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Molecular polarizability in quantum defect theory: Nonpolar molecules

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The method of reduced-added Green's function in quantum defect approximation [V. E. Chernov, D. L. Dorofeev, I. Yu. Kretinin, and B. A. Zon, Phys. Rev. A **71**, 022505 (2005)] is generalized for calculation of dynamic polarizabilities of nonpolar molecules. The method is applied to alkali-metal dimers Li_2, Na_2, and Rb_2. The accuracy achieved in benchmark calculation (H_2 molecule) is comparable to that of *ab initio* calculations.

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I. INTRODUCTION

The knowledge of dynamic polarizabilities of molecules is important for the description of a number of physical phenomena such as ac Stark effect, Raman and Rayleigh light scatterings, Faraday and Kerr effects [1], long-range intermolecular interactions [2], alignment and orientation of molecules in laser field [3], and manipulations (e.g., aligning [4] and Stark deceleration [5]) with trapped ultracold molecules.

Frequency-dependent polarizabilities of molecules are actively studied using various methods of computational chemistry [6–9]. However, calculation of dynamic polarizabilities involves contributions of highly excited and continuum states for which the accuracy of *ab initio* methods is essentially lower as compared to the ground and low-excited states.

A comparatively simple and physically transparent way to bypass these disadvantages is the quantum defect theory (QDT) well-known in atomic and molecular physics [10]. Since the main contribution to the one-electron matrix elements is given by the distances far from the atomic or molecular core the effective one-electron potential has Coulomb form. In practice, it allows one to obtain analytical expression for the optical electron wave function which involves some parameters (quantum defects, QDs) resulting from the knowledge of the experimental spectrum. This enables to account for the influence of the core on the optical electron and, effectively, for some many-electron effects.

Since the Schrödinger equation for the optical electron is exactly solvable, the calculation of polarizabilities can be easily done using Green's function (GF) technique. The GF formalism in QDT framework (QDGF) was elaborated for simple atoms a long time ago [11]; its application to calculation of dynamical polarizabilities of ground and low-excited states of alkali-metal atoms showed a good agreement with experiment [12].

While the highly excited states of molecules are well described by QDT, there are several difficulties in quantum-defect treatment of their ground and low-excited states. The rare exceptions are, e.g., excimer molecules of noble gas hydrides whose oscillator strengths are successively calculated in QDT framework [13]. Since the low-excited molecular states are reliably described by *ab initio* methods, it seems advisable to combine the advantages of both methods. Such a combined method, the reducing-adding procedure for QDGF, was proposed in [14] and consists in changing the wave functions of some low-excited states in spectral expansion of QDGF with wave functions obtained by *ab initio* methods.[1] For the polarizabilitiy it means a change of some first-order matrix elements in the sum-over-states expression by correspondent matrix elements calculated *ab initio* or by oscillator strengths taken from experiment. Usage of the experimental spectroscopic data in the QDT ideology ensures the proper positions of the poles of the frequency-dependent polarizabilitiy. This method has proved its efficiency in calculations of scalar, vector, and tensor polarizabilities of excited atomic states [15] including fine structure of their terms [16,17].

In the present work we generalize the above approach to nonpolar molecules. The proposed theory is applicable to simple molecules whose electronic terms can be classified in the united-atom limit scheme. As a rule, the intervals between the electronic levels of such molecules are much greater than those between its vibrational levels and, in turn, the latter are much greater than the intervals between the rotational levels. This implies that the vibrational and (or) rotational contributions to the total molecular polarizability at optical frequencies should not exceed a few percent. This is not the case for several polyatomic molecules [18] especially when hyperpolarizabilities are concerned [19]. In this work we consider only the electronic part of molecular polarizability and neglect the nuclear motion.

Note that an attempt to apply QDGF formalism to calculation of second-order properties of simplest molecules was made many years ago for H_2^+ ion. Its dynamic polarizability

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[1] It was considered for a long time that QDT description is successful only for one electron over complete shells, e.g., for alkali-metal-like atoms and ions. After an error in earlier QDT has been corrected in Ref. [14], the modified QDT is capable to treat optical electron states in any complex atom. The wave function of such a state is determined by the QDs of the whole spectral series (not only by the QD of the given state).

[20] and two-photon ionization cross section [21] were calculated using the spheroidal functions to describe the two-center potential of the molecular core. The difference between this potential and the spherically symmetric Coulomb potential is due to higher multipolar moments of the molecular core. Due to a short-range nature of these multipolar potentials and the spectroscopic information contained in QDs, the radial part of GF was assumed to have Coulomb form with a good accuracy [21].

With the help of the above-mentioned reducing-adding procedure we construct here the QDGF of optical electron in many-electron nonpolar molecules and apply it to the calculation of their dynamic polarizabilities. Our benchmark calculations for the simplest H_2 molecule demonstrate a good agreement with *ab initio* calculations and with experimental data. As further applications of the developed technique the dynamic polarizabilities are calculated for alkali-metal dimers Li_2, Na_2, and Rb_2. Atomic units are used throughout.

II. GENERAL FORMALISM

Since the QDGF formalism for spherically symmetric potential describing an optical electron in atoms was presented in detail in Ref. [14], in this section we give only the main equations of this formalism in a form generalized with an account for nonspherical symmetry of the molecular core potential.

The $G(E,\boldsymbol{r},\boldsymbol{r}')$ of the optical electron satisfies the Schrödinger equation

$$\{\hat{H}-E\}G(E,\boldsymbol{r},\boldsymbol{r}')=\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{1}$$

$$\hat{H}=-\frac{1}{2}\nabla^2+U(\boldsymbol{r})-\frac{Z}{r}, \tag{2}$$

where E is the electron's virtual energy and $U(\boldsymbol{r})$ is the non-Coulomb part of the molecular core potential. For nonpolar molecules this part of the potential is formed by higher multipole moments of the core so that $U(\boldsymbol{r})$ can be considered as a short-range potential: $U(\boldsymbol{r})=0$ for $r>r_c$, where r_c is molecular core radius. We neglect here any relativistic effects (responsible, e.g., for spin-orbit coupling, etc.)

In QDT framework Rydberg molecular states are characterized by the electron orbital momentum l and its projection m onto the molecular axis so that the electron part of their energy is given by the Rydberg formula

$$E_{nlm}=-\frac{1}{2\nu_{nlm}^2}\equiv-\frac{1}{2(n-\mu_{lm})^2}. \tag{3}$$

The integer number n enumerates the spectral lm series. For labeling the electronic states of diatomics we will use the united-atom notation which implies $n\geq l+1$. Note that the axial symmetry of the molecular potential results in m dependence of the QDs μ_{lm} in molecular states unlike the QDs μ_l [14] of spherically symmetric atomic states.

Keeping in mind that further calculation of polarizability will use *ab initio* description for low-excited states and QDGF for Rydberg and continuum states, we assume the above symmetry considerations to separate the radial and angular variables in Eq. (1) for $r>r_c$ and decompose the three-dimensional GF

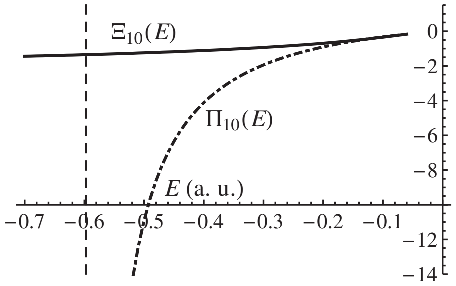

FIG. 1. $\Xi_{10}(E)$ and $\Pi_{10}(E)$ functions for $p\sigma$ state of H_2 molecule. The vertical dashed asymptote of $\Pi_{10}(E)$ corresponds to the "extra" $1p\sigma$ pole at $E=-0.597$ a.u. In the earlier QDT one has $\Xi(E)=\Pi(E)$.

$$G^{\mathrm{QD}}(E,\boldsymbol{r},\boldsymbol{r}')=\sum_{lm}g_{lm}^{\mathrm{QD}}(E,r,r')Y_{lm}(\boldsymbol{r})Y_{lm}^{*}(\boldsymbol{r}') \tag{4}$$

over spherical harmonics to obtain the equation for the radial QDGF $g_{lm}^{\mathrm{QD}}(E,r,r')$ for $r>r_c$, as follows:

$$\left\{\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)-\frac{l(l+1)}{2r^2}+\frac{Z}{r}+E\right\}g_{lm}^{\mathrm{QD}}(E,r,r')=\frac{1}{rr'}\delta(r-r'). \tag{5}$$

The solution of Eq. (5) can be given [14] in terms of Whittaker functions as follows:

$$g_{lm}^{\mathrm{QD}}(E,r,r')=\frac{\nu}{Zrr'}\frac{\Gamma(l+1-\nu)}{\Gamma(l+1+\nu)}W_{\nu,l+1/2}\left(\frac{2Zr_>}{\nu}\right)\times\left[\frac{\Gamma(l+1+\nu)}{\Gamma(2l+2)}M_{\nu,l+1/2}\left(\frac{2Zr_<}{\nu}\right)+\frac{\sin\pi(\mu_{lm}+l)}{\sin\pi(\mu_{lm}+\nu)}\frac{\Xi_{lm}(E)}{\Pi_{lm}(\nu)}W_{\nu,l+1/2}\left(\frac{2Zr_<}{\nu}\right)\right],$$

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

$$\nu=1/\sqrt{-2E}, \tag{6}$$

where $\Gamma(\cdot)$ is the Euler's gamma function. The integer number q is chosen to eliminate the "extra" poles corresponding to the $|nlm\rangle$ states either occupied by the core electrons or those with $n<l+1$. The entire function $\Xi_{lm}(E)$ of energy can be restored from its values at discrete set of points corresponding to the experimental energy levels (3)

$$\Xi_{lm}(E_{nlm})=\Pi_{lm}(n),\quad n\geq l+1. \tag{7}$$

Condition (7) ensures that QDGF (6) has poles at proper (experimental) points E_{nlm}. Figure 1 shows $\Xi_{10}(E)$ and $\Pi_{10}(E)$ functions corresponding to $p\sigma$ state of H_2 molecule; these functions were used in calculation of H_2 polarizability in Sec. III. As it should be expected, both the curves coincide near the threshold $E=0$.

TABLE I. Convergence of the reducing-adding procedure [substitution of N first-excited states according to Eq. (14)] for H_2.

0ω (a.u.)	α_{xx} (a.u.) $N=0$	$N=1$	$N=2$	$N=3$
0.0	4.2975	4.5927	4.5856	4.5833
0.06	4.3451	4.6449	4.6378	4.6354
0.12	4.4964	4.8108	4.8034	4.8010
0.18	4.7793	5.1214	5.1136	5.1110
0.24	5.2574	5.6479	5.6392	5.6364
0.30	6.0791	6.5563	6.5462	6.5431
0.36	7.6592	8.3139	8.3016	8.2978

TABLE II. Static polarizabilities (in a.u.) of H_2 molecule.

Method	α_{xx}	α_{zz}	$\bar{\alpha}$
Expt. [47]	6.303	4.913	5.376
Exact variational [22]	6.3805	4.5777	5.1786
Double perturbation [23]	6.349	4.912	5.433
Sum-over states [24]	6.41	4.57	5.18
Sum-over states with account for nonadiabatic effects [25]	6.3866	4.5786	5.1812
Variation perturbation [26]	6.3873	4.5786	5.1815
Full CI [27]	6.4104	4.5282	5.1556
Full CI [28]	6.3992	4.5765	5.1841
MC-SCF [29]	6.416	4.597	5.203
James-Coolidge wave functions [30]	6.3866	4.5786	5.1812
SOPPA [31]	6.4495	4.5676	5.1949
QMC [32]	6.42	4.53	5.16
TDGI [32]	6.4310	4.5944	5.2066
MP4(SD) [33]	6.407	4.585	5.192
TDDFT [34]			5.1816
Finite-difference Hartree-Fock [35]	6.4487		
Sum-over states [36]	6.3943	4.5825	5.1864
Variationally stable [38]	6.3838	4.5769	5.1792
CISD [37]	6.3970	4.5749	5.1891
TD-CISD [37]	6.3989	4.5845	5.1893
QDGF (this work)	6.3822	4.5926	5.1892

The frequency-dependent dipole polarizability tensor of a system consisting of p_s equivalent optical electrons in quantum state $|s\rangle$ can be expressed through the one-electron GF as follows:

$$\alpha_{ij}(\omega) = p_s \langle s | D_i \hat{G}(E_s+\omega) D_j + D_j \hat{G}(E_s-\omega) D_i | s\rangle . \tag{8}$$

Here $i,j=x,y,z$; the electron dipole moment $\boldsymbol{D}=\boldsymbol{r}$ or $\boldsymbol{r}'$. The GF $\langle \boldsymbol{r}|\hat{G}(E)|\boldsymbol{r}'\rangle = G(E,\boldsymbol{r},\boldsymbol{r}')$ can be expressed in terms of spectral expansion over discrete $|d\rangle$ and continuous $|c\rangle$ states

$$G(E,\boldsymbol{r},\boldsymbol{r}') = \sum_d \frac{\Psi_d^*(\boldsymbol{r}')\Psi_d(\boldsymbol{r})}{E-E_d} + \int dE_c \frac{\Psi_c^*(\boldsymbol{r}')\Psi_c(\boldsymbol{r})}{E-E_c} . \tag{9}$$

Normally the polarizabilities calculated for the ground state $|d\rangle = |0\rangle$. As it was mentioned above, for a realistic description of molecular electron's dynamics the wave functions of highly excited and continuum states can be chosen in QDT approximation while those of the first N low-excited states (including the ground one) can be substituted by *ab initio* wave functions obtained with the help of computational chemistry (CC) methods

$$\langle \boldsymbol{r}|c\rangle = \Psi^{\mathrm{QD}}_{E_c lm}(\boldsymbol{r}), \tag{10}$$

$$\langle \boldsymbol{r}|d\rangle = \Psi^{\mathrm{QD}}_{nlm}(\boldsymbol{r}), \quad d \geq N, \tag{11}$$

$$\langle \boldsymbol{r}|d\rangle = \Psi^{\mathrm{CC}}_{d}(\boldsymbol{r}), \quad 0 \leq d < N. \tag{12}$$

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 $N=0$ and none of $\langle \boldsymbol{r}|d\rangle$ wave functions (12) equal to $\Psi^{\mathrm{CC}}_d(\boldsymbol{r})$.

Such substitution in the spectral expansion (9) leads to reduced-added QDGF

$$\mathcal{G}(E,\boldsymbol{r},\boldsymbol{r}') = G^{\mathrm{QD}}(E,\boldsymbol{r},\boldsymbol{r}') - \sum_{d=0}^{N-1} \frac{\Psi_d^{\mathrm{QD}*}(\boldsymbol{r}')\Psi_d^{\mathrm{QD}}(\boldsymbol{r})}{E-E_d} + \sum_{d=0}^{N-1} \frac{\Psi_d^{\mathrm{CC}*}(\boldsymbol{r}')\Psi_d^{\mathrm{CC}}(\boldsymbol{r})}{E-E_d} . \tag{13}$$

Again, $N=0$ means the absence of the reducing-adding procedure so that the sums in Eqs. (13) and (14) vanish and $\mathcal{G} = G^{\mathrm{QD}}$ for $N=0$.

The reduced-added QDGF (13) was used in calculations of molecular polarizabilities below according to Eq. (8) with $G=\mathcal{G}$. Since more reliable results can be obtained by using the reported theoretical (calculated *ab initio*) or experimental (e.g., from measured oscillator strengths) values $\langle 0|\hat{D}_i|d\rangle$, $0 < d < N$, of the transition dipole moments, we give the corresponding expression for the diagonal components of the polarizability tensor

$$\alpha_{ii}(\omega) = \alpha_{ii}^{\mathrm{QD}}(\omega) - p_0 \sum_{\substack{nlm(15)\\ N\ \text{first levels}}} \left(\frac{|\langle 0|\hat{D}_i|nlm\rangle|^2}{E_0 - E_{nlm} - \omega} + \frac{|\langle 0|\hat{D}_i|nlm\rangle|^2}{E_0 - E_{nlm} + \omega} \right) + p_0 \sum_{d=0}^{N-1} \left(\frac{|\langle 0|\hat{D}_i|d\rangle|^2}{E_0 - E_d - \omega} + \frac{|\langle 0|\hat{D}_i|d\rangle|^2}{E_0 - E_d + \omega} \right). \tag{14}$$

Here $i=x$ or y for the perpendicular and $i=z$ for parallel polarizability; the mean polarizability $\bar{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz})$ determines the refractivity index of a gas of molecules and is also frequently reported in literature. The first term in Eq. (14), α^{QD}, is calculated according to Eq. (8) with $G=G^{\mathrm{QD}}$. As it is seen from Eq. (14), one needs *ab initio* calculation for the initial (ground) state wave function $\Psi_0^{\mathrm{CC}}(\boldsymbol{r})$ to evaluate its

TABLE III. Dynamic polarizability α_{zz} of H_2 in a.u.

ω (a.u.)	QDGF	Ref. [36]	Ref. [26]	Ref. [31]	Ref. [32]	Ref. [24]
0.0	6.3822	6.3943	6.3873	6.4495	6.42	6.4067
0.07	6.5052	6.5136				
0.072	6.5124		6.5164	6.5812	6.55	6.5467
0.08	6.5439	6.5511				
0.0834	6.5584		6.5618	6.6276	6.59	6.59
0.1	6.6390	6.6432				
0.1045	6.6637		6.6659	6.7338	6.69	6.6967
0.13	6.8298	6.8282				
0.1363	6.8781		6.8776	6.9501	6.90	
0.15	6.9997	6.9872				
0.1535	7.0258		7.0235	7.0990	7.04	7.0567
0.19	7.4299	7.4107				
0.1979	7.5366		7.5256	7.6136	7.52	7.5567
0.23	8.0589	8.0219				
0.2354	8.1633		8.1412	8.2437	8.09	
0.25	8.4739	8.4254	8.4481	8.5568	8.37	
0.3	10.0029	9.8861	9.9160	10.0649	9.68	
0.35	12.7310	12.5902	12.6126	12.8558		
0.3748	15.1443		14.9610	15.3084		15.1
0.4	19.2819	19.0694	18.9847	19.5639		
0.45	58.2152	58.2120	54.3276	62.0977		
0.48	−77.3505	−76.6628				
0.51	−12.0085	−12.6516				
0.54	23.3734	23.7352				
0.57	25.6037	34.1702				

TABLE IV. Dynamic polarizability α_{xx} of H_2 in a.u.

ω (a.u.)	QDGF	Ref. [36]	Ref. [26]	Ref. [31]	Ref. [32]	Ref. [24]
0.0	4.5927	4.5825	4.5786	4.5676	4.53	4.5667
0.07	4.6641	4.6532				
0.072	4.6683		4.6562	4.6445	4.60	4.6467
0.08	4.6866	4.6754				
0.0834	4.6950		4.6834	4.6715	4.62	4.67
0.1	4.7417	4.7298				
0.1045	4.7558		4.7457	4.7331	4.68	4.7367
0.13	4.8513	4.8384				
0.1363	4.8788		4.8715	4.8576	4.79	
0.15	4.9448	4.9313				
0.1535	4.9631		4.9576	4.9427	4.87	4.9467
0.19	5.1914	5.1762				
0.1979	5.2510		5.2503	5.2328	5.13	5.2367
0.23	5.5399	5.5238				
0.2354	5.5970		5.6017	5.5800	5.43	
0.25	5.7660	5.7496	5.7738	5.7493	5.57	
0.3	6.5563	6.5427	6.5713	6.5367		
0.35	7.9185	7.9177	7.9320	7.8834		
0.3748	9.0206		9.0182	8.9633		8.98
0.4	10.7426	10.7849	10.6930	10.6421		
0.45	20.5823	20.7920	19.4400	20.0551		
0.48	101.4130	103.6960				
0.51	−14.7166	−13.7345				
0.54	7.4775	10.7884				
0.55	129.8770	341.0165				

matrix elements with the QD states even without reducing-adding substitution.

III. BENCHMARK: H_2 MOLECULE

The molecular hydrogen is one of the simplest molecules with well-studied properties, so it is a good benchmark for testing any methods before their application to more complex systems. The polarizability of H_2 has been calculated for several decades up to now by various methods. Good accuracy achieved by semianalytical variational approaches [22–26] was validated by various computational methods [27–38] among whose configuration interaction (CI) [27,28], multiconfigurational self-consistent field (MC-SCF) [29], second-order polarization propagator approximation (SOPPA) [31], quantum Monte Carlo (QMC), time-depended gauge invariant (TDGI) [32] time-depended density-functional theory (TDDFT) [34], and CI with single and double excitations (TD-CISD) [37] (for more detailed review of H_2 polarizability calculations see, e.g., Refs. [36–38]. and reference therein). In this section we present our calculations of H_2 polarizabilities and compare them to other theoretical and experimental values available.

The ground $X\,^1\Sigma_g^+$ state configuration of hydrogen molecule includes two equivalent electron in $1s\sigma$ orbital that implies $p_0=2$ in Eq. (14). This wave function was calculated in GAUSSIAN98 package [39] by relativistic Hartree-Fock (RHF) method [40] with the 6-31G* basis set [41]. The ionization threshold was determined by interpolation the data presented in Refs. [42,43] at the equilibrium internuclear separation 1.401 a.u. of the neutral H_2 molecule. To build the QD-related functions $\mu_{lm}(\nu)$ and $\Xi_{lm}(\nu)$ which enter Eq. (6) we used the excited-state energies reported in Refs. [44,45] for $^1\Sigma_u$ and $^1\Pi_u$ correspondingly. Due to the dipole selection rules for homonuclear diatomics, only $^1\Sigma_u^+$ states contribute into the parallel dipole polarizability α_{zz} and only $^1\Pi_u$ states into the perpendicular polarizability α_{xx}.

The reducing-adding procedure (14) consisted in substituting the transition moments to low-excited states by their values taken from Refs. [45,46] at the equilibrium internuclear separation. For α_{xx} it was sufficient to substitute only $N=1$ state; for α_{zz} the convergence was achieved at $N=3$. The further increasing of N changes the results by not more than 0.2%. The convergence of the reducing-adding procedure for H_2 is shown in Table I.

Comparison of QDGF calculations for parallel, perpendicular, and mean static polarizabilities of molecular hydrogen to other calculations and experiment is given in Table II. Our values are in good agreement (within 0.4%) with the presented results.

The QDGF results for dynamic polarizabilities are presented in Tables III and IV together with results of other calculations. When comparing these values it should be kept in mind that the positions of the excited levels [and therefore the poles, i.e., resonances in the frequency dependencies $\alpha(\omega)$] are different in various sources. We used the energy levels from Refs. [45,46] as did the authors of Ref. [36]. The first resonance occurs at $\omega=0.4858$ a.u. for α_{xx} and at $\omega=0.4687$ a.u. for α_{zz}; the second resonance occurs at $\omega=0.5509$ a.u. for α_{xx} and at $\omega=0.5458$ a.u. for α_{zz}. These resonances are seen in the Fig. 2 as poles of the frequency dependence of the mean polarizability $\bar{\alpha}(\omega)$.

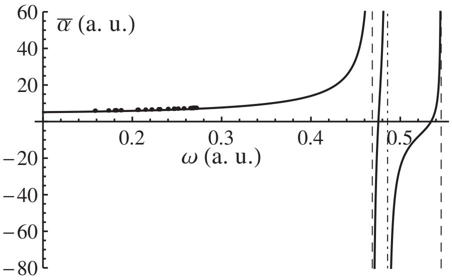

FIG. 2. Mean polarizability $\bar{\alpha}(\omega)$ of H_2 molecule. Dashed asymptotes show the poles coming from $\alpha_{zz}(\omega)$. Dot-dashed asymptote corresponds to the first resonance of $\alpha_{xx}(\omega)$. Circles show the experimental values extracted from the refractivity measurement [48].

IV. RESULTS AND DISCUSSION: ALKALI-METAL DIMERS

In this section we present the results of calculation of dynamic polarizability for alkali-metal dimers Li_2, Na_2, and Rb_2. In the united-atom model all these molecules in the ground $X\,^1\Sigma_g^+$ states contain two $s\sigma$ electrons over the core molecular orbitals ($p_0=2$).

A. Li_2

The ground-state wave function of lithium dimer was calculated using Hartree-Fock (HF) method (with Møller-Plesset correlation energy correction) [40] with the 6-31G* basis set. The QD-related functions were built using the spectroscopic data from the Ref. [49]. for the equilibrium internuclear separation 5.051 a.u. Tables V and VI contain the values of parallel and perpendicular dynamic polarizabilities calculated according to Eq. (14) without reducing-adding procedure (α^{QD}, the second column) and with substitution of the transition moment to the first-excited state by the moments reported in the literature (columns 3–6). Substitution of the second-excited state results in only slight (about 0.8%) modification so we have $N=1$ for lithium

TABLE V. Parallel polarizability $\alpha_{zz}(\omega)$ (in a.u.) of Li_2 (the first resonance at $\omega=0.067\,489$ a.u.) calculated using different sources for dipole transition moments.

ω (a.u.)	$\langle X\,^1\Sigma_g^+\lvert D_z\rvert 1\,^1\Pi_u\rangle$ from QDT	Ref. [52]	Ref. [50]	Ref. [51]	Ref. [54]
0.0	406.84	302.13	317.30	303.48	306.16
0.003	407.67	302.75	317.95	304.10	306.79
0.006	410.17	304.62	319.91	305.98	308.68
0.009	414.41	307.80	323.25	309.18	311.90
0.012	420.49	312.36	328.03	313.76	316.52
0.015	428.57	318.41	334.37	319.84	322.65
0.018	438.87	326.14	342.47	327.60	330.48
0.021	451.69	335.76	352.55	337.25	340.22
0.024	467.44	347.57	364.93	349.11	352.18
0.027	486.64	361.97	380.04	363.58	366.77
0.03	510.03	379.53	398.44	381.21	384.55
0.033	538.58	400.97	420.91	402.75	406.27
0.036	573.71	427.36	448.57	429.25	432.99
0.039	617.40	460.19	482.97	462.22	466.24
0.042	672.61	501.71	526.47	503.92	508.29
0.045	743.88	555.35	582.66	557.78	562.60
0.048	838.61	626.70	657.41	629.44	634.86
0.051	969.72	725.61	760.98	728.76	735.00
0.054	1161.87	870.83	913.00	874.59	882.04
0.057	1469.10	1103.84	1156.77	1108.57	1117.91
0.06	2039.36	1539.83	1612.21	1546.28	1559.06
0.063	3603.59	2789.38	2907.36	2799.90	2820.72

TABLE VI. Perpendicular polarizability $\alpha_{xx}(\omega)$ (in a.u.) of Li_2 (the first resonance at $\omega=0.0931$ a.u.) calculated using different sources for dipole transition moments.

ω, a.u.	$\langle X\,^1\Sigma_g^+\vert D_z\vert 1\,^1\Pi_u\rangle$ from				
	QDT	Ref. [53]	Ref. [50]	Ref. [51]	Ref. [54]
0.0	153.04	168.42	174.38	169.99	169.19
0.006	153.67	169.10	175.09	170.69	169.89
0.012	155.57	171.20	177.26	172.81	171.99
0.018	158.84	174.81	181.00	176.45	175.62
0.024	163.67	180.14	186.52	181.32	180.97
0.03	170.33	187.49	194.14	189.25	188.35
0.036	179.27	197.34	204.35	199.20	198.26
0.042	191.13	210.43	217.91	212.42	211.41
0.048	206.97	227.91	236.02	230.06	228.97
0.054	228.49	251.66	260.64	254.04	252.83
0.06	258.66	284.94	295.14	287.65	286.28
0.066	303.07	333.96	345.94	337.14	335.53
0.072	373.66	411.90	426.72	415.83	413.83
0.078	501.48	553.03	573.01	558.33	555.64
0.084	799.17	881.77	913.80	890.27	885.96
0.09	2248.95	2483.00	2573.76	2507.10	2494.87

dimer. In Table VII the calculated static (at $\omega=0$) polarizabilities α_{xx}, α_{zz}, and $\bar{\alpha}$ are compared to the *ab initio* calculations and to the experiment. The slight discrepancy seen in Table VII can be explained by the difference between the transition moment values reported in various sources. Indeed, with transition moments substituted by their values given in Refs. [50,51], our static polarizabilities are in very good agreement with those reported in these references.

B. Na_2

For calculation of the ground-state wave function of sodium dimer we used the same method of that for lithium. The QD-related functions were built with the help of Na_2 Rydberg spectra given using the spectroscopic data from the Ref. [58]. The results of the polarizability calculation are presented in Table X. The columns with $N=0$ contain the results without reducing-adding procedure, i.e., without substitution of the transition moments. Good convergence is achieved after substitution of $N=1$ excited states for both perpendicular and parallel polarizabilities. The results in the corresponding columns are calculated using the *ab initio* transition moments reported in Ref. [59]. Unlike the case of Li_2 there is no experimental oscillator strengths for Na_2 available in literature, to our knowledge. The first resonances occur at $\omega=0.09257$ a.u. for α_{xx} and $\omega=0.0669$ a.u. for α_{zz}.

Table IX contain a comparison of our static polarizability calculation with other theoretical and experimental results. Our α_{zz} values exceed significantly the DFT (B3PW91) results (while α_{xx} are in good accordance with other calculations). It was pointed out in Ref. [56], that DFT gives good results for the perpendicular polarizability and underestimates the parallel one. Overall, our QDGF method with substitution of only one excited state for both the polarizability components gives results with an accuracy comparable to other methods [in particular, CCSD(T)].

C. Rb_2

To calculate the ground-state wave function we used LANL2DZ basis set, which included D95V basis set [62] on first-row atoms, and Los Alamos National Laboratory electron-correlated pseudopotentials plus double-zeta basis sets on Na-Bi [63]. For reconstruction of the QD-related functions we use Rb_2 spectrum from Ref. [64]. Calculation of α_{xx} required substitution of $N=2$ excited states while α_{zz} was calculated with $N=1$. The transition moments for sub-

TABLE VII. Static polarizabilities (in a.u.) of Li_2 molecule.

Method	α_{xx}	α_{zz}	$\bar{\alpha}$
Multideterminant ket with polynomial factor [50]	174	318	222
As above, without polynomial factor [50]	170	314	218
TDGI [51]	160	303	207.67
CI(ν)+CPP [55]	163.9	301.8	209.87
CCSD(T) [56]	169.2	309.7	216.03
QDGF (this work with transition moments from Refs. [52,53]	168.42	302.13	212.99
As above, Ref. [50]	174.38	317.30	222.02
As above, Ref. [51]	169.99	303.48	214.49
As above, Ref. [54]	169.19	306.16	214.85
Experiment [57]			229.45 ± 20.24

TABLE VIII. Dynamic polarizability (in a.u.) of Na_2 (for $N=1$ the transition dipole moments are substituted from Ref. [59]).

ω (a.u.)	α_{xx}		α_{zz}	
	$N=0$	$N=1$	$N=0$	$N=1$
0.0	196.01	209.10	555.23	399.72
0.003			556.34	400.51
0.006	196.85	209.99	559.68	402.92
0.009			565.34	406.97
0.012	199.40	212.71	573.47	412.80
0.015			584.28	420.54
0.018	203.78	217.38	598.05	430.41
0.021			615.21	442.70
0.024	210.92	224.23	636.27	457.80
0.027			661.99	476.23
0.03	218.98	233.61	693.33	498.69
0.033			731.66	526.15
0.036	230.67	246.09	778.86	559.97
0.039			837.65	602.10
0.042	246.05	262.54	912.11	655.45
0.045			1008.53	724.53
0.048	266.45	284.35	1137.20	816.72
0.051			1316.25	945.01
0.054	293.97	313.81	1580.73	1134.51
0.057			2007.82	1440.48
0.06	332.33	354.90	2809.58	2014.87
0.063			4849.90	3476.56
0.066	388.65	415.28		
0.072	478.50	511.64		
0.078	642.91	688.06		
0.084	1037.95	1112.09		
0.09	3276.71	3515.89		

stitution were taken from Ref. [65]. The results for the dynamic polarizabilities are presented in Table X in a form similar to those in Table VIII for Na_2. The first resonances occur at $\omega=0.0668$ a.u. for α_{xx} and $\omega=0.0492$ a.u. for α_{zz}.

Our static value of Rb_2 polarizability is compared in Table XI to other calculations [56,66]. Our results differ from those of Ref. [56] which overestimates the experimental value because the calculations of Ref. [56] used an internuclear separation greater than the experimental value for Rb_2 molecule. As it was for Na_2, our results differ from those calculated using DFT and agree well with CCSD(T) calculations [66].

TABLE IX. Static polarizabilities (in a.u.) of Na_2.

Method	Reference	α_{xx}	α_{zz}	$\bar{\alpha}$
CI(ν)+CPP	[55]	197.2	375.5	256.63
CCSD(T)	[56]	209.7	389.9	269.77
B3PW91	[60]	205.73	351.78	254.41
CCSD(T)	[60]	206.07	377.71	263.28
CI(ν)+CPP	[61]	201.6	370.1	257.77
QDGF	This work	209.10	399.72	272.64
Expt.	[57]			269.9 ± 20.2

TABLE X. Dynamic polarizability (in a.u.) of Rb_2 (for $N>0$ the transition dipole moments are substituted from Ref. [65]).

ω (a.u.)	α_{xx}		α_{zz}	
	$N=0$	$N=2$	$N=0$	$N=1$
0.0	476.39	402.13	994.93	830.45
0.002			996.35	831.74
0.004			1000.65	835.60
0.005	479.03	404.35		
0.006			1007.9	842.13
0.008			1018.26	851.47
0.010	487.12	411.16	1031.93	863.79
0.012			1049.2	879.37
0.014			1070.48	898.58
0.015	501.25	423.04		
0.016			1096.27	921.91
0.018			1127.25	949.96
0.020	522.74	441.17	1164.87	984.12
0.022			1208.52	1023.72
0.024			1261.46	1071.89
0.025	552.53	466.18		
0.026			1325.25	1130.05
0.028			1402.75	1200.87
0.030	594.39	501.38	1498.07	1288.15
0.032			1617.22	1397.51
0.034			1769.42	1537.54
0.035	652.96	550.62		
0.036			1969.48	1722.06
0.038			2242.8	1974.77
0.040	736.93	621.19	2636.85	2339.98
0.042			3251.85	2911.26
0.044			4342.1	3926.12
0.045	863.08	727.19		
0.050	1068.28	899.53		
0.055	1451.88	1221.61		
0.060	2404.69	2021.34		
0.065	8611.63	7229.85		

TABLE XI. Static polarizabilities (in a.u.) of Rb_2.

Method	Ref.	α_{xx}	α_{zz}	$\bar{\alpha}$
CCSD(T)	[66]	419.9	815.2	551.7
B3LYP	[66]	394.4	761.1	516.63
CCSD(T)	[56]	445.4	916.1	602.0
QDGF	This work	402.13	830.45	544.90
Expt.	[57]			533 ± 40

TABLE XII. Cauchy moments (in a.u.) for the molecules considered.

Molecule	$S_{\parallel}(-4)$	$S_{\perp}(-4)$	$S_{\parallel}(-6)$	$S_{\perp}(-6)$
H_2, this work	24.8929	14.3347	97.8995	51.8380
H_2, Ref. [36]	23.79 ± 1.87	14.14 ± 2.59	100.5 ± 6.0	54.11 ± 8.58
Li_2, this work[a]	6.88×10^4	1.92×10^4	1.47×10^7	2.12×10^6
Li_2, Ref. [67]	$(6.16..6.54) \times 10^4$	$(1.78..1.82) \times 10^4$	$(1.31..1.42) \times 10^7$	$(1.94..2.02) \times 10^6$
Na_2, this work	8.86×10^4	2.47×10^4	1.63×10^7	2.39×10^6
Rb_2, this work	3.24×10^5	8.84×10^4	1.03×10^8	1.96×10^7

[a] Transition dipole moments from Ref. [51].

D. Cauchy moments

Far away from the resonances the frequency dependence of polarizability can be expressed in terms of Cauchy moments $S(-2k-2)$ as

$$\alpha(\omega) = \sum_{k=0}^{\infty} S(-2k-2)\omega^{2k}.$$

Although the set of Cauchy moments reduces the amount of data needed to present the $\alpha(\omega)$ curve, they are normally calculated with an error greater than the error of the $\alpha(\omega)$ data [36]. Nevertheless, we present in Table XII the Cauchy moments for all the molecules considered above up to $k=2$ for parallel and perpendicular polarizabilities. Since $S(-2) = \alpha(0)$ and the static polarizabilities are presented in the tables above, Table XII contains $S(-4)$ and $S(-6)$ only.

V. CONCLUDING REMARKS

The QDGF with the reducing-adding procedure of the low-excited states provides an exact account for the high-excited and continuum electronic states. As an application, we present simple and efficient semianalytical methods for calculation of electric frequency-dependent dipole polarizability for simple homonuclear diatomics (alkali-metal dimers). Our benchmark calculation of polarizability of molecular hydrogen shows that the accuracy of the proposed method is comparable to that of the existing methods of computational quantum chemistry.

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