Dynamic hyperpolarizability of the one-dimensional hydrogen atom with a \( \delta \)-function interaction

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The dynamic hyperpolarizability of a particle bound by the one-dimensional \( \delta \)-function potential is obtained in closed form. On the first step, we analyze the singular structure of the non-linear response function as given by the sum-over-state expression. We express its poles and residues in terms of the wave-number \( k \). On the second step, we calculated the frequency dependence of the response function by integration over \( k \). Our method provides a unique opportunity to check the convergence of numerical methods, and is in a perfect agreement with the static and high frequency limits obtained by different theories. The former is obtained using the approach of Swenson and Danforth (J. Chem. Phys. 57, 1734 (1972)). The asymptotic decay is studied using the method of Scandolo and Bassani (Phys. Rev. B 51, 6925 (1995)). Its extension to the case of quadrupole polarizability reveals a universal (not dependent on the choice of the system) asymptotic behavior of the hyperpolarizability.

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I. INTRODUCTION

There is only a small number of exactly solvable realistic quantum systems. The hydrogen atom is one of the most experimentally and theoretically studied. Remarkably, expressions for the Green function \([1]\), transition matrix elements between the ground and excited states \([2]\), and a number of other properties of this system exist in closed form. However, the complexity of the matrix elements as well as of the sum-over-states (SOS) expressions for the nonlinear optical response functions \([3]\) hinders an analytic computation of its dynamic hyperpolarizabilities. Already expressions for the dynamic polarizability of hydrogen atom are very complicated \([4]\).

To describe the multiphoton ionization of atomic hydrogen it is sufficient to consider summations over all intermediate bound states \([5]\). In contrast, the computation of the nonlinear optical response is much more involved since summations over the continuum states should also be performed \([6]\). This considerably complicates derivations and calls for the development of new methods. Thus, Mizuno \([7]\) used the sturmian coulomb Green function \([8]\) in order to compute the third harmonic generation coefficient of the hydrogen atom. These results were extended by Shelton \([9]\) to other third order processes. Although written in analytical form, they still contain infinite sums, and thus can only be analyzed numerically. Therefore, it is desirable to have a simpler model system that would allow for a closed-form solution for non-linear optical responses.

A particle bound by a one-dimensional \( \delta \)-function potential bears a close resemblance to the three-dimensional hydrogen atom with Coulomb potential. Despite its simplicity, the system is attractive for the theoretical analysis because like the hydrogen atom it contains both discrete and continuum eigenstates. Also the Green function of these two systems shows remarkable analogies \([10]\). The \( \delta \)-potential allows for a great simplification of the analytic work since one only needs to carry out the integration of relatively simple functions.

The frequency-dependent electric polarizability of this system has previously been computed by explicit solution of the time-dependent Schrödinger equation with uniform time-dependent electric field and expansion of the charge density in the perturbed ground state up to and including terms linear in applied electric fields \([11]\). Recently, the result has been confirmed using a perturbation technique \([12]\) based on the work by Nozières \([13]\). Here, we present results for the lowest order non-zero hyperpolarizability due to the combination of two electric-dipole and one electric-quadrupole transitions. This response function describes the second-harmonic generation (SHG) process. SHG due to only dipole transitions is forbidden because the system possesses an inversion symmetry. The next order non-linear response (the third harmonic generation) due to the combination of four dipole transition should have a comparable magnitude and will be analyzed elsewhere.

As a starting point, in Sec. II we study singular properties of the SHG response function as given by equations of Orr and Ward \([5]\). We assume that all conditions of validity of these formulas are fulfilled. The reader is referred to the book of Shen \([14]\) for the discussion of relevance of these expressions for a certain experimental situation. Using expressions for the poles and residues of the response function obtained here we perform the actual computation for the one-dimensional hydrogen in Sec III. Finally, we qualitatively analyze obtained results in the low and high frequency limits and compare them with prediction of other theories (Sec. IV).

In this respect we refer to the work of Fernández and Castro \([15]\) which gives an introduction to the method that avoids an integration over the continuum spectrum. Based on the original idea of Swenson and Danforth \([16]\), and extending the derivation of Austin \([17]\), they obtained a recursive equation that relates the expectation values of \( x^N \) operator at different level of the perturbation expansion. They used the method to find a perturbative correction to the ground state energy and to describe the appearance of resonant states in the presence of static electric field. As will be shown below, the same approach can be used to obtain an arbitrary order static hyperpolarizability \([18]\). We performed corresponding calculations for our model system and found an agreement with the static limit of our SOS-derived expression.

The high frequency limit of the second-harmonic genera-
tion in dipole approximation was obtained by Scandolo and Bassani [19]. Later, this result was generalized to higher harmonic generation processes using the general quantum theory of Kubo optical response function [20]. It yields $1/\omega^{2n+2}$ decay of $n$-th order response function. We show that non-local response (the quadrupole polarization) dictates a different asymptotic behavior, $1/\omega^4$ for the SHG process, in agreement with our SOS results.

In Appendix A we outline calculations of the transition matrix elements for this system, and in Appendix B we derive the frequency dependence of the SHG response function from the corresponding residues. An extensive use of the complex analysis and generalized functions is made. All calculations are done analytically. The final results are expressed in terms of elementary functions.

II. SINGULARITIES OF THE SHG RESPONSE FUNCTION

The poles and residues of the second-order response functions can be derived from the microscopic expressions for the nonlinear polarizations (as, for example, given by Eq. (43) of Ref. 3) assuming certain form of the light-matter interaction. It is important to notice that corresponding perturbation operators $V$ as well the polarization operator $P$ must be used in the renormalized form with vanishing expectation values in the ground state

$$V = \tilde{V} - \langle \tilde{V} \rangle_{gg},$$  
$$P = \tilde{P} - \langle \tilde{P} \rangle_{gg},$$

where $\tilde{V}$ and $\tilde{P}$ are the bare operators. Other forms of presenting the non-linear response functions are also known. For example, lifting the requirement on the diagonal elements to be zero leads to the appearance of additional terms [21]. They can be traced back to the secular divergence problem. Clearly, both forms lead to identical results at the end. To make our manuscript self-contained, we reproduce here the equation of Orr and Ward for a general second-order process ($\omega_r = \omega_1 + \omega_2$) using slightly simplified notations:

$$P^{\omega} = \frac{K(\omega_1, \omega_2)}{(-\hbar)^2} I_{1,2} \sum_{m,n} \frac{\langle P \rangle_{gm} \langle V^{\omega_1} \rangle_{mn} \langle V^{\omega_2} \rangle_{ng}}{(\Omega_{mg} - \omega_\sigma)(\Omega_{ng} - \omega_1)} + \frac{\langle V^{\omega_1} \rangle_{gm} \langle V^{\omega_2} \rangle_{mn} \langle P \rangle_{ng}}{(\Omega_{mg} + \omega_2)(\Omega_{ng} + \omega_\sigma)} + \frac{\langle V^{\omega_2} \rangle_{gm} \langle P \rangle_{mn} \langle V^{\omega_1} \rangle_{ng}}{(\Omega_{mg} + \omega_2)(\Omega_{ng} - \omega_1)}. \tag{3}$$

The simplification concerns the use of only renormalized operators, while in the original formulation the authors had both renormalized and bare operators. Such transformation is always possible since $\langle V \rangle_{ng} = \langle V \rangle_{ng}$ (the same also holds for $P$). As a consequence, the expression acquires a more symmetrical form. Here, $I_{1,2}$ denotes the average of all terms generated by permuting $\omega_1$ and $\omega_2$. $K$ is a numerical factor that depends on the permutational symmetry of incident photons. For the SHG process it is equal to $\frac{1}{2}$. The summations are running over all excited states excluding the ground state. $\Omega_{mg}$ denotes the energy difference between the excited state $m$ and the ground state (labeled by $g$). In order to avoid divergencies at the resonances, a phenomenological damping ($i\Gamma$) of excited states is introduced, $\Omega_{mg} = E_m - E_g + i\Gamma$. This shifts the poles of the response functions away from the real axis on the complex plane.

If the damping constant $i\Gamma$ is small, it has no relevance for the derivation of residues. That is why we provisionally assume that all poles lie on the real axis ($\Omega_{mg} = \Omega_{ng}$). Furthermore, a simple analysis of Eq. (3) shows that the poles of nonlinear polarization are symmetrically situated around $\omega = 0$. Additional symmetry also exists for their residues.

$$\text{Res}_{\Omega_{ng}} P^{2\omega} = -\frac{1/2}{(-\hbar)^2} \sum_{m} \left\{ \frac{\langle P \rangle_{gm} \langle V^{\omega} \rangle_{mn} \langle V^{\omega} \rangle_{ng}}{\Omega_{mg} - 2\Omega_{ng}} \right\} + \frac{\langle P \rangle_{mn} \langle V^{\omega} \rangle_{ng} \langle V^{\omega} \rangle_{gm}}{\Omega_{mg} + \Omega_{ng}} \tag{6}.$$
Here, we substituted the frequencies and the symmetry factor $K$ and expanded the symmetrization operator. A bar over the matrix elements denotes their symmetrization, which signifies the equivalence of two incident photons and follows from the application of $I_{1,2}$ to the whole expression. In the same way, we write an expression for the residue of the polarization at $\omega = \Omega m_{g}/2$ where only one term contributes:

$$\text{Res}_{\Omega m_{g}/2} P^{2\omega} = -\frac{1}{4} \left(\frac{-\hbar}{\hbar}\right)^{2} \sum_{n} \left\{ \frac{\langle P\rangle_{gm} \langle V\rangle_{mn} \langle V\rangle_{ng}}{\Omega_{ng} - 1/2\Omega m_{g}} \right\}.$$

Equations (6) and (7) are obtained from the general theory, and, therefore, are valid for systems of arbitrary dimensionality and for different light-matter interaction mechanisms. They are not only useful in present theoretical analysis, but also can bring a substantial computational savings when used in \textit{ab initio} calculations for realistic systems. This directly follows from the estimates on the number of floating-point operations needed to directly evaluate Eq. (5) ($N_{\text{sos}} = O(N_{\omega} \cdot N^{2})$) in comparison with a two-step procedure, where the residues (Eqs. (6) and (7)) are computed with numerical cost of $N_{\text{sos}} = O(N_{\omega})$ only, and the frequency dependence is obtained on the second step using $N_{\text{sos}} = O(N_{\omega} \cdot N)$ operations. Here we assumed that the system has $N$ excited states and $N_{\omega}$ frequency points are required.

On the last step, we specify Eqs. (6) and (7) for the model system. Since the SHG is strictly forbidden in centrosymmetric systems within the electric dipole approximation ($\chi^{(2)}_{\omega} = 0$), we will be considering a one-component response function $\chi^{(2)}_{\omega}$ with the dipole perturbation operator $V = -e x F$, and the quadrupole polarization $\tilde{P} = e x^{2}$. Furthermore, we make use of atomic units, the conversion is done by setting the electron charge $e = -1$, and $\hbar = 1$. Finally, the differentiation with respect to the external electric field $F$ are performed according to the definition of the response function (Eq. (4)).

We will denote two contributions to $A^{(\omega)}_{ijk}(m)$ as $A^{I}(k)$ and $A^{II}(k)$, and $B^{(\omega)}_{ijk}(m)$ will be denoted as $B(k)$. It is natural to name them as \textit{spectral functions of the second-order nonlinear response} in analogy with the spectral functions in the many-body perturbation theory.

\begin{align*}
A^{I}(k) &= -\frac{1}{2} \sum_{q} \frac{\langle x^{2}\rangle_{0q} \langle x \rangle_{k0} \langle x \rangle_{k0}}{\Omega_{q0} - 2\Omega_{k0}}, \quad \text{(8a)} \\
A^{I}(k) &= -\frac{1}{2} \sum_{q} \frac{\langle \Delta x^{2} \rangle_{qk} \langle x \rangle_{k0} \langle x \rangle_{q0}}{\Omega_{k0} + \Omega_{q0}}, \quad \text{(8b)} \\
B(k) &= -\frac{1}{2} \sum_{q} \frac{\langle x^{2}\rangle_{0q} \langle x \rangle_{k0} \langle x \rangle_{q0}}{2\Omega_{q0} - 2\Omega_{k0}}. \quad \text{(8c)}
\end{align*}

Instead of a discrete state number $m$, these functions now depend on the wave-number $k > 0$ that characterizes excited states of the system as will be shown below. In order to be consistent with naming of states of the one-dimensional hydrogen that will be introduced below we changed the notation for the ground state to 0. We also introduced the notation $\Delta x^{2} = x^{2} - \langle x^{2}\rangle_{00}$ and took into account that $\langle x \rangle_{00} = 0$ for our model system.

## III. DYNAMIC HYPERPOLARIZABILITY OF THE ONE-DIMENSIONAL HYDROGEN

The system discussed here is described by the one-dimensional time-independent Schrödinger equation that can be written in the dimensionless form:

$$H_{0}\phi = -\phi''/2 - \delta(x)\phi = E\phi. \quad \text{(9)}$$

The solution of the eigenvalue problem (Eq. (9)) yields a single bound state with the energy and wave-function:

$$E_{0} = -1/2, \quad \phi_{0}(x) = \exp(-|x|), \quad \text{(10)}$$

and a continuum of unbound states $|11, 22\rangle$. Since the Hamiltonian of the system is invariant with respect of space inversion, the wave-functions can also be constructed to have a well defined parity:

\begin{align*}
\phi_{+}(k; x) &= \frac{k}{\sqrt{\pi} \sqrt{1 + k^{2}}} \left[ \cos(kx) - \frac{1}{k} \sin(k|x|) \right], \quad \text{(11)} \\
\phi_{-}(k, x) &= \frac{1}{\sqrt{\pi}} \sin(kx). \quad \text{(12)}
\end{align*}

They are degenerate and have the energy $E(k) = k^{2}/2$ in resemblance with the unperturbed states of a free particle. However, in contrast to the free-particle case the wave-number $k$ can only attain \textit{positive} real values. One can readily demonstrate the completeness and the normalization of the above set of eigenfunctions.

As a starting point for $A^{I}(k)$, $A^{II}(k)$ and $B(k)$ computation, we need the bound-free and free-free transition matrix elements of the electric dipole:
\[\langle \phi_0 | x | \phi_- (k') \rangle = \frac{4}{\sqrt{\pi}} \frac{k}{(k^2 + 1)^2}, \quad (13a)\]
\[\langle \phi_+(k) | x | \phi_- (k') \rangle = -\frac{k}{\sqrt{1 + k'^2}} \left[ \delta(1)(k' - k) - 4 \frac{k'}{\pi (k'^2 - k^2)^2} \right], \quad (13b)\]
\[\langle \phi_+(k') | x | \phi_- (k) \rangle = \frac{k'}{\sqrt{1 + k'^2}} \left[ \delta(1)(k' - k) + \frac{4}{\pi} \frac{k}{(k'^2 - k^2)^2} \right]. \quad (13c)\]

For the non-local SHG, we also need the quadrupole transition matrix elements between the ground and even unbound states:
\[\langle \phi_0 | x^2 | \phi_+ (k) \rangle = -\frac{8}{\sqrt{\pi}} \frac{1}{\sqrt{1 + k^2} (1 + k^2)^2} \quad (14a)\]

and between two free odd states:
\[\langle \phi_- (k') | \Delta x^2 | \phi_- (k) \rangle = \langle \phi_- (k') | x^2 - \langle \phi_0 | x^2 | \phi_0 \rangle | \phi_- (k) \rangle \langle \phi_0 | x | \phi_- (k') \rangle = -\left[ \frac{d^2}{dk'^2} + \frac{1}{2} \right] \delta(k' - k). \quad (14b)\]

The derivation of the matrix elements is done in Appendix [A].

The spectral functions are computed according to Eqs. (6), replacing the summations with integrations over the wave-number \(k'\):
\[A^I (k) = -\frac{1}{2} \int_0^\infty \frac{\langle \phi_0 | x^2 | \phi_+ (k') \rangle \langle \phi_+(k') | x | \phi_- (k') \rangle \langle \phi_-(k') | x | \phi_0 \rangle \langle \phi_0 | x | \phi_- (k') \rangle}{\omega_0 (k') - 2 \omega_0 (k)} \, dk' \]
\[= -\frac{32}{\pi} \frac{k}{(k^2 + 1)^2} \int_0^\infty \frac{1}{2k'^2 - k'^2 + 1} \frac{k'^2}{(1 + k'^2)^2} \left[ \frac{1}{\pi} \frac{4k}{(k'^2 - k^2)^2} \right] \, dk' = -\frac{32}{\pi} \frac{k}{(k^2 + 1)^2} \left[ \frac{1}{\pi} \frac{4k}{(k'^2 - k^2)^2} \right] \, dk' = -\frac{32}{\pi} \frac{k}{(k^2 + 1)^2} \lambda_1 (k) + \frac{4}{\pi} \lambda_2 (k), \quad (15)\]

where we introduced notation \(\omega_0 (k) = \frac{1}{2} (E(k) - E_0) = (k^2 + 1)/2\). Integrals \(\lambda_1 (k)\) and \(\lambda_2 (k)\) are computed in Appendix [A].

\[A^{II} (k) = -\frac{1}{2} \int_0^\infty \frac{\langle \phi_- (k') | \Delta x^2 | \phi_- (k) \rangle \langle \phi_- (k) | x | \phi_0 \rangle \langle \phi_0 | x | \phi_- (k') \rangle}{\omega_0 (k) + \omega_0 (k')} \, dk' \]
\[= \frac{16}{\pi} \frac{k}{(k^2 + 1)^2} \int_0^\infty \left[ \frac{d^2}{dk'^2} + \frac{1}{2} \right] \delta(k' - k) \left[ \frac{k'}{k'^2 + 2(k'^2 + 1)^2} \right] \, dk' \]
\[= \frac{16}{\pi} \frac{k}{(k^2 + 1)^2} \int_0^\infty \left[ \frac{d^2}{dk'^2} + \frac{1}{2} \right] \delta(k' - k) \, dk' = 4 \frac{k^2}{\pi} \frac{k^2}{(k^2 + 1)^2} \frac{4k^2 + 40k^2 - 29}{(k^2 + 1)^2}. \quad (16)\]

Here, we use twice the integration by parts and the fact that the integrand vanishes at the ends of interval. Thus, the final expression for \(A(k) = A^I (k) + A^{II} (k)\) results from the addition of Eq. (15) and Eq. (16):
\[A(k) = \frac{8}{\pi} \frac{k^2 (6k^2 + 5)}{(k^2 + 1)^2}. \quad (17)\]

Computation of \(B(k)\) is slightly more involved since the resulting function appears to be non-analytic:
\[B(k) = -\frac{1}{2} \int_0^\infty \frac{\langle \phi_0 | x^2 | \phi_+ (k) \rangle \langle \phi_+(k) | x | \phi_- (k') \rangle \langle \phi_- (k') | x | \phi_0 \rangle}{2 \omega_0 (k') - \omega_0 (k)} \, dk' \]
\[= -\frac{32}{\pi} \frac{k^2}{(1 + k^2)^3} \int_0^\infty \frac{1}{2k'^2 - k'^2 + 1} \frac{k'}{(k'^2 + 1)^2} \left[ \frac{d}{dk'} \left( \frac{k'}{(k'^2 + 1)^2} \right) \right] \, dk' \]
\[= -\frac{32}{\pi} \frac{k^2}{(1 + k^2)^3} \left[ \lambda_3 (k) - \frac{4}{\pi} \lambda_4 (k) \right] \quad (18)\]
Before the evaluation of $\chi_{qee}(\omega,\omega)$ it is instructive to analyze the properties of the spectral functions $A^I(k)$, $A^{II}(k)$, and $B(k)$. They describe different excitation pathways (Fig. 1) in the system. A peak slightly below $k = \frac{1}{2}$ related to the existence of the excitation threshold is common for them. It is interesting to observe that $A^I(k)$ and $A^{II}(k)$ decay as $k^{-8}$ for large wave-number $k$. There is, however, a cancellation of two terms in their sum leading to the same asymptotic behavior as $B(k)$ ($k^{-10}$).

We compute the SHG response using the following representation:

$$\chi_{qee}(\omega,\omega) = \int_0^\infty dk \frac{A(k)}{\omega - \omega_0(k) + i\Gamma} + \int_0^\infty dk \frac{-A(k)}{\omega + \omega_0(k) + i\Gamma} + \int_0^\infty dk \frac{B(k)}{\omega - \omega_0(k)/2 + i\Gamma/2} + \int_0^\infty dk \frac{-B(k)}{\omega + \omega_0(k)/2 + i\Gamma/2}$$

$$= \frac{1}{2} \int_{-\infty}^\infty dk \left[ \frac{A(k)}{\omega - \omega_0(k) + i\Gamma} - \frac{A(k)}{\omega + \omega_0(k) + i\Gamma} + \frac{B(k)}{\omega - \omega_0(k)/2 + i\Gamma/2} - \frac{B(k)}{\omega + \omega_0(k)/2 + i\Gamma/2} \right],$$

where $\Gamma > 0$ is infinitesimally small broadening of the states that ensures the causality of the response function. We transform the integration to the whole real axis using the fact that $A(k)$ and $B(k)$ are even functions. In this form the residue theorem can
FIG. 2: SHG response functions of the one-dimensional hydrogen with a \( \delta \)-function interaction. The axes are labeled in atomic units. Dotted curves represent parabolic dispersion of the response functions in the vicinity of \( \omega = 0 \), as given by Eqs. (25,26).

It is convenient to introduce following auxiliary functions:

\[
\begin{align*}
\alpha(\omega) &= \frac{1}{2} \int_{-\infty}^{\infty} dk \frac{A(k)}{\omega - \omega_0(k) + i\Gamma} = \frac{4}{\pi} \int_{-\infty}^{\infty} dk \frac{k^2(6k^2 + 5)}{(k^2 + 1)^2(\omega - 1/2(k^2 + 1) + i\Gamma)}, \\
\beta(\omega) &= \frac{1}{2} \int_{-\infty}^{\infty} dk \frac{B(k)}{\omega - \omega_0(k)/2 + i\Gamma/2} = b_1(\omega) + b_2(\omega),
\end{align*}
\]

and to split the integration of \( B(k) \) into two parts:

\[
\begin{align*}
b_1(\omega) &= -\frac{16}{\pi} \int_{-\infty}^{\infty} dk \frac{k^2\lambda_3(k)}{(1 + k^2)^3(\omega - \omega_0(k)/2 + i\Gamma/2)} = -\frac{16}{\pi} \int_{-\infty}^{\infty} dk \frac{k^2(7k^2 - 1)}{(1 + k^2)^2(\omega - 1/4(k^2 + 1) + i\Gamma/2)}, \\
b_2(\omega) &= \frac{64}{\pi^2} \int_{-\infty}^{\infty} dk \frac{k^2}{(1 + k^2)^3(\omega - \omega_0(k)/2 + i\Gamma/2)} \lambda_4(k).
\end{align*}
\]

Thus, the response function can be written as \( \chi^{(\omega,\omega)}_{\text{qee}} = \tilde{A}(\omega) + \tilde{B}(\omega) \), with \( \tilde{A}(\omega) = \alpha(\omega) + \alpha^*(-\omega) \), and \( \tilde{B}(\omega) = \beta(\omega) + \beta^*(-\omega) \). Although one can apply Sokhotsky’s formula in order to quickly get its imaginary part, we will explicitly perform the integrations in order to obtain the real part. The calculations are quite cumbersome involving numerous applications of the residue theorem. Since \( \lambda_4(k) \) is not an analytic function, we were forced to use its integral representation and to exchange the
order of integrations. Details of these calculations are presented in AppendixB. Thus, final expressions are given by:

\[
\begin{align*}
\text{Im} \tilde{A}(\omega) &= \frac{1}{16\omega^7} \begin{cases}
(1 - 12|\omega|)\sqrt{2|\omega| - 1} & |\omega| > \frac{1}{2}, \\
0 & |\omega| < \frac{1}{2};
\end{cases} \\
\text{Re} \tilde{A}(\omega) &= \frac{53\omega^4 + 44\omega^2 - 104}{64\omega^6} + \frac{1}{16\omega^7} \begin{cases}
-\sqrt{1 - 2|\omega|(1 - 12\omega)} & \omega < -\frac{1}{2}, \\
\sqrt{1 + 2\omega(1 + 12\omega)} - \sqrt{1 - 2\omega(1 - 12\omega)} & |\omega| < \frac{1}{2}, \\
\sqrt{1 + 2\omega(1 + 12\omega)} & \omega > \frac{1}{2};
\end{cases} \\
\text{Im} \tilde{B}(\omega) &= \frac{\sqrt{4|\omega| - 1}}{16\omega^6} \begin{cases}
2|\omega| - 1 & |\omega| > \frac{1}{2}, \\
0 & |\omega| < \frac{1}{2};
\end{cases} \\
\text{Re} \tilde{B}(\omega) &= -\frac{53\omega^4 + 12\omega^2 - 8}{64\omega^6} - \frac{1}{16\omega^7} \begin{cases}
\sqrt{1 - 4\omega} & |\omega| < \frac{1}{2}; \\
\sqrt{1 - 4\omega} & |\omega| > \frac{1}{2}; \\
\sqrt{1 - 4\omega} & |\omega| > \frac{1}{2};
\end{cases}
\end{align*}
\]

\[
\text{Im} \tilde{B}(\omega) = \frac{\sqrt{4|\omega| - 1}}{16\omega^6} \begin{cases}
2|\omega| - 1 & |\omega| > \frac{1}{2}, \\
0 & |\omega| < \frac{1}{2};
\end{cases}
\]

\[
\text{Re} \tilde{B}(\omega) = -\frac{53\omega^4 + 12\omega^2 - 8}{64\omega^6} - \frac{1}{16\omega^7} \begin{cases}
\sqrt{1 - 4\omega} & |\omega| < \frac{1}{2}; \\
\sqrt{1 - 4\omega} & |\omega| > \frac{1}{2}; \\
\sqrt{1 - 4\omega} & |\omega| > \frac{1}{2};
\end{cases}
\]

\[
\begin{align*}
\text{Re} \tilde{A}(\omega) &= -\frac{219}{128} - \frac{4433}{1024}\omega^2 + \ldots \\
\text{Re} \tilde{B}(\omega) &= \frac{963}{128} + \frac{82849}{1024}\omega^2 + \ldots \\
\text{Re} \chi^{(2)}(\omega) &= \frac{93}{16} + \frac{4901}{64}\omega^2 + \ldots
\end{align*}
\]

At small \(\omega\), one observes a quadratic dependence of the SHG response on the frequency of incident photon. This behavior was already found in many realistic systems and proved analytically [24, 25].

Let us now obtain the static limit closely following the derivation of [15]. We consider the one-dimensional stationary Schrödinger equation:

\[
H \psi = \epsilon \psi, \quad H = -D^2 + V(x), \quad D = d/dx,
\]

where the boundary conditions are supposed to be

\[
\psi(x \to \pm \infty) = 0,
\]

and \(V(x) = -\delta(x) + \lambda x\). Using the method of Swenson and Danforth [16], one can obtain recursive equations

\[
\begin{align*}
X_0^{(N-1)} &= (N - 1)(N - 2)X_0^{(N-3)}, \\
X_p^{(N-1)} &= (N - 1)(N - 2)X_p^{(N-3)} + 4 \sum_{q=1}^{p} X_{q-1}^{(N-1)} X_{p-q}^{(N-1)} - 2(N + 1)X_p^{(N-1)},
\end{align*}
\]

for the expectation values of of \(x^N\), i.e. \(X^{(N)} = \langle x^N \rangle\) at different orders of the Rayleigh-Schrödinger perturbation theory:

\[
\epsilon = \sum_{p=0}^{\infty} \epsilon_p \lambda^p, \quad \epsilon_0 = -\frac{1}{4}, \quad X^{(N)} = \sum_{p=0}^{\infty} X_p^{(N)} \lambda^p.
\]

From \(X_0^{(0)} = 1\) and \(X_0^{(1)} = 0\) one obtains with a help of Eq. (29)

\[
X_0^{(2)} = 2, \quad X_0^{(4)} = 24, \quad X_0^{(6)} = 720, \ldots, \quad X_0^{(2N+1)} = 0.
\]

Starting from these values other coefficients can be recursively computed using Eq. (30). Simple symmetry consideration
show that $X_i^{(N)} = 0$ if $N + p$ is an odd number. First few nonzero values are

$$
X_1^{(1)} = -10, \quad X_3^{(3)} = -168,
X_2^{(2)} = 744, \quad X_4^{(3)} = 36960,
X_3^{(3)} = -3520, \quad X_3^{(3)} = -184080.
$$

The knowledge of $X_p^{(N)}$ allows to compute the static response functions. Let us make a rescaling $q = x/2$, $\phi(q) = \psi(x)$, $F = -i\lambda$, $E = 2\varepsilon$, and $E_0 = 2\varepsilon_0 = -\frac{1}{2}$ in order to bring Eq. (28) to the form:

$$
H_0\phi(q) = -\frac{\dot{q}^2}{2} - \delta(q)\phi(q) - Fq\phi(q) = E\phi(q). \quad (32)
$$

As a consequence an expansion

$$
Q^{(N)} = \sum_{p}^{\infty} Q_p^{(N)} F_p, \quad (33)
$$

must be compared with Eq. (31) yielding:

$$
Q_p^{(N)} = (-1)^p \frac{X_p^{(N)}}{2N^4p^4}. \quad (34)
$$

Hence, the first few values are:

$$
\alpha(0) = Q_1^{(1)} = -\frac{1}{8} X_1^{(1)} = \frac{5}{4}, \quad 2\chi_{qee}^{(0,0)} = Q_2^{(2)} = \frac{1}{224} X_2^{(2)} = \frac{93}{8}.
$$

We see that $Q_1^{(1)}$ correctly reproduces the static polarizability of our model system. The frequency dependent polarizability was obtained in [11, 12]. Taking a limit $\omega \to 0$ yields $\alpha(0) = \frac{5}{4}$. There is an additional factor of 2 that must be multiplied with $\chi_{qee}^{(0,0)}$ in order to equate it to $Q_2^{(2)}$. Appearance of this factor is due to different representations of electric fields for static and dynamic case used in [3]. The resulting difference in terminology is discussed in details in [26], alternatively one can see it from the difference in factor $K(\omega_1, \omega_2)$ adopted by Orr and Ward for static and dynamic cases (for SHG $K(\omega, \omega) = 1/2$, while in the static case $K(0, 0) = 1$, see Tab. 1 of [3]).

Following the prescription of [19] the $\omega \to \infty$ behavior will be obtained by i) defining the $\chi_{qee}^{(\omega, \omega)}$ in terms of its Fourier transform:

$$
\chi_{qee}^{(\omega, \omega)} = \int d\tau^+ \int d\tau^- G^{(2)}(t_1, t_2) e^{i\omega \tau^+}, \quad (35)
$$

where $\tau^+ = t_1 + t_2$, $\tau^- = (t_1 - t_2)/2$ and

$$
G^{(2)}(t_1, t_2) \propto -f(t_1, t_2)g(t_1, t_2), \quad f(t_1, t_2) = \theta(t_1)\theta(t_2 - t_1) + \theta(t_2)\theta(t_1 - t_2) \quad (36)
$$

ii) integrating Eq. (35) by parts

$$
\chi_{qee}^{(\omega, \omega)} = -\sum_{m} \int \frac{d\tau^-}{\tau^-} \frac{\partial}{\partial \tau^-} G^{(2)}(t_1, t_2) \big|_{\tau^- = 0^+} \big|_{\tau^+ = 0^+} \quad (38)
$$

iii) seeking the lowest nonvanishing order of the time derivative $\frac{\partial}{\partial \tau^-} g(t_1, t_2)$ of the correlation function

$$
g(t_1, t_2) = \langle [x(-t_2), [x(-t_1), x^2]] \rangle_0. \quad (39)
$$

Since we consider here the one-dimensional case, spatial indices are omitted. After some algebra one can show that the first nonzero term is:

$$
\frac{\partial^2}{\partial \tau^+ \partial \tau^-} g(t_1, t_2) = \frac{\partial^2 g}{\partial t_1 \partial t_2} = -4. \quad (40)
$$

Thus, the first nonvanishing derivative in Eq. (38) is of the third order

$$
\frac{\partial^3}{\partial \tau^+ \partial \tau^- \partial \tau^-} G^{(2)}(t_1, t_2) \propto 4[\delta(t_1)\theta(t_2 - t_1) + \delta(t_2)\theta(t_1 - t_2)]
$$

By inserting this expression in Eq. (38), performing the integration and taking the limit we obtain

$$
\chi_{qee}^{(\omega, \omega)} \propto \frac{1}{\omega^4}
$$

for $\omega \to \infty$. The same behavior is seen indeed from Eqs. (23, 24). One can also note a delicate cancellation of $\omega^{-2}$ terms in the sum $A(\omega) + B(\omega)$.

Another important conclusion that immediately follows from our asymptotic analysis is the prefactor of $1/\omega^4$ decay. In the SHG case due to dipole transitions the response function $\chi_{i, j k}^{(\omega, \omega)}$ behaves as $\langle \frac{\partial^3 V}{\partial \varepsilon_i \partial \varepsilon_j \partial \varepsilon_k} \rangle_0 \propto \frac{1}{\omega^4}$, where the average is performed in the ground state of the system [19]. The potential $V$ describes the electron-ion interaction. For the third harmonic generation one obtains in the same way

$$
\chi_{i, j k}^{(\omega, \omega)} = \langle \frac{\partial^3 V}{\partial \varepsilon_i \partial \varepsilon_j \partial \varepsilon_k} \rangle_0 \propto \frac{1}{\omega^4}. \quad (27)
$$

It is clear that in both cases the potential and its partial derivatives are system specific. In contrast, the quadrupole SHG response function does not contain derivatives of the potential, it only depends on the system density in the high frequency limit.

V. CONCLUSIONS

In this work, we analyzed the singular structure of the second-order response function based on the sum-over-states expression. As an illustration of the method the non-local second harmonic generation is obtained for the one-dimensional hydrogen atom with a $\delta$-function interaction. It provides a new paradigm where the sum over continuum states can be analytically evaluated. Finally we analyze the static and high-frequency limits, which we are also able to compute using different methods.

Our results lead to the fast algorithm for the calculation of non-linear response using the sum-over-state approach. The analytic expression for the SHG response can be used as a valuable test of the numerical convergence of SOS methods. The analysis of the high-frequency behavior shows a universal $\omega^{-4}$ behavior, which can easily be tested experimentally.
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APPENDIX A: MATRIX ELEMENTS

One of the simplest matrix elements is the bound-free transition dipole moment. The integrand belongs to the space of square-integrable functions. The integration can be done using elementary methods:

$$\langle \phi_0 | x | \phi_-(k) \rangle = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx x e^{-|x|^2} x \sin(kx) = -\frac{2}{\sqrt{\pi}} \frac{d}{dk} \int_{0}^{\infty} dx e^{-x^2} \cos(kx) = \frac{4}{\sqrt{\pi}} \frac{k}{(k^2 + 1)^2}. \quad (A1)$$

Similarly, one obtains the matrix element for the quadrupole transition between the ground and even excited state:

$$\langle \phi_0 | x^2 | \phi_+(k) \rangle = \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{1 + k^2}} \int_{-\infty}^{\infty} dx x^2 e^{-|x|^2} \left( \cos(kx) - \frac{1}{k} \sin(k|x|) \right)$$

$$= -\frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{1 + k^2}} \left( \frac{d^2}{dk^2} \int_{0}^{\infty} dx e^{-x^2} \cos(kx) - \frac{1}{k} \frac{d^2}{dk^2} \int_{0}^{\infty} dx e^{-x^2} \sin(kx) \right)$$

$$= -\frac{8}{\sqrt{\pi}} \frac{1}{1 + k^2} \frac{1}{(1 + k^2)^2}. \quad (A2)$$

All other matrix elements mentioned in this manuscript cannot be represented in terms of only elementary functions. This is due to the fact that free particle states are not square integrable, but rather normalized on the $\delta$-function. Thus, the quadrupole transition moment between the odd states can be computed as follows:

$$\langle \phi_- (k') | x^2 | \phi_-(k) \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} dx \sin(k'x) x^2 \sin(kx) = -\frac{1}{\pi} \frac{1}{(2i)^2} \frac{d^2}{dk^2} \int_{-\infty}^{\infty} dx \left( e^{i k'x} - e^{-i k'x} \right) \left( e^{i kx} - e^{-i kx} \right)$$

$$= \frac{d^2}{dk^2} \left[ \delta(k + k') - \delta(k' - k) \right] = -\delta^{(2)}(k' - k), \quad (A3)$$

where the last transition is valid because of $k, k' > 0$ in our case. The calculation of the dipole transition moments between the free states of different parity can be done as follows:

$$\langle \phi_+(k) | x | \phi_- (k') \rangle = \frac{1}{\pi} \frac{k}{\sqrt{1 + k^2}} \left[ \int_{-\infty}^{\infty} dx \cos(kx) x \sin(k'x) - \frac{1}{k} \int_{-\infty}^{\infty} dx \sin(k|x|) x \sin(k'x) \right]$$

$$= -\frac{k}{\sqrt{1 + k^2}} \left[ \delta^{(1)}(k' - k) - \frac{4}{\pi} \frac{k'}{k^2 - k'^2} - \frac{4}{k^2 - k'^2} \right], \quad (A4)$$

using following integrals

$$\frac{1}{\pi} \int_{-\infty}^{\infty} dx \cos(kx) x \sin(k'x) = -\frac{1}{\pi} \frac{1}{2i} \frac{d}{dk'} \int_{-\infty}^{\infty} dx \left( e^{i k'x} + e^{-i k'x} \right) \left( e^{i kx} + e^{-i kx} \right)$$

$$= -\frac{d}{dk'} \left[ \delta(k + k') + \delta(k' - k) \right] = -\delta^{(1)}(k' - k), \text{ for } k, k' > 0$$

$$\frac{1}{k} \int_{-\infty}^{\infty} dx \sin(k|x|) x \sin(k'x) = -\frac{1}{k} \frac{d}{dk'} \int_{-\infty}^{\infty} dx \operatorname{sgn}(x) \sin(kx) \cos(k'x)$$

$$= -\frac{1}{k} \frac{d}{dk'} \left[ \operatorname{sgn}(x) \frac{e^{i k'x} + e^{-i k'x}}{i k} \right] \left( e^{i kx} - e^{-i kx} \right)$$

$$= -\frac{1}{k} \frac{d}{dk'} \left[ \frac{1}{k' + k} - \frac{1}{k' - k} \right] = \frac{2}{d} \frac{2}{k'^2 - k^2} = -\frac{4k'}{(k'^2 - k^2)^2},$$
cumbersome calculations, which involve application of the residue theorem. For \( a(\omega) \), the number of poles in the upper complex half-plane encircled by the contour of integration depends on the value of frequency \( \omega \) (Fig. 4). When \( \omega < \frac{1}{2} \), i.e. the energy of incident photon is insufficient to generate optical transition from the ground state to the continuum of unbound states. The imaginary part of the function \( a(\omega) \) vanishes. While the real part has a contribution from two

APPENDIX B: HILBERT TRANSFORMS

Below, we evaluate integrals \( a(\omega) \), \( b_1(\omega) \) and \( b_2(\omega) \). They are defined by Eqs. (20,22a,22b), respectively. These are quite cumbersome calculations, which involve application of the residue theorem. For \( a(\omega) \), the number of poles in the upper complex half-plane encircled by the contour of integration depends on the value of frequency \( \omega \) (Fig. 4). When \( \omega < \frac{1}{2} \), i.e. the energy of incident photon is insufficient to generate optical transition from the ground state to the continuum of unbound states. The imaginary part of the function \( a(\omega) \) vanishes. While the real part has a contribution from two
FIG. 4: Integration of $a(\omega)$, $k = \pm i$ are poles of the seventh order. $k = \pm \sqrt{2\omega - 1}$ are simple poles. It is important to notice that due to the presence of small imaginary part ($\omega \to \omega + i\Gamma$, $\Gamma > 0$) they are shifted away from the real axis even in the case of $\omega > \frac{1}{2}$. Thus, only one pole of this pair is encircled by the contour for any value of $\omega$. However, when $\omega > \frac{1}{2}$, its residue is real, thus contributing to the imaginary part of the integral. In all other cases, the poles have imaginary residues. This fact is reflected by different notations for singularities with real (crossed circle) and imaginary (black circle) residues.

poles. For the energy of an incident photon above the ionization threshold, i.e. $\omega > \frac{1}{2}$, one pole contributes to the real and one pole contributes to the imaginary part of the function.

\[
\begin{align*}
\text{Re } a(\omega) &= \pi i \left\{ \begin{array}{ll}
\text{Res}_{k=i} & \omega > \frac{1}{2}, \\
\text{Res}_{k=i\sqrt{2\omega - 1}} & \omega < \frac{1}{2},
\end{array} \right. \frac{A(k)}{\omega - \omega_0(k) + i\Gamma} \\
&= \frac{147\omega^6 + 106\omega^5 + 86\omega^4 + 88\omega^3 + 184\omega^2 - 208\omega + 16}{256\omega^7} - \frac{1}{16\omega^2} \left\{ \begin{array}{ll}
0 & \omega > \frac{1}{2}, \\
\sqrt{1 - 2\omega(-12\omega + 1)} & \omega < \frac{1}{2};
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\text{Im } a(\omega) &= \pi i \left\{ \begin{array}{ll}
0 & \omega > \frac{1}{2}, \\
\frac{A(k)}{\omega - \omega_0(k) + i\Gamma} & \omega < \frac{1}{2},
\end{array} \right. = \frac{1}{16\omega^7} \left\{ \begin{array}{ll}
\sqrt{2\omega - 1(-12\omega + 1)} & \omega > \frac{1}{2}, \\
0 & \omega < \frac{1}{2}.
\end{array} \right.
\end{align*}
\]

Calculations for $b_1(\omega)$ can be done along the same line with a small distinction that now $\omega = \frac{1}{4}$ is a point, in which the function changes its behavior. This is because $b_1(\omega)$ describes resonant $2\omega$ transitions. The result works out to be:

\[
\begin{align*}
\text{Re } b_1(\omega) &= \frac{28\omega^6 + 14\omega^5 + 8\omega^4 + 6\omega^3 + 10\omega^2 - 11\omega + 2}{64\omega^7} - \frac{1}{64\omega^2} \left\{ \begin{array}{ll}
0 & \omega > \frac{1}{4}, \\
\sqrt{1 - 4\omega} & \omega < \frac{1}{4};
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\text{Im } b_1(\omega) &= \frac{1}{64\omega^2} \left\{ \begin{array}{ll}
\sqrt{4\omega - 1(7\omega - 2)} & \omega > \frac{1}{4}, \\
0 & \omega < \frac{1}{4}.
\end{array} \right.
\end{align*}
\]

The computation of $b_2(\omega)$ brings us to the following double integral:

\[
b_2(\omega) = \frac{32}{\pi^2} \int_{-\infty}^{\infty} dq \frac{q^2}{(q^2 + 1)^2} \int_{-\infty}^{k^2} dk \frac{(1 + k^2)^2(\omega - \omega_0(k)/2 + i\Gamma/2)(2q^2 - k^2 + 1)(q^2 - k^2)^2}{(1 + k^2)^3(\omega - \omega_0(k)/2 + i\Gamma/2)(2q^2 - k^2 + 1)(q^2 - k^2)^2}.
\]

After simple but lengthy consideration of all cases (Fig. [3] we obtain:

\[
\begin{align*}
\text{Re } b_2(\omega) &= s(\omega) + u_2(\omega) + \left\{ \begin{array}{ll}
t_5(\omega) & \omega > \frac{1}{4}, \\
0 & \frac{1}{2} > \omega > \frac{1}{4}, \\
t_1(\omega) + u_3(\omega) & \omega < \frac{1}{4};
\end{array} \right.
\end{align*}
\]

\[
\begin{align*}
\text{Im } b_2(\omega) &= \left\{ \begin{array}{ll}
t_1(\omega) & \omega > \frac{1}{2}, \\
t_1(\omega) + t_2(\omega) & \frac{1}{2} > \omega > \frac{1}{4}, \\
0 & \omega < \frac{1}{4};
\end{array} \right.
\end{align*}
\]
where the auxiliary functions \( s(\omega) \), \( t_i(\omega) \), and \( u_i(\omega) \), \( i = 1, \ldots, 3 \) are given by:

\[
\begin{align*}
  s(\omega) &= \text{Res}_{q=1} (\text{Res}_{k=i}[f(k, q, \omega)]) = -\frac{197\omega^2 + 50\omega + 10}{256\omega^3}, \\
  t_1(\omega) &= \text{Res}_{q=1} (\text{Res}_{k=\sqrt{4\omega - T}}[f(k, q, \omega)]) = \frac{\sqrt{4\omega - 1}(\omega - 2)}{16\omega^2}, \\
  t_2(\omega) &= \text{Res}_{q=i\sqrt{1 - 2\omega}} (\text{Res}_{k=\sqrt{4\omega - T}}[f(k, q, \omega)]) = \frac{\sqrt{4\omega - 1}\sqrt{1 - 2\omega}}{16\omega^2}, \\
  t_3(\omega) &= \text{Res}_{q=\sqrt{2\omega - 1}} (\text{Res}_{k=\sqrt{4\omega - T}}[f(k, q, \omega)]) = \frac{\sqrt{4\omega - 1}\sqrt{2\omega - 1}}{16\omega^2}, \\
  u_1(\omega) &= \text{Res}_{q=i} (\text{Res}_{k=i\sqrt{1 - 2\omega}}[f(k, q, \omega)]) = -\frac{\sqrt{1 - 4\omega}(\omega - 2)}{64\omega^2}, \\
  u_2(\omega) &= \text{Res}_{q=i\sqrt{1 - 4\omega}} (\text{Res}_{k=i\sqrt{1 - 2\omega}}[f(k, q, \omega)]) = \text{Res}_{q=\sqrt{2\omega - 1}} (\text{Res}_{k=\sqrt{4\omega - T}}[f(k, q, \omega)]) = -\frac{7\omega - 2}{64\omega^2}, \\
  u_3(\omega) &= \text{Res}_{q=i\sqrt{1 - 2\omega}} (\text{Res}_{k=i\sqrt{1 - 4\omega}}[f(k, q, \omega)]) = -\frac{\sqrt{1 - 4\omega}\sqrt{1 - 2\omega}}{16\omega^2}.
\end{align*}
\]

Here we denote the function under the integrals as \( f(k, q, \omega) \).

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