nu}{Zrr'}\frac{\Gamma(l+1-\nu)}{\Gamma(2l+2)} \times M_{\nu,l+1/2}\left(\frac{2Zr_<}{\nu}\right)W_{\nu,l+1/2}\left(\frac{2Zr_>}{\nu}\right), \qquad (5)$$

where $\nu = Z/\sqrt{-2E}$ is the so-called effective principal quantum number, $r_>(r_<)$ are the greater (least) of r and r' values, and M and W are well-known Whittaker functions [40]. The first term in Fig. 4, which is a partial solution of the inhomogeneous equation (3), is a pure-Coulomb GF $g_l^C(E,r,r')$ whereas the second term, which enters with an r-independent coefficient A, is a solution of the homogeneous equation. Its other solution containing a double product of M functions must not appear in the expression for the GF since the latter should be regular at $r,r'\rightarrow\infty$ for $E<0$. This can be easily seen from the properties of the Whittaker functions [40]:

$$M_{\nu,l+1/2}\left(\frac{2Zr}{\nu}\right) = \exp(i\pi\nu)\Gamma(2l+2)\times\left[\frac{W_{-\nu,l+1/2}\left(-\frac{2Zr}{\nu}\right)}{\Gamma(1+l-\nu)} - (-1)^l\frac{W_{\nu,l+1/2}\left(-\frac{2Zr}{\nu}\right)}{\Gamma(1+l+\nu)}\right],$$

$$W_{\pm\nu,l+1/2}\left(\pm\frac{2Zr}{\nu}\right)\underset{r\rightarrow+\infty}{\sim}\left(\pm\frac{2Zr}{\nu}\right)^{\pm\nu}\exp\left(\mp\frac{Zr}{\nu}\right). \qquad (6)$$

B. QDGF for $E>0$ and the phase shift

For $E>0$ the M and W functions are more conveniently expressed in the following way [40]:

$$W_{\pm\nu,l+1/2}\left(\pm\frac{2Zr}{\nu}\right)\leftrightarrow(\mp\mathrm{i})^{l+1}\exp\left(\frac{\pi Z}{2k}\mp\mathrm{i}\sigma_l\right)\times[F_l(k,r)\mp\mathrm{i}G_l(k,r)],$$

$$M_{\nu,l+1/2}\left(\frac{2Zr}{\nu}\right)\leftrightarrow(-\mathrm{i})^{l+1}\exp\left(-\frac{\pi Z}{2k}+\mathrm{i}\sigma_l\right)\times\frac{2\Gamma(2l+2)}{\Gamma(l+1-iZ/k)}F_l(k,r). \qquad (7)$$

Here $\sigma_l=\arg\Gamma(l+1-iZ/k)$, $k=\sqrt{2E}$, and ↔ sign corresponds to the replacement

$$\nu\leftrightarrow\mathrm{i}Z/k. \qquad (8)$$

The functions $F_l(k,r)$ and $G_l(k,r)$ in Eqs. (7) are the regular and irregular Coulomb functions [40]. Given the asymptotic form of Whittaker functions (6) we can write the asymptotics of these Coulomb functions:

$$F_l(k,r)r\rightarrow+\infty\sim\sin\Delta_l(r),$$

$$G_l(k,r)_{r\rightarrow+\infty}\sim\cos\Delta_l(r), \qquad (9)$$

where $\Delta_l(r)=kr+Z\ln(2kr)/k-\pi l/2+\sigma_l$. Then, taking into account Eqs. (7) and (9), one obtains, for $E>0$,

$$g_l^{\mathrm{C}}(E,r,r')_{r,r'\rightarrow+\infty}\sim\frac{2\sin\Delta_l(r_<)}{krr'}\exp[i\Delta_l(r_>)]. \qquad (10)$$

It can be shown [41] that the asymptotic expression for QDGF (4) differs from that for the pure-Coulomb GF (10) only by the phase shift $\delta_l(E)$ due to the non-Coulomb potential term $U(r)$:

$$g_l(E,r,r')_{r,r'\rightarrow+\infty}\sim\frac{2\sin[\Delta_l(r_<)+\delta_l]}{krr'}\exp[i(\Delta_l(r_>)+\delta_l)]. \qquad (11)$$

The parameter A can be determined from the correspondence between the asymptotic representations of the QDGF for $E>0$, Eq. (11), and for $E<0$. Indeed, making the replacement (8) in Eq. (4) and using Eq. (6), one obtains

$$A=\exp[2i\sigma_l+i\pi(\nu-l)][1-\exp(2i\delta_l)]. \qquad (12)$$

Given expression (12) for A, we use Eq. (7) to express the QDGF (4) for $E>0$ in the following form:

$$g_l(E,r,r')=\frac{2i\exp(i\delta_l)}{krr'}[F_l(k,r_<)\cos\delta_l+G_l(k,r_<)\sin\delta_l]\times[F_l(k,r_>)-iG_l(k,r_>)]. \qquad (13)$$

C. QD functions and phase relationship

Thus, for a complete definition of the QDGF it is necessary to know the non-Coulomb parts of the scattering phases δ_l and their analytic continuation onto the $E>0$ domain. To determine these quantities we use a well-known relation of scattering theory. Since the discrete spectrum points are the poles of the S matrix, one obtains, for the phase shift in those points [42],

$$\cot(\delta_l+\sigma_l)-i=0,\quad \text{when } E=E_{nl}, \qquad (14)$$

where E_{nl} are the energy levels of the optical electron without account for the fine structure, n and l being its principal and orbital quantum number.

Rewriting Eq. (14) in the form

$$\cot(\delta_l+\sigma_l)-i=\frac{(\cot\delta_l-i)(\cot\sigma_l-i)}{\cot\delta_l+\cot\sigma_l}=0, \qquad (15)$$

one can easily see that the roots of Eq. (15) constitute two subsets. The first subset

$$\cot\sigma_l(E_n)-i=0,\quad E_n=-Z^2/2n^2, \qquad (16)$$

corresponds to a pure-Coulomb (hydrogenlike atom) spectrum and thus should not appear among the S-matrix poles, while the second subset

$$\cot\delta_l(E_{nl})=i \qquad (17)$$

does correspond to a real atom spectrum. The second subscript of the energy eigenvalue is absent in Eq. (16) due to the l degeneracy of the pure-Coulomb spectrum.

Since $E_{nl}\rightarrow0$ as $n\rightarrow\infty$, it then follows from Picard's great theorem [43] that the point $E=0$ is an essential singularity point for the $\cot\delta_l(E)$ function in the complex E plane. Let us assume that the S matrix has no other poles except those determined by formula (17). Then the expression for $\cot\delta_l$

can be defined for all complex E values through the relation

$$\cot \delta_l(E) - i = -2i \exp(i\pi\nu) \frac{\sin \pi(\mu_l + \nu)}{\sin(\pi\mu_l)} \frac{\Pi_l(\nu)}{\Xi_l(E)},$$

$$\Pi_l(\nu) = \nu^{2l} \left[\prod_{m=0}^{l-1} (m + \mu_l + \nu)(m + 1 - \mu_l - \nu) \right]^{-1}, \quad (18)$$

where $\nu = Z/\sqrt{-2E}$ and $\Xi_l(E)$ is an entire function of energy. Recall that an entire function cannot have singularities nowhere in the complex plane except infinity.

Let us define the quantum defect μ_l entering Eq. (18) through the relation

$$\mu_l(E_{nl}) + \nu_{nl} = n, \quad (19)$$

where $\nu_{nl} = Z/\sqrt{-2E_{nl}}$ and n is an integer number satisfying the $n \geqslant l+1$ condition. Then the fundamental condition (17) is obviously valid for all discrete spectrum energies E_{nl}. To eliminate the pure-Coulomb roots (16), the function $\Xi_l(E)$ should be defined at $E = E_n$ in the following way:

$$\Xi_l(E_n) = \Pi_l(n), \quad n \geqslant l + 1. \quad (20)$$

Indeed, for $\nu = n$ taking into consideration Eq. (20) one obtains from formula (18) that

$$\cot \delta_l(E_n) = -i.$$

It is easy to see that for $E = E_n$ the pure-Coulomb roots disappear from the set (15) and therefore from the set (14).

Since the function $\Xi_l(E)$ is defined on the countable set E_n which has the accumulation point $E = 0$, then the relation (20) defines the function $\Xi_l(E)$ unambiguously in the whole complex energy plane [43].

Now we derive the relationship between the phase shifts and quantum defects. Using

$$\frac{\sin \pi(\mu_l + \nu)}{\sin(\pi\mu_l)} = \sin(\pi\nu)[\cot(\pi\nu) + \cot(\pi\mu_l)]$$

and assuming $E \to 0$ in Eq. (18), which means $\sin(\pi\nu) \to \frac{1}{2} i \exp(-i\pi\nu)$, $\cot(\pi\nu) \to -i$, $\Pi_l(\nu) \to (-1)^l$ at $\nu \to i\infty$ and $\Xi_l(E_n) \to (-1)^l$ at $n \to \infty$, one recovers the well-known Seaton relation [20]

$$\cot \delta_l(E) = \cot \pi\mu_l(\nu).$$

D. QDGF for $E < 0$ and bound-state wave functions

Taking into account expression (18) for the phase shift, Eq. (12) can be rewritten to yield

$$A = \frac{\Gamma(l + 1 - \nu)}{\Gamma(l + 1 + \nu)} \frac{\sin \pi(\mu_l + l)}{\sin \pi(\mu_l + \nu)} \frac{\Xi_l(E)}{\Pi_l(\nu)}. \quad (21)$$

Substituting Eq. (21) into Eq. (4) the expression for QDGF $g_l(E, r, r')$ can be rewritten in the following final form:

$$g_l(E,r,r') = \frac{\nu}{Zrr'} \frac{\Gamma(l + 1 - \nu)}{\Gamma(l + 1 + \nu)} W_{\nu,l+1/2}\left(\frac{2Zr_>}{\nu}\right) \times \left[\frac{\Gamma(l + 1 + \nu)}{\Gamma(2l + 2)} M_{\nu,l+1/2}\left(\frac{2Zr_<}{\nu}\right) + \frac{\sin \pi(\mu_l + l)}{\sin \pi(\mu_l + \nu)} \frac{\Xi_l(E)}{\Pi_l(\nu)} W_{\nu,l+1/2}\left(\frac{2Zr_<}{\nu}\right) \right]. \quad (22)$$

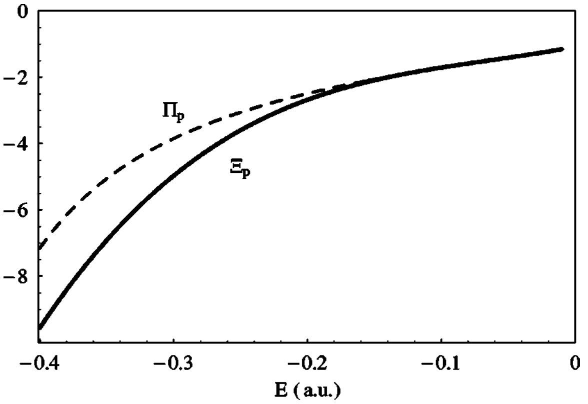

FIG. 1. The $\Xi_l(E)$ and $\Pi_l(Z/\sqrt{-2E})$ functions for Li ($Z=1$, $l=1$).

Evidently, QDGF (22) has poles at the E_{nl} points, which correspond to the atomic spectrum energies; moreover, the QDGF residues in these poles equal to the products of two radial QDT wave functions:

$$R_{nl}(r) = \frac{Z^{1/2}}{r\nu_{nl}} \left[\frac{\Xi_l(E_{nl})}{\Pi_l(\nu_{nl})} \right]^{1/2} W_{\nu_{nl},l+1/2}\left(\frac{2Zr}{\nu_{nl}}\right) \times \left[\Gamma(l + 1 + \nu_{nl})\Gamma(\nu_{nl} - l)\left(1 + \frac{\partial\mu_l(\nu_{nl})}{\partial\nu}\right) \right]^{-1/2}. \quad (23)$$

The $[\Xi_l/\Pi_l]^{1/2}$ factor in the bound-state wave functions (23) makes their normalization different from that used normally in QDT [20,37]. This fact shows the fundamental role played by the function $\Xi_l(E)$ in QDT together with the $\mu_l(E)$ function. This normalization can be important for a QDT description of various effects in the interaction of atoms and molecules with an external field—for instance, in tunneling ionization [44–47].

A typical behavior of the functions $\Xi_l(E)$ and $\Pi_l(Z/\sqrt{-2E})$ is shown in Figs. 1 and 2 for Li ($Z=1$, $l=1$) and Ar ($Z=1$, $l=2$) correspondingly. The functions $\Xi_l(E)$ and $\Pi_l(Z/\sqrt{-2E})$ coincide when $E \to 0$ as it should be according to Eq. (7). In fact, the small difference between $\Pi_l(Z/\sqrt{-2E})$ and $\Xi(E)$ for the alkali-metal atoms (and their significant difference for rare-gas atoms) is responsible for the opinion that a satisfactory QDT description could be performed only for the atoms and ions with one electron over the closed shells. The results below (especially for He atom) show that the domain of applicability of QDT is essentially wider due to the proposed reduce-adding procedure.

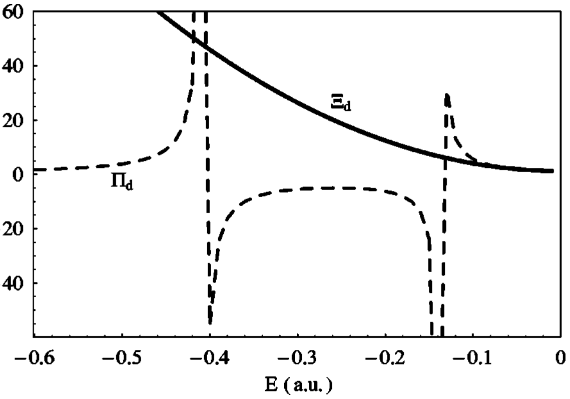

FIG. 2. The $\Xi_l(E)$ and $\Pi_l(Z/\sqrt{-2E})$ functions for Ar ($Z=1$, $l=2$).

E. Reduced-added GF and dynamic polarizability

Besides the definition through the differential equation (1), the GF can be expressed in the form of an expansion over the one-electron Hamiltonian eigenfunctions:

$$G(E,\boldsymbol{r},\boldsymbol{r}')\sum_l \sum_{n\geqslant n_{\min}(l)} \sum_m \frac{\langle r|nlm\langle nlm|r'\rangle}{E-E_{nl}}, \qquad (24)$$

which is equivalent to Eq. (2) with $\langle r|nlm\rangle \equiv R_{nl}(r)Y_{lm}(\boldsymbol{r})$ and

$$g_l(E,r,r') = \sum_{n\geqslant n_{\min}(l)} \frac{R_{nl}(r)R_{nl}(r')}{E-E_{nl}}, \qquad (25)$$

where E_{nl} are the energy levels of the optical electron (without account for the fine structure).

Due to the Pauli principle, the summation in Eqs. (24) and (25) starts from the principal quantum number $n_{\min}(l)$ of the lowest (in a well-defined l series) state of the optical electron and goes through a complete set of nonoccupied one-electron states including the continuum spectrum. Taking in mind that expression (22) contains this summation implicitly, we subtract for each l from the series (25) the states with principal quantum number satisfying $n_{\min}(l)\leqslant n\leqslant n_{\max}(l)$. These boundaries should be chosen so that the excluded states were the first $N=\sum_l[n_{\max}(l)-n_{\min}(l)+1]$ excited states, for which QDT gives the low-accurate wave functions R_{nl}. Instead of them we add N analogous terms containing the wave functions $\mathcal{R}_{nl}$ calculated using *ab initio* computational methods. The resulting reduced-added GF

$$\mathcal{G}(E,\boldsymbol{r},\boldsymbol{r}') = G(E,\boldsymbol{r},\boldsymbol{r}') + \sum_l \sum_{n=n_{\min}(l)}^{n_{\max}(l)} \frac{\mathcal{R}_{nl}(r)\mathcal{R}_{nl}(r') - R_{nl}(r)R_{nl}(r')}{E-E_{nl}} \times \sum_m Y_{lm}(\boldsymbol{r})Y^*_{lm}(\boldsymbol{r})' \qquad (26)$$

will, on the one hand, contain an exact addition of the high-excited $[n>n_{\max}(l)]$ and continuum states, and on the other hand, it will provide an account of the many-electron effects through the *ab initio* treatment of the low-excited states, for which these effects are most significant.

The N value is chosen empirically to achieve convergence—that is, a weak change of the calculated values with increasing N. The analysis of the results below shows

TABLE I. Frequency-dependent polarizabilities $\alpha_{2s}(\omega)$ of lithium, $\alpha_{3s}(\omega)$ of sodium, and $\alpha_{4s}(\omega)$ of potassium (a.u.).

ω (a.u.)	0.000	0.005	0.010	0.015	0.020	0.025	0.030	0.035
Lithium								
$N=0$	168.40	169.31	172.09	176.93	184.20	194.48	208.73	228.56
$N=1$	164.20	165.08	167.79	172.52	179.60	189.62	203.51	222.84
QDT [23]	165.25	166.14	168.87	173.63	180.77	190.87	204.87	224.342
CI [56]	164.1	165.0	167.7	172.4	179.5	189.6	203.4	222.8
MCSCF [56]	164.91	165.80	168.53	173.29				
TDMP2 [56]	165.01	165.90	168.63	173.38	180.52	190.61	204.61	224.09
TDROHF [56]	170.13	171.07	173.95	178.97	186.52	197.22	212.11	232.92
Experiment [57]	164(3)							
Sodium								
$N=0$	178.02	178.77	181.05	184.98	190.79	198.81	209.57	223.90
$N=1$	160.68	161.36	163.41	166.96	172.20	179.44	189.16	202.09
Experiment [62]	162.5(8)							
Potassium								
$N=0$	353.78	356.32	364.14	377.98	399.22	430.30		
$N=1$	280.73	282.74	288.95	299.94	316.79	341.45		
QDT [23]	310.80	313.01	319.83	331.90	350.41	377.49		
TDMP2 [56]	285.23	286.71	291.18	298.59	308.58	319.49		
TDROHF [56]	416.27	420.50	433.71	457.71	496.22	556.55		
Experiment [57]	292.8(6.1)							

that small N values are sufficient as a rule. The asymptotical convergence of the proposed algorithm is also evident: when $N\to\infty$, the whole discrete spectrum is completely taken into account by the *ab initio* methods. In principle, the continuum can be considered in the same way; however, our results below show that good agreement with experiment can be achieved without such a consideration.

Thus, using *ab initio* calculations for a very few excited-state wave functions, the above method gives an improved reduced-added GF, with the help of which one can calculate various multiphoton processes. As an application, we consider the simplest example of such processes.

The frequency-dependent scalar polarizability of an atom with $k_{n_il_i}$ optical electrons in the $|n_il_i\rangle$ state is

$$\alpha_{n_il_i}(\omega) = \frac{k_{n_il_i}}{2l_i+1}\sum_m \langle n_il_im|z\mathcal{G}(E_{n_il_i}+\omega,\mathbf{r},\mathbf{r}')z' + z\mathcal{G}(E_{n_il_i}-\omega,\mathbf{r},\mathbf{r}')z'|n_il_im\rangle. \tag{27}$$

We supposed for simplicity that the polarizability is determined only by the electron transition from the outer $|n_il_i\rangle$ shell. It is the case for the comparatively low frequencies which are considered here. For high frequencies, an account of the transitions from inner electron shells may be required. Note also that neither is a particular atomic term (allowed for $k_{n_il_i}$ electrons in the $|n_il_i\rangle$ state) specified in Eq. (27) nor its multiplet structure taken into account. The results given in the next section for atoms with two and more electrons in the outer shell are in good (2%-3%) agreement with the data reported for the ground atomic terms without their multiplet structure resolved. To our knowledge, there are only a few data available for polarizabilities of individual multiplet components (see, e. g., [48]). In the QDT framework the corresponding accuracy could be attained by an account of the dependence of the energy levels and QD-related functions μ and Ξ on the quantum numbers which characterize the multiplet structure (see, for instance, [49]).

III. RESULTS AND DISCUSSION

In this section we present the results for the polarizabilities of some atoms (Li, Na, K, Be, Mg, Ca, Si, P, S, O, Al, Ge, C, N, F, He, Ne, Ar, Kr, Xe). The *ab initio* wave functions were calculated using the GAUSSIAN98W quantum chemistry program [50]. The wave functions of the initial (ground) $\langle r|n_il_im\rangle=\mathcal{R}_{n_il_i}(r)Y_{l_im}(\mathbf{r})$ state were calculated in the Hartree-Fock (HF) approach [51,52]—restricted for rare-gas and alkaline-earth–metal atoms and unrestricted for the other. The excited-state wave functions were calculated using a configuration interaction with single substitutions (CIS) [53]. The standard basis sets were used: 3-21G** [54] with five-dimensional (5D) polarized functions for xenon and 6-311++G(3df,3pd) [55] for the other atoms. In this section N means the total number of subtracted excited states with l satisfying the dipole and parity selection rules $|l_i-l|=1$.

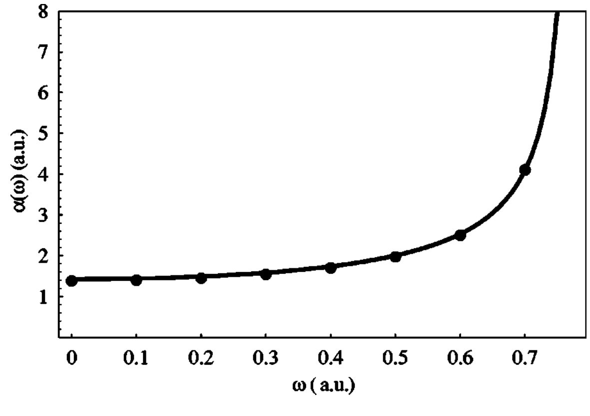

FIG. 3. Dynamic polarizability of He below the first resonance: this work (solid line) and Ref. [58] (circles).

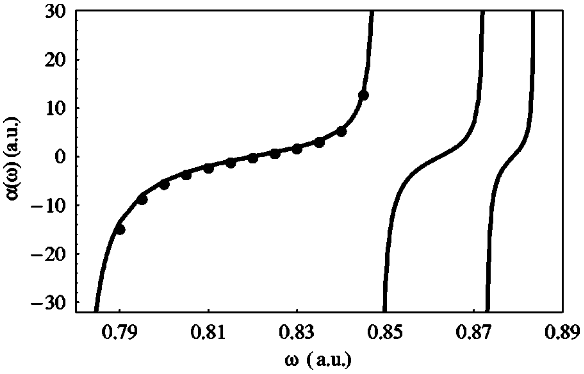

FIG. 4. The same as Fig. 3 between the second and fourth resonances.

A. Lithium, sodium, and potassium

The frequency-dependent polarizabilities of the alkali-metal atoms in their ground states (2s for Li, 3s for Na, and 4s for K) are compared in Table I with the *ab initio* calculations performed in Ref. [56] by various methods time-dependent restricted open-shell Hartree-Fock (TDROHF), time-dependent second-order Møller-Plesset perturbation (TDMP2), CI, and multiconfiguration self-consistent field (MCSCF). Reasonable agreement with the time-dependent *ab initio* calculations of the polarizability is achieved by substituting only one (N=1) excited state (2p for Li, 3p for Na, and 4p for K correspondingly). We also compare these results with those from the Ref. [23], where the QDGF was

TABLE II. Frequency-dependent polarizability $\alpha_{2p}(\omega)$ of neon (a.u.).

ω (a.u.)	N=0	N=2	Ref. [59]	Expt. [60]
0.0	1.915	2.725	2.673	2.669
0.1	1.923	2.746	2.701	
0.2	1.950	2.814	2.794	
0.3	1.997	2.939	2.974	
0.4	2.080	3.148	3.311	
0.5	2.316	3.533	4.089	
0.6	11.773	8.430		

TABLE III. Frequency-dependent polarizabilities $\alpha_{2s}(\omega)$ of beryllium, $\alpha_{3s}(\omega)$ of magnesium, and $\alpha_{4s}(\omega)$ of calcium (a.u.).

	Beryllium			*Magnesium*			*Calcium*		
ω (a.u.)	$N=0$	$N=1$	Ref. [61]	$N=0$	$N=2$	Experiment [62]	$N=0$	$N=1$	Experiment [62]
0.00	43.177	37.034	37.755	97.533	69.544	71.5(31)	231.406	162.113	168.7(135)
0.02	43.626	37.416	38.150	99.009	70.526		239.342	167.578	
0.04	45.032	38.615	39.388	103.729	73.661		266.918	186.553	
0.06	47.597	40.803	41.646	112.732	79.614		331.065	230.644	
0.08	51.745	44.342	45.290	128.465	89.952		502.942	348.593	
0.10	58.326	49.958	51.059	156.956	108.509		1596.16	1097.51	
0.12	69.167	59.213	60.533	216.653	146.942				
0.14	88.870	76.042	77.684	401.204	264.089				
0.16	132.982	113.748	115.903						
0.18	306.585	262.263	265.673						
0.2	−674.340	−577.514	−571.442						
0.22	−152.750	−131.327	−125.566						
0.24	−89.300	−77.738	−66.761						

used with the ground state treated in the QDT model. Table I therefore shows that QDT gives a good approximation for alkali-metal atoms even without using *ab initio* data for the ground-state wave functions.

B. Helium and neon

In Figs. 3 and 4 we compare our calculations for He with those of the Ref. [58] which uses a variationally stable treatment with a coupled-channes hyperspherical representation of the wave functions and provides very close agreement with experiment. Even without the reduce-adding procedure, our calculations are in good agreement (within 2%) with Ref. [58] for He. Our analysis shows that use of more *ab initio* excited states ($N \geqslant 1$) results in a lower accuracy for helium. This fact can be explained by the low accuracy given by the *ab initio* methods we used for the excited states. We can hardly achieve better accuracy without account of relativistic effects.

In Table II we present our calculations of the dynamical polarizability for the ground state of Ne. For the Ne polarizability, adequate accuracy is attained by the substitution of two excited state ($3s,3d$; $N=2$) wave functions.

C. Beryllium, magnesium, and calcium

The frequency-dependent polarizabilities of alkaline-earth atoms in their ground states ($2s$ for Be, $3s$ for Mg, and $4s$ for Ca) are presented in Table III. Like the alkali-metal atoms the polarizability calculations for Be, Ca, and Mg required the use of the reduce-adding procedure. We substitute one ($2p$; $N=1$) excited state for Be, two ($3p,4p$; $N=2$) excited states for Mg, and one ($4p$; $N=1$) for Ca to achieve good agreement (within 2% for Be and 3% for static Mg and Ca) with reference and experimental data.

D. Silicon, phosphorus, and sulfur

The frequency-dependent polarizabilities of Si, P, and S in their ground states [$3p^2(^3P)$, $3p^3(^4S)$, and $3p^4(^3P)$, respectively] are presented in Table IV. Here we substituted one

TABLE IV. Frequency-dependent polarizabilities $\alpha_{3p}(\omega)$ of silicon, phosphorus, and sulfur (a.u.).

	Silicon			*Phosphorus*			*Sulfur*	
ω (a.u.)	$N=0$	$N=1$	Ref. [63]	$N=0$	$N=2$	Ref. [63]	$N=0$	Ref. [63]
0.00	33.096	37.317	38.39	21.888	25.014	25.03	18.474	18.78
0.02	33.308	37.581	38.61	21.943	25.101	25.11	18.513	18.82
0.04	33.971	38.408	39.31	22.114	25.366	25.33	18.632	18.93
0.06	35.162	39.902	40.55	22.406	25.827	25.73	18.836	19.13
0.08	37.051	42.292	42.49	22.835	26.517	26.31	19.136	19.42
0.10	39.979	46.044	45.40	23.425	27.490	27.10	19.551	19.81
0.12	44.722	52.231	49.91	24.216	28.839	28.17	20.110	20.31
0.14	53.481	63.930	57.61	25.270	30.724	29.58	20.868	20.95
0.16	76.465	95.521	75.06	26.703	33.444	31.46	21.927	21.77
0.18	1016.89	1303.59	299.6	28.741	37.624	34.08	23.513	22.82

TABLE V. Frequency-dependent polarizability $\alpha_{2p}(\omega)$ of oxygen (a.u.).

ω (a.u.)	$N=0$	$N=2$	Ref. [64]
0.00	6.146	5.389	5.337
0.04	6.152	5.392	
0.08	6.175	5.395	
0.10	6.195	5.396	5.392
0.14	6.264	5.403	
0.16	6.320	5.415	
0.20	6.504	5.472	5.583
0.24	6.872	5.616	
0.26	7.192	5.754	
0.30	8.5851	6.382	6.281

$(4s;N=1)$ excited state for Si, two $(4s,3d;N=2)$ excited states for P, and for S there is no need in the reduce-adding procedure. The static limits for polarizabilities of these atoms are within 1% error reference data. The discrepancy between our results and the data reported in Ref. [63] for the frequency-dependent polarizability of Si and P increases while the frequency reaches a first resonant value. The authors of Ref. [63] note less accuracy of their polarizability values near the resonances due to insufficient accuracy in the resonance positions calculated. Given the fact that the QDGF method uses exact (experimental) resonance positions, we consider our data on dynamical polarizabilities near the resonances more reliable.

E. Oxygen

The frequency-dependent polarizability of the O atom in its ground state, $2p^4(^3P)$, is presented in Table V. Here we substituted two $(3s,3d;N=2)$ excited states for O.

F. Aluminum, germanium, carbon, nitrogen, and fluorine

The frequency-dependent polarizabilities of Al, Ge, C, N, and F in their ground states $[3p(^2P)$ for Al, $4p^2(^3P)$ for Ge, $2p^2(^3P)$ for C, $2p^3(^4S)$ for N, and $2p^5(^2P)$ for F, respectively$]$ are presented in Table VI. Here we substituted three $(4s,5s,3d;N=3)$ excited states for Al, three $(4s,5s,4d;N=3)$ excited states for Ge, one $(3s;N=1)$ excited state for C, three $(3s,4s,3d;N=3)$ excited states for N, and three $(3s,4s,3d;N=3)$ excited states for F. The static polarizabilities for these atoms were computed using GAUSSIAN98W quantum chemistry program (see footnote) and they are within 2% error with present results.

G. Argon, krypton, and xenon

The frequency-dependent polarizabilities of Ar, Kr, and Xe in their ground states are shown in Table VII. For Ar the adequate accuracy is attained after the substitution of two $(4s\ 3d;N=2)$ first excited-state wave functions. For Kr and Xe it is necessary to substitute four excited states $(5s,6s,4d,5d;N=4)$ and $(6s,7s,5d,6d;N=4)$ correspondingly.

We illustrate the convergence of the proposed method for Ar in Fig. 5. It is evident that the proposed modification of the QDGF via the reduce-adding procedure demonstrates its increasing accuracy with an increase of the number N of substituted states. In this sense the accuracy of the proposed method (without taking into consideration the relativistic effects which lead to a fine structure of the energy levels) is determined only by the accuracy of *ab initio* calculation of wave functions or the corresponding oscillator strengths.

IV. CONCLUSIONS

The proposed modification of the one-electron Green function method for the calculation of the dynamical polarizability consists in a so-called reduce-adding procedure, i.e., in the substitution of the ground- and some first excited-state wave functions in the GF eigenfunction expansion (or corresponding oscillator strengths in the expression for the polarizability) by their values obtained using nonempirical (*ab initio*) calculations. This procedure provides an account of the many-electron effects, which are significant in the low-excited states. The account of the high-excited and continuum states is included in an analytical form, and this simple treatment of the excited states is an advantage of the

TABLE VI. Frequency-dependent polarizabilities $\alpha_{3p}(\omega)$ of aluminum, $\alpha_{4p}(\omega)$ of germanium, and $\alpha_{2p}(\omega)$ of carbon, nitrogen, and fluorine (a.u.).

	Aluminum		*Germanium*		*Carbon*		*Nitrogen*		*Fluorine*	
ω (a.u.)	$N=0$	$N=3$	$N=0$	$N=3$	$N=0$	$N=1$	$N=0$	$N=3$	$N=0$	$N=2$
0.00[a]		52.808[a]		40.169[a]		9.288[a]		6.724[a]		2.950[a]
0.00	74.919	53.663	30.657	39.986	7.257	9.447	5.012	6.141	1.704	2.949
0.02	78.808	57.039	30.822	40.207	7.274	9.475	5.018	6.150	1.704	2.951
0.04	88.462	65.009	31.333	40.888	7.325	9.562	5.037	6.177	1.704	2.957
0.06	100.640	73.761	32.243	42.095	7.414	9.713	5.068	6.222	1.704	2.967
0.08	117.199	83.537	33.663	43.961	7.543	9.935	5.113	6.288	1.705	2.981
0.10	160.201	110.205	35.828	46.753	7.721	10.244	5.173	6.375	1.705	3.000

[a] MP2(FULL)/6-311++G$(3df,3pd)$ SCF(TIGHT) POLAR.

TABLE VII. Frequency-dependent polarizabilities $\alpha_{3\mathrm{p}}(\omega)$ of argon, $\alpha_{4\mathrm{p}}(\omega)$ of krypton, and $\alpha_{5\mathrm{p}}(\omega)$ of xenon (a.u.).

ω (a.u.)	0.0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
Argon									
$N=0$	14.039	14.252	14.401	14.897	15.695	16.964	19.131	23.676	42.811
$N=1$	11.715	11.849	11.941	12.244	12.713	13.417	14.515	16.508	23.017
$N=2$	10.666	10.775	10.851	11.097	11.476	12.042	12.924	14.552	20.358
Ref. [65]	10.62	10.68	10.88	11.22	11.75	12.56	13.80	15.94	20.98
Ref. [66]	10.76	10.83	11.02	11.38	11.93	12.76	14.04	16.25	21.49
Experiment [67]	11.08								
Krypton									
$N=0$	24.731	24.966	25.711	27.114	29.528	33.888	43.672	100.491	
$N=2$	22.930	23.155	23.869	25.216	27.545	31.783	41.396	97.969	
$N=4$	17.871	18.031	18.541	19.509	21.207	24.390	32.098	84.198	
Experiment [67]	16.754								
Xenon									
$N=0$	42.899	43.447	45.223	48.728	55.431	71.223	204.155		
$N=2$	33.177	33.573	34.858	37.419	42.440	55.053	180.527		
$N=4$	27.785	28.091	29.088	31.091	35.096	45.648	160.724		
Experiment [67]	27.292								

proposed method in comparison with the most *ab initio* methods.

In a simple semianalytic calculation of the polarizability for the closed-shell atoms (He, Ne, Ar, Kr, Xe), the method gives good accuracy comparable with the accuracy of computational chemistry methods. For the open-shell atoms (Li, Na, K) the method provides even better agreement with experiment. For more complex systems (Be, Mg, Ca, Si, P, S, O, Al, Ge, C, N, F) the method provides reasonable (2%-3%) agreement with the available data.

Computational simplicity is not the main advantage of the proposed method. We extend the single-channel QDT method which was previously used for atoms with simple hydrogenlike spectra. More complex spectral structures are taken into account by an energy-dependent QD-related function $\Xi_l(E)$.

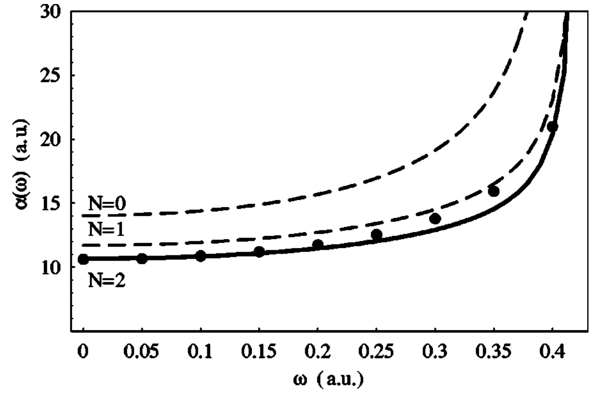

FIG. 5. Convergence of the reduce-adding procedure for the dynamic polarizability of Ar with the number $N=0$, 1 (dashed lines) and $N=2$ (solid line) of the added *ab initio* states. The circles correspond to Ref. [65].

The accuracy of QDGF calculations depends strongly on the accuracy of the available QD values, the latter being determined by the quality of the experimental spectroscopy data. In QDGF calculations, this dependence influences significantly the procedure of extrapolation of the $\mu_l(\nu)$ functions using their values at the ν_{nl} points (19) and also the procedure of the reconstruction of the $\Xi_l(E)$ functions by their values at the Coulomb points E_n, Eq. (20). It turns out that more accurate restoration of Ξ_l functions is attained when Ξ_l is treated as a function of the effective principal quantum number ν rather than a function of energy.

It is clear physically that for the polarizabilities of excited states the proposed method should provide a higher accuracy. In these cases the advantages of the GF method becomes even more significant. We also suppose that this method can be efficient for calculations of the nonlinear susceptibilities of atoms. With some modifications this method can also be spread to calculations of the linear and nonlinear susceptibilities of molecules, including polar ones.

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