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Molecular polarizability in quantum defect theory: polar molecules

E. V. Akindinova, V. E. Chernov,* I. Yu. Kretinin,† and B. A. Zon‡
Voronezh State University, Voronezh RU-394693, Russia

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The reduced-added Green's function technique in the quantum defect theory combines the advantages of analytical and *ab initio* methods in calculating frequency-dependent (dynamic) polarizabilities of atoms and molecules, providing an exact account for the high-excited and continuum electronic states. In the present paper this technique is modified to take into account the long-range dipole potential of a polar molecule core. The method developed is applied to calculation of the dynamic polarizability tensors of alkali-metal hydrides LiH and NaH as well as to some fluorides (CaF and BF) in the frequency range up to the first resonances. The results are in good agreement with *ab initio* calculations available for some frequencies.

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I. INTRODUCTION

The previous papers of the present series discussed the modifications of the quantum defect theory (QDT) which allowed us to use it for calculation of frequency-dependent (dynamic) polarizabilities of different (close- and open-shell) atoms [1] and nonpolar diatomic molecules [2]. In the present paper we develop the theory further to calculate the dynamic polarizabilities of polar diatomic molecules.

Besides the traditional molecular physics applications, such as ac Stark effect, Raman and Rayleigh light scattering, Faraday and Kerr effects [3], and long-range intermolecular interactions [4], the computation of dynamic polarizabilities are relevant for studies of cold and ultracold molecules, such as for modeling the Stark deceleration and trapping of polar molecules in external electromagnetic fields, or to predict their possible orientation and alignment in a superposition of static and oscillating electric fields [5].

The dynamic polarizabilities of homonuclear alkali-metal dimers, which were among the first cold molecules produced experimentally, was calculated in the previous paper [2]. In this context there is growing interest in electronic properties of polar alkali-metal hydrides, LiH and NaH [5,6], whose polarizabilities are presented in this paper. It should be mentioned that these molecules are interesting also from the astrophysical and astrochemical points of view: They are detected in the interstellar clouds [7], in the atmosphere of Jupiter and Saturn [8], and in quasars spectra [9]. Since LiH was one of the first molecules formed in the universe, their radiation and collisional properties are important study of the early universe chemistry [10]. The boron monofluoride molecule, BF, is also of astrochemical interest; it has been recently detected in the sunspot spectra [11]. This molecule plays an important role in coordination chemistry due to its high bond polarity [12]. Among the metal monofluorides, the CaF molecule is a well-known object for studying the Rydberg electron states [13–20]. The large dipole moment of CaF^+ makes the Rydberg spectra of CaF completely different from those of the nonpolar molecules.

A Rydberg electron spends most of its time at a long distance away from a molecular core. Therefore, the motion of this electron is mostly affected only by long-range parts of the core potential. Apart from the Coulomb field of the molecular core, the terms of a multipole expansion of the core potential also play a role of such long-range potentials. In particular, the core of polar molecules possesses a moment of the lowest multipolarity, a dipole moment; therefore, the theory of Rydberg states in polar molecules should be constructed taking consistently into account the core dipole moment. A variant of such consistent consideration taking into account the above-mentioned important difference from the nonpolar molecules was described in terms of so-called dipole-spherical angular functions which give the exact analytical solutions of Schrödinger equation for an electron in the field of a point charge combined with a point dipole [21–23].

It seems that the above dipole-spherical functions were used for the first time by Debye [24] in the analysis of the Stark effect for a symmetric rotator, with this problem actually leading to the angular functions. These functions were used for the description of the Rydberg states of polar molecules within the framework of the Born-Oppenheimer [21,22] and the inverse-Born-Oppenheimer [23] rotational approximations. The oscillator strengths of excimer Rydberg molecules were calculated with the help of the dipole-spherical functions in Refs. [25,26]. These functions were also used for studying the photodetachment of atomic anions in a strong field [27], and for studying the single-photon photodetachment of dipole-bound molecular anions [28,29]. In Ref. [30] the dipole-spherical angular functions were applied to the Zeeman effect in rotational-Rydberg states of polar molecules.

In the present paper we give the further development of the quantum defect Green's function (QDGF) technique [1,2] and generalize it for calculation of polarizabilities of polar molecules. This technique combines the *ab initio* description of the ground and low-excited molecular states with the analytical description of the high-excited and continuum states of the optical electron in polar molecules using the dipole-spherical functions as exact solutions for the Schrödinger equation with dipole-Coulomb potential. A brief sketch of this model is given below; atomic units are used throughout.

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[*] chernov@niif.vsu.ru

[†] Present address: Troitsk Institute of Innovative and Thermonuclear Research (TRINITI), Troitsk, 142190, Moscow Region, Russia.

[‡] Also at Belgorod State University, Belgorod RU-308015, Russia.

II. GENERAL FORMALISM

The Hamiltonian of the electron moving in a "Coulomb + point dipole" field can be written as

$$\hat{H}^{\mathrm{C+d}} = \widehat{T} + \hat{V}; \tag{1}$$

$$\widehat{T} = -\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\boldsymbol{l}}^2}{2r^2}; \tag{2}$$

$$\hat{\boldsymbol{l}}^2 = -\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) - \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial^2\varphi} \tag{3}$$

$$\hat{V} = -\frac{Z}{r} + \frac{(\boldsymbol{d}\cdot\boldsymbol{r})}{r^3}. \tag{4}$$

Here $\widehat{T}$ is the electron kinetic energy operator, $\hat{\boldsymbol{l}}^2$ is the squared electron angular momentum, and $\hat{V}$ is the interaction between the electron and the molecular core with the charge Z and the dipole moment $\boldsymbol{d}$.

The Schrödinger equation with the dipole-Coulomb Hamiltonian (1) can be separated in spherical coordinates r, ϑ, φ with the z axis along the dipole moment direction $\boldsymbol{d}$:

$$\begin{gathered} \hat{H}^{\mathrm{C+d}}\Psi^{\mathrm{C+d}}(\boldsymbol{r}) = E\Psi^{\mathrm{C+d}}(\boldsymbol{r}); \\ \Psi^{\mathrm{C+d}}(\boldsymbol{r}) = \mathcal{R}^{\mathrm{C+d}}(r)\mathcal{Z}_{\ell m}(\vartheta,\varphi), \end{gathered} \tag{5}$$

where the dipole-spherical functions $\mathcal{Z}_{\ell m}(\vartheta,\varphi)$ satisfy

$$(\hat{\boldsymbol{l}}^2 + 2d\cos\vartheta)\mathcal{Z}_{\ell m} = \eta_{\ell m}\mathcal{Z}_{\ell m}. \tag{6}$$

The separation constant, that is, the eigenvalue $\eta_{\ell m}$ of the two-dimensional angular operator (6) is enumerated by two quantum numbers; one of them is the projection m of the electron's orbital momentum onto the molecular z axis. To understand the meaning of the second quantum number, ℓ, we expand the dipole-spherical functions over the familiar spherical harmonics:

$$\mathcal{Z}_{\ell m}(\vartheta,\varphi) = \sum_{L>|m|} a^m_{\ell,L} Y_{Lm}(\vartheta,\varphi), \tag{7}$$

and substitute the expansion (7) into Eq. (6) to obtain the recurrence relation for the expansion coefficients $a^m_{\ell l}(d)$:

$$\begin{gathered} A^-_L a^m_{\ell,L-1} + A^+_L a^m_{\ell,L+1} = (\eta_{\ell m} - L_+L_-)a^m_{\ell,L}, \\ A^\pm_L = 2d\left[\frac{L^2_\pm - m^2}{4L^2_\pm - 1}\right]^{1/2}; \quad L_\pm = L + \frac{1}{2} \pm \frac{1}{2}. \end{gathered} \tag{8}$$

The expansion (7) explicitly demonstrates the l mixing due to nonspherical (axial) symmetry of the polar molecule's core potential (4), so the convenient orbital momentum l is not a good quantum number. Instead of it we introduce the "quasimomentum" $\ell = \ell_{lm}(d)$ according to $\eta = \ell(\ell+1)$. The noninteger quasimomentum values are enumerated by the integer l, m numbers so that in the zero dipole limit we have

$$\eta_{\ell m}(d\to 0) \longrightarrow l(l+1); \quad a^m_{\ell,L}(d\to 0) \longrightarrow \delta_{l,L}, \tag{9}$$

and therefore the dipole-spherical functions $\mathcal{Z}_{\ell m}(\vartheta,\varphi)$ turn to the convenient spherical functions $Y_{lm}(\vartheta,\varphi)$. Since the quasimomentum $\ell = \ell_{lm}$ is completely determined by the values of l and m (and also by the value d of the dipole moment), the dipole-spherical functions can be written in the form $\mathcal{Z}_{lm}$.

The condition (9) uniquely defines the solution of the homogeneous eigenvalue difference problem (8), (9). It can be explicitly shown [22,25] that in the small dipole limit,

$$d \ll l(l+1), \tag{10}$$

which can be also treated as the quasiclassical limit for the angular equation (6), the quasimomentum tends to the convenient orbital quantum number:

$$\begin{gathered} \ell_{lm} \simeq l + 2d^2\frac{l(l+1) - 3m^2}{l(l+1)(4l^2-1)(2l+3)}, \quad l \geqslant 1; \\ \ell_{00} \simeq -\frac{2}{3}d^2. \end{gathered} \tag{11}$$

The expansion coefficients $a^m_{\ell L}$ corresponding to the state with the quasimomentum ℓ_{lm} are expressed in the low dipole limit (10) as

$$\begin{gathered} a^m_{\ell,L} \simeq \delta_{l,L} + \frac{1}{2}\left[\delta_{L_-,l}\frac{A^-_L}{L_-} - \delta_{L_+,l}\frac{A^+_L}{L_+}\right], \quad l \geqslant 1; \\ a^0_{\ell,L} \simeq \delta_{L,0} + \frac{d}{\sqrt{3}}\delta_{L,1}, \quad l = 0; \end{gathered} \tag{12}$$

where $L \geqslant |m|$ according to Eq. (10).

The radial function corresponding to the bound state with radial quantum state n (which is equal to the number of nodes in r) and the angular quantum numbers l, m (which define the quasimomentum $\ell = \ell_{lm}$) is expressed in the dipole-Coulomb model as

$$\mathcal{R}^{\mathrm{C+d}}_{nlm}(r) = \frac{2Z^{3/2}}{N^2_{nlm}}x^\ell \mathrm{e}^{-x}\sqrt{\frac{n!}{\Gamma(2\ell+2+n)}}L^{2\ell+1}_n(x), \tag{13}$$

where $x = 2Zr/N_{nlm}$ and L is the Laguerre polynomial [31]. The functions (13) have Coulomb form with the noninteger quasimomentum instead of the orbital quantum number and noninteger principal quantum number N_{nlm} which determines the discrete energy levels in the dipole-Coulomb model:

$$\varepsilon_{nlm} = -\frac{Z^2}{2\mathcal{N}^2_{nlm}}; \quad \mathcal{N}_{nlm} = n + \ell_{lm} + 1. \tag{14}$$

The noninteger value of $\mathcal{N}_{nlm}$ in Eq. (14) provides the account for the long-range (dipole) part of the molecular core's potential. In the QDT framework the account of the short-range part can be provided in terms of the "short-range" quantum defect μ^{s}_{lm}:

$$E_{nlm} = -\frac{Z^2}{2\nu^2_{nlm}}; \quad \nu_{nlm} = \mathcal{N}_{nlm} - \mu^{\mathrm{s}}_{lm}. \tag{15}$$

The total (long- plus short-range) quantum defect, which is normally reported in the literature, can be expressed as $\mu_{lm} = \ell_{lm} - l + \mu^{\mathrm{s}}_{lm}$. Note that the "atom-like" spectroscopic notation $|nlm\rangle$ does not imply the l mixing and is normally assigned to the molecular states in the united atom limit.

The Green's function $G(E, \boldsymbol{r}, \boldsymbol{r}')$ of the optical electron in the dipole-Coulomb QDT model (QDGF) satisfies the following equation outside the molecular core:

$$(E - \hat{H}^{\mathrm{C+d}})G^{\mathrm{QD}}(E, \boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad r > r_{\mathrm{c}}, \tag{16}$$

where E is the virtual energy of the optical electron. Inserting the expansion of the three-dimensional Green's function,

$$G^{\mathrm{QD}}(E, \boldsymbol{r}, \boldsymbol{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_{lm}^{\mathrm{QD}}(E, r, r')\mathcal{Z}_{lm}(\boldsymbol{r})\mathcal{Z}_{lm}^{*}(\boldsymbol{r}'), \tag{17}$$

over the dipole-spherical functions into Eq. (16) we obtain the equation for the radial QDGF $g_{lm}^{\mathrm{QD}}(E, r, r')$ in the $r > r_{\mathrm{c}}$ domain:

$$\left[\frac{1}{2r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) - \frac{\ell(\ell+1)}{2r^2} + E + \frac{Z}{r}\right] g_{lm}^{\mathrm{QD}}(E, r, r') = \frac{1}{rr'}\delta(r - r'), \tag{18}$$

whose solution can be given in terms of Whittaker functions [31] (see Refs. [1,2] for the details),

$$\begin{aligned} g_{lm}^{\mathrm{QD}}(E, r, r') = {} & \frac{\nu}{Zrr'}\frac{\Gamma(\ell+1-\nu)}{\Gamma(\ell+1+\nu)} W_{\nu,\ell+\frac{1}{2}}\left(\frac{2Zr_{>}}{\nu}\right) \\ & \times \left[\frac{\Gamma(\ell+1+\nu)}{\Gamma(2\ell+2)}\, M_{\nu,\ell+\frac{1}{2}}\left(\frac{2Zr_{<}}{\nu}\right)\right. \\ & + \frac{\sin\pi\left(\mu_{lm}^{\mathrm{s}}(\nu)\right)}{\sin\pi\left(\mu_{lm}^{\mathrm{s}}(\nu) + \nu - \ell\right)}\frac{\Xi_{lm}(E)}{\Pi_{lm}(\nu)} \\ & \left.\times W_{\nu,\ell+\frac{1}{2}}\left(\frac{2Zr_{<}}{\nu}\right)\right]; \quad \nu = 1/\sqrt{-2E}. \end{aligned} \tag{19}$$

Equation (19) differs from the corresponding expression for nonpolar molecules [2] by the dependence on dipole moment via the noninteger quasimomentum ℓ_{lm}. By the similar way we introduce the function,

$$\Pi_{lm}(\nu) = \nu^{2q}\left[\prod_{k=0}^{q-1}(k - \ell + \mu_{lm} + \nu)(k + 1 + \ell - \mu_{lm} - \nu)\right]^{-1}, \tag{20}$$

and the function $\Xi_{lm}(E)$ which coincides with $\Pi_{lm}(\nu)$ in the dipole-Coulomb eigenstates (14):

$$\Xi_{lm}(\varepsilon_{nlm}) = \Pi_{lm}(\mathcal{N}_{nlm}). \tag{21}$$

The quantum defect function $\mu_{lm}^{\mathrm{s}}(\nu)$ in Eq. (19) should be constructed by interpolation from the experimental Rydberg spectrum according to (15):

$$\mu_{lm}^{\mathrm{s}}(E_{nlm}) = \mathcal{N}_{nlm} - \nu_{nlm}. \tag{22}$$

The radial wave functions in QDT can be obtained as a residue of the radial QDGF (19) in the discrete spectrum points E_{nlm} [1]. Here we write the three-dimensional QDT wave function of the optical electron for the $r > r_{\mathrm{c}}$ domain:

$$\Psi_{nlm}^{\mathrm{QD}}(\boldsymbol{r}) = \frac{Z^{1/2}}{r\nu_{nlm}}\left[\frac{\Xi_{lm}(E_{nlm})}{\Pi_{lm}(\nu_{nlm})}\right]^{\frac{1}{2}} \times \frac{(-1)^n W_{\nu_{nlm},\ell+\frac{1}{2}}\left(\frac{2Zr}{\nu_{nlm}}\right)\mathcal{Z}_{lm}(\vartheta, \varphi)}{\sqrt{\Gamma(\ell+1+\nu_{nlm})\Gamma(\nu_{nlm}-\ell)\left(1 + \frac{\partial\mu_{lm}^{\mathrm{s}}(\nu_{nlm})}{\partial\nu}\right)}}. \tag{23}$$

The GF in $\boldsymbol{r}, \boldsymbol{r}'$ representation $\langle\boldsymbol{r}|\hat{G}(E)|\boldsymbol{r}'\rangle = G(E, \boldsymbol{r}, \boldsymbol{r}')$ can be expressed in terms of spectral expansion over discrete $|d\rangle$ and continuous $|c\rangle$ states:

$$G(E, \boldsymbol{r}, \boldsymbol{r}') = \sum_{d} \frac{\Psi_d^{*}(\boldsymbol{r}')\Psi_d(\boldsymbol{r})}{E - E_d} + \int \mathrm{d}E_c \frac{\Psi_c^{*}(\boldsymbol{r}')\Psi_c(\boldsymbol{r})}{E - E_c}. \tag{24}$$

The "reduce-adding" procedure used here and in the previous papers [1,2] consists of substitution of the first N low-excited states (including the ground one) wave functions $\Psi_d^{\mathrm{QD}}(\boldsymbol{r})$ in Eq. (24) by *ab initio* wave functions obtained with the help of computational chemistry (CC) methods:

$$\mathcal{G}(E, \boldsymbol{r}, \boldsymbol{r}') = G^{\mathrm{QD}}(E, \boldsymbol{r}, \boldsymbol{r}') - \sum_{d=0}^{N-1} \frac{\Psi_d^{\mathrm{QD}*}(\boldsymbol{r}')\Psi_d^{\mathrm{QD}}(\boldsymbol{r})}{E - E_d} + \sum_{d=0}^{N-1} \frac{\Psi_d^{\mathrm{CC}*}(\boldsymbol{r}')\Psi_d^{\mathrm{CC}}(\boldsymbol{r})}{E - E_d}. \tag{25}$$

The number N of the substituted states should be determined from convergence of the numerical values. If no states are substituted, then formally we have $N = 0$ that means the absence of the reducing-adding procedure so that the sums in Eq. (25) vanish and $\mathcal{G} = G^{\mathrm{QD}}$ for $N = 0$.

The "reduce-adding" formalism for calculation of polarizabilities in terms of the reduced-added GF $\mathcal{G}$ (25) is similar to that given in Ref. [2].

III. RESULTS AND DISCUSSION

The *ab initio* calculations for the low-excited states was calculated using the GAUSSIAN98 package [32]. For the basis expansion coefficients of the low-excited states, this package gives accuracy of about five significant digits. The QD-related function $\Xi_{lm}(\varepsilon)$ is built by interpolation of the quantum defects (or energy level values) from literature where they are given four-digit accuracy. The results for transition moments and static polarizabilities reported in the papers, which are used for comparison with our calculations, have the same accuracy and therefore our results are presented with four significant digits. It should be expected that this accuracy does not sufficiently decrease for near-resonant frequencies since the behavior of the GF near resonances is determined by (i) the position of a resonance which is taken from the experimental data and (ii) by the residue in the resonance which is determined by the product of the corresponding bound state's wave functions [in the case of low-excited states corresponding to first or second resonances, these residues are determined by *ab initio* wave functions in Eq. (25)]. The overall accuracy of our calculation should also not decrease when increasing the number N of the substituted states since GF should then converge to

TABLE I. Parallel polarizability $\alpha_{zz}(\omega)$ (in a.u.) LiH (the first resonance at $\omega = 0.1314$ a.u.).

	QDT (this work)			
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$	Ref. [37]
0.0	41.09	24.70	26.01	26.08
0.01	41.27	24.79	26.10	26.17
0.02	41.83	25.06	26.38	26.45
0.03	42.81	25.52	26.86	26.93
0.04	44.28	26.22	27.58	27.65
0.05	46.37	27.21	28.60	28.67
0.06	49.28	28.58	30.00	30.07
0.07	53.37	30.49	31.96	32.00
0.08	59.27	33.24	34.76	34.75
0.09	68.25	37.38	38.97	38.84
0.10	83.15	44.21	45.89	45.44
0.11	112.2	57.46	59.24	57.85
0.12	192.6	93.90	95.80	89.86

its "*ab initio*" value. However, significant increase of N is meaningless because of, for example, relativistic, vibrational, rotational corrections, etc.

A. LiH

The ground-state wave function for the LiH molecule was calculated by the MP2 method (i.e., Hartree-Fock calculation followed by a Møller-Plesset correlation energy correction [33]) using the 6–31 G* basis at the equilibrium internuclear separation $R_e(\text{LiH}) = 3.015$ a.u. [34]. The quantum defect function was interpolated using the spectroscopic data taken from Ref. [35]. The dipole moment of the molecular core is $d(\text{LiH}^+) = 0.703$ D at $R_e(\text{LiH}^+) = 4.15$ a.u. [36]. In Tables I and II we present the results of calculations of the parallel, $\alpha_{zz}(\omega)$, and the perpendicular, $\alpha_{xx}(\omega)$, dynamic polarizabilities calculated according to Eq. (24) of our previous work [2] without the "reduce-adding" procedure ($N = 0$, the first column) and with $N = 1, 2$ first dipole transition moments substituted by the values calculated *ab initio* [35]. Substitution of more than $N = 2$ states does not result in significant change in the calculated values of polarizability. For instance, substitution of $N = 3$ states changes the $\alpha_{zz}(\omega)$ value by 0.6%, and the $\alpha_{zz}(\omega)$ value by 0.07%; this demonstrates the convergence of the "reduce-adding" procedure. As it is seen from Tables I and II, our calculations are in good agreement with time-dependent gauge independent (TDGI) *ab initio* results [37]. Table III compares the static ($\omega = 0$) values of the perpendicular, parallel, and mean polarizabilities α_{xx}, α_{zz}, and $\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz})$ calculated by different methods.

TABLE II. Perpendicular polarizability $\alpha_{xx}(\omega)$ (in a.u.) LiH (the first resonance at $\omega = 0.1684$ a.u.).

	QDT (this work)			
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$	Ref. [37]
0.0	21.57	30.07	29.36	29.75
0.01	21.62	30.16	29.44	29.83
0.02	21.79	30.41	29.70	30.09
0.03	22.07	30.85	30.13	30.52
0.04	22.47	31.49	30.77	31.16
0.05	23.03	32.35	31.63	32.02
0.06	23.75	33.49	32.77	33.16
0.07	24.69	34.96	34.25	34.63
0.08	25.89	36.87	36.15	36.52
0.09	27.45	39.35	38.63	38.98
0.10	29.52	42.64	41.92	42.24
0.11	32.31	47.12	46.40	46.66
0.12	36.28	53.51	52.79	52.92
0.13	42.28	63.24	62.53	
0.14	52.41	79.78	79.06	

TABLE III. Static polarizabilities (in a.u.) of LiH molecule.

Method	α_{xx}	α_{zz}	$\bar{\alpha}$
Multideterminant ket with polynomial factor [35]	30.8	26.9	29.5
DQMC [38]	30.9	24.6	28.8
TDGI [39]	29.96	27.04	28.99
CCSD(T) [40]	29.57	25.79	28.31
MCSCF [41]	29.76	26.36	28.63
TDGI [37]	29.75	26.08	28.53
CCSD(T) [42]	30.01	26.81	28.94
QDGT (this work)	29.36	26.01	28.24

B. NaH

We calculated the wave function of the LiH ground state by MP2 method using the 6–31 G** basis at the equilibrium internuclear separation $R_e(\text{NaH}) = 3.566$ a.u. [43]. Since the experimental energies are known only for the $A^1\Sigma$, $B^1\Pi$, $C^1\Sigma$ states, we used the energy level values calculated *ab ininio* in Refs. [39] and [44] for interpolation of $\mu_{lm}(\nu)$ function. The transition dipole moments used in the "reduce-adding" procedure were also taken from Refs. [39,44]. Tables IV and

TABLE IV. Parallel polarizability $\alpha_{zz}(\omega)$ (in a.u.) NaH (the first resonance at $\omega = 0.1157$ a.u.).

	QDT		
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$
0.0	88.63	54.41	55.95
0.01	89.25	54.77	56.32
0.02	91.16	55.87	57.44
0.03	94.54	57.83	59.42
0.04	99.79	60.86	62.48
0.05	107.5	65.33	67.00
0.06	118.9	71.93	73.66
0.07	136.3	81.97	83.78
0.08	164.6	98.33	100.2
0.09	216.6	128.5	130.5
0.10	340.1	199.8	202.0
0.11	962.0	559.7	562.1

TABLE V. Perpendicular polarizability $\alpha_{xx}(\omega)$ (in a.u.) NaH (the first resonance at $\omega = 0.150858$ a.u.).

	QDT		
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$
0.0	35.49	39.09	40.35
0.01	35.61	39.23	40.49
0.02	35.98	39.65	40.92
0.03	36.62	40.38	41.66
0.04	37.57	41.45	42.76
0.05	38.88	42.93	44.27
0.06	40.64	44.92	46.30
0.07	42.98	47.58	49.00
0.08	46.13	51.14	52.63
0.09	50.44	56.03	57.60
0.10	56.55	62.98	64.64
0.11	65.75	73.44	75.23
0.12	80.94	90.75	92.69
0.13	110.6	124.6	126.7
0.14	194.2	220.1	222.5
0.15	2208.	2526.	2529.

V show the results of calculations without the "reduce-adding" procedure ($N = 0$) and with the substitution of $N = 1, 2$ states. In calculation of the static polarizabilities, a good agreement with the other authors was achieved even for $N = 1$ for both $\alpha_{xx}(0)$ and $\alpha_{zz}(0)$ values. These results are presented in Table VI.

C. BF

As for the case of NaH, the ground-state wave function for LiH molecule was calculated by MP2 method using the 6–31 G** basis at the equilibrium internuclear separation $R_e(\mathrm{BF}) = 2.386$ a.u. [47]. The dipole moment $d(\mathrm{BF}^+) \simeq 3$ D of the molecular core ion was taken from Fig. 2 of Ref. [47]. To build the interpolation function $\mu_{lm}(\nu)$ we used the spectroscopic data from Ref. [48]. The results of the calculations for the polarizabilities of BF molecule are shown in Tables VII and VIII. The number of the substituted states $N = 1$ for the perpendicular polarizability and $N = 2$ for the parallel polarizability. Tables VII and VIII contain also the results for $N = 3, 4$ to illustrate the convergence of the "reduce-adding" procedure. The convergence for $\alpha_{xx}(\omega)$ is not monotonic, but the agreement with *ab initio* TDGI calculations [49] is satisfactory: for the static value the difference is 4.8% and 0.9% for $\alpha_{xx}(\omega)$ and $\alpha_{zz}(\omega)$ correspondingly. This discrepancy is probably due to differences in the experimental [48] and the TDGI calculated [49] BF energy spectra.

TABLE VI. Static polarizabilities (in a.u.) of NaH molecule.

Method	α_{xx}	α_{zz}	$\bar{\alpha}$
CCSD(T) [39]	39.60	58.30	45.80
TDGI [39]	41.37	58.01	46.92
QCISD(T) [45]	39.97	56.53	45.99
CCSD(T) [42]	39.70	58.90	46.10
Finite field method [46]	38.80	53.70	43.70
QDT (this work)	40.35	55.95	45.55

TABLE VII. Parallel polarizability $\alpha_{zz}(\omega)$ (in a.u.) BF (the first resonance at $\omega = 0.298$ a.u.).

	QDT (this work)					
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$	$N = 3$	$N = 4$	Ref. [49]
0.0	33.41	34.40	17.63	18.04	16.74	17.48
0.02	33.53	34.52	17.68	18.10	16.80	
0.04	33.89	34.90	17.85	18.26	16.95	
0.06	34.50	35.53	18.12	18.55	17.23	
0.072	35.00	36.06	18.35	18.79	17.43	17.75
0.08	35.40	36.47	18.53	18.97	17.61	
0.0885	35.88	36.97	18.75	19.19	17.81	18.03
0.0933	36.18	37.28	18.89	19.33	17.94	18.12
0.0995	36.61	37.72	19.08	19.53	18.13	18.25
0.10	36.64	37.76	19.10	19.55	18.14	
0.1045	36.97	38.10	19.25	19.70	18.28	18.36
0.12	38.29	39.47	19.84	20.31	18.85	
0.1252	38.80	40.00	20.07	20.54	19.07	18.92
0.1294	39.24	40.46	20.27	20.75	19.26	19.06
0.14	40.47	41.74	20.82	21.31	19.79	
0.16	43.35	44.74	22.11	22.63	21.02	
0.18	47.23	48.79	23.84	24.40	22.68	
0.20	52.59	54.39	26.23	26.84	24.98	
0.22	60.33	62.51	29.66	30.35	28.29	
0.24	72.25	75.07	34.91	35.69	33.38	
0.28	135.3	143.9	63.02	64.16	60.95	

D. CaF

The ground-state ${}^2\Sigma^+$ of CaF contains only $p_0 = 1$ electron over the closed core subshells. This makes it similar to

TABLE VIII. Perpendicular polarizability $\alpha_{xx}(\omega)$ (in a.u.) BF (the first resonance at $\omega = 0.233$ a.u.).

	QDT (this work)			
ω (a.u.)	$N = 0$	$N = 1$	$N = 2$	Ref. [49]
0.0	7.320	20.93	20.78	21.99
0.02	7.349	21.06	20.91	
0.04	7.439	21.46	21.31	
0.06	7.596	22.17	22.02	
0.072	7.727	22.77	22.62	23.71
0.08	7.831	23.26	23.10	
0.0885	7.959	23.86	23.70	24.73
0.0933	8.040	24.25	24.09	25.09
0.0995	8.154	24.80	24.63	25.60
0.10	8.164	24.84	24.68	
0.1045	8.255	25.29	25.12	26.07
0.12	8.626	27.15	26.98	
0.1252	8.774	27.91	27.73	28.56
0.1294	8.903	28.58	28.41	29.26
0.14	9.276	30.57	30.39	
0.16	10.23	35.98	35.78	
0.18	11.73	45.48	45.27	
0.20	14.58	66.29	66.05	
0.22	23.77	149.2	148.9	

TABLE IX. Parallel $\alpha_{zz}(\omega)$ and perpendicular $\alpha_{xx}(\omega)$ polarizabilities (in a.u.) CaF.

	QDT		
ω (a.u.)	α_{zz}	α_{xx}	$\bar{\alpha}$
0.0	37.85	75.50	62.95
0.005	37.84	75.84	63.18
0.01	38.21	76.90	64.00
0.015	38.77	78.72	65.40
0.02	39.59	81.42	67.48
0.025	40.71	85.16	70.34
0.03	42.16	90.22	74.20
0.035	44.04	97.01	79.35
0.04	46.46	106.2	86.28
0.045	49.60	118.9	95.80
0.05	53.73	137.1	109.3
0.055	59.31	164.9	129.7
0.06	67.17	211.4	163.4
0.065	78.91	304.0	229.0
0.07	98.18	571.6	413.8
0.075	135.4	8881.	5966.
0.08	236.7		
0.085	1580.		

one-electron alkali-metal-like systems which are well described by QDT, and the large dipole moment $d(\mathrm{CaF}^+) \simeq 9$ D of the molecular core makes this molecule an ideal object for studying Rydberg states in polar molecules. Indeed, the Rydberg states of CaF are very well described [13–20]; to build the interpolated function $\mu_{lm}(\nu)$ we used the experimental data from Refs. [13,14,16,50]. Table IX contains the results for dynamic polarizabilities calculated without the "reduce-adding" procedure. It can be justified by good agreement of the static polarizabilities (Table X) with the *ab initio* calculations [51]. This fact is not surprising due to the above-mentioned similarity between the alkaline-metal-earth halides and alkali-metal atoms. For the latter the calculation of polarizability does not require substitution of any states [1].

TABLE X. Mean polarizability (in a.u.) and polarizability anisotropies of CaF molecule.

Method	$\bar{\alpha}$	γ
TEK [51]	61.88	−38.94
D-shell(−1) [51]	62.83	−35.09
D-shell(q) [51]	60.94	−27.20
QDT (this work)	62.95	−37.64

IV. CONCLUDING REMARKS

This paper continues the series [1,2] where we develop the quantum defect theory (QDT) for simple calculation of dynamic polarizability of molecules in a wide frequency range. The Green's function of the optical electron in this technique (QDGF) with the reducing-adding procedure of the low-excited states provides an exact account for the high-excited and continuum electronic states. In the description of the latter states, the dipole moment of the molecular core is taken into account using the formalism of dipole-spherical functions giving exact analytical solution of the Schrödinger equation for the electron moving in the field of point charge and point dipole. As an application, we present simple and efficient semianalytical method for calculation of electric frequency-dependent dipole polarizability for simple diatomics (LiH, NaH, BF, and CaF). We consider the proposed method to be a helpful addition to *ab initio* methods of computational quantum chemistry [52–55]; its accuracy is comparable with the accuracy of the *ab initio* methods. The method is also applicable for calculation of other polarizability-related electromagnetic properties of simple molecules, such as depolarization ratios [56] or magneto-optical constants [57].

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