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Generalized Miller Formulae for Quantum Anharmonic Oscillators

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Abstract

Miller's rule originated as an empirical relation between the nonlinear and linear optical coefficients of materials. It is now accepted as a useful tool for guiding experiments and computational materials discovery, but its theoretical foundation had long been limited to a derivation for the classical Lorentz model with a weak anharmonic perturbation. Recently, we developed a mathematical framework which enabled us to prove that Miller's rule is equally valid for quantum anharmonic oscillators, despite different dynamics due to zero-point fluctuations and further quantum-mechanical effects. However, our previous derivation applied only to one-dimensional oscillators and to the special case of second- and third-harmonic generation in a monochromatic electric field. Here we extend the proof to three-dimensional quantum anharmonic oscillators and also treat all orders of the nonlinear response to an arbitrary multi-frequency field. This makes the results applicable to a much larger range of physical systems and nonlinear optical processes. The obtained generalized Miller formulae rigorously express all tensor elements of the frequency-dependent nonlinear susceptibilities in terms of the linear susceptibility and thus allow a computationally inexpensive quantitative prediction of arbitrary parametric frequency-mixing processes from a small initial dataset.

Keywords: Miller's rule; generalized Miller formulae; nonlinear optics; nonlinear susceptibility; harmonic generation; frequency mixing; quantum anharmonic oscillator; time-dependent perturbation theory

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1. Introduction

Nonlinear optical effects arise from the fact that the induced polarization in atoms, molecules, or solids is, in general, not simply proportional to an applied external electric field. The nonlinear response is especially relevant for strong fields [1]. The necessary field strengths were achieved for the first time in the 1960s with the invention of the laser by Theodore Maiman [2]. Shortly afterwards, Peter Franken and co-workers discovered the doubling of the irradiation frequency of a ruby optical maser when interacting with a quartz crystal [3]. Since then, nonlinear optical processes have become fundamental to modern photonics, underpinning applications such as frequency conversion [4,5], tunable coherent light sources [6], ultrafast spectroscopy [7], optical microscopy of biological systems [8], and quantum information processing [9]. For the latter, parametric down-conversion [10] is a key process for single-photon sources [11].

A critical challenge in advancing these technologies is the identification of materials with tailored nonlinear optical properties. Traditional approaches rely on experimental trial-and-error or numerically intensive computations, such as simulations based on many-body perturbation theory [12]. However, these are usually too cumbersome for applications in the rapidly developing field of data-driven materials science [13], where high-throughput screening methods [14], machine learning [15], and the computer-aided discovery of new materials [16,17] typically require a highly efficient evaluation of the specific nonlinear optical coefficients in question for a large number of materials. In this situation, empirical relations like Miller's rule [18] provide a convenient way to quickly estimate the desired nonlinear susceptibilities from previously measured or computed data for the linear optical properties, thus opening a practical pathway for efficient materials screening.

In its original formulation, Miller's rule states that the nonlinear optical coefficient for second-harmonic generation is approximately proportional to a certain product of linear susceptibilities evaluated at different frequencies [19]. Initially based on experimental data for a small set of inorganic crystalline solids, Miller's rule was subsequently confirmed for a large and diverse range of materials, including organic molecular crystals [20], ferroelectrics [21], and chalcogenide glasses [22], while more notable deviations were reported for optical metamaterials [23,24]. Similar relations were also found for other nonlinear coefficients, such as third-harmonic generation [25].

Despite its repeated empirical validation, the theoretical foundations of Miller's rule remain unsatisfactory, as a proper mathematical derivation had for a long time been limited to the classical Lorentz model [26], whose assumptions of classical particle dynamics and velocity-dependent damping are notably different from the actual quantum-mechanical behavior of electrons in real solids. In a recent work [27], we presented a rigorous derivation for driven quantum anharmonic oscillators, based on a solution of the time-dependent Schrödinger equation in the presence of an external electric field, which finally established that Miller's rule is, in principle, equally applicable to quantum-mechanical systems despite fundamental differences in the underlying dynamics, such as zero-point fluctuations or tunneling into the barriers. However, the main focus of [27] was on the development of the necessary mathematical tools. As a consequence, the actual derivation was restricted to one-dimensional oscillators and to the special case of second- and third-harmonic generation driven by a monochromatic electric field with just a single frequency component.

In this work, we extend our previous treatment substantially along three lines. First, we consider realistic three-dimensional systems, which gives access to all tensor components of the nonlinear optical susceptibilities in real anisotropic materials. Second, we assume an arbitrary multi-frequency driving field instead of a monochromatic field, so that processes like sum-frequency or difference-frequency generation with different input frequencies, which had previously been neglected, can also be described. These are essential for many technological applications, such as optical parametric amplification or parametric down-conversion. Third, we include all orders of the electric field in a nonperturbative manner so that the resulting formulae are not limited to second- and third-harmonic generation but equally cover high harmonics and other high-order nonlinear processes.

From the time-dependent Schrödinger equation, we derive explicit solutions for the nonlinear susceptibilities of quantum anharmonic oscillators up to arbitrary order for electric fields with multiple frequency components. Furthermore, we demonstrate that all elements of the nonlinear susceptibilities can be written in terms of the linear optical susceptibility. The resulting generalized Miller formulae mirror expressions previously derived for the classical Lorentz model [28] and can be used for high-throughput screening of nonlinear optical materials [29–31]. In particular, they allow a numerically very efficient estimate of arbitrary nonlinear coefficients, such as high-harmonic generation or multi-wave mixing, based solely on data for the linear susceptibility. By leveraging existing databases of measured or computed linear optical properties, such as refractive indices or susceptibilities, it is thus feasible to predict the nonlinear response with modest computational resources.

After such an initial screening, more numerically intensive methods can then be focused on the most promising configurations.

This paper is organized as follows. In Section 2, we describe the driven quantum anharmonic oscillator model that is considered in this work. In Section 3, we solve the time-dependent Schrödinger equation analytically up to first order in the anharmonicity and derive the generalized Miller formulae that allow us to express the nonlinear optical susceptibilities up to arbitrary order in terms of the linear susceptibility. The practical application is further illustrated by means of a numerical example. Finally, our conclusions are summarized in Section 4.

2. Methods

In this work, we consider independent electrons in a confining three-dimensional anharmonic potential $V(\boldsymbol{r})$ with a global minimum at $\boldsymbol{r} = \boldsymbol{0}$ that are driven by an external electric field. Within a quantum-mechanical treatment, the dynamics are governed by the time-dependent Schrödinger equation

$$i\hbar\partial_t \Psi(\boldsymbol{r},t) = \Big(H^{(0)}(\boldsymbol{r},t) + H^{(1)}(\boldsymbol{r})\Big)\Psi(\boldsymbol{r},t)\,, \tag{1}$$

where the Hamiltonian operator is written as the sum of the time-dependent Hamiltonian of a driven harmonic oscillator

$$H^{(0)}(\boldsymbol{r},t) = -\frac{\hbar^2}{2m}\nabla_{\boldsymbol{r}}^2 + \frac{m}{2}\boldsymbol{r}^\top\Omega^2\boldsymbol{r} + e_0\boldsymbol{E}(t)\cdot\boldsymbol{r} \tag{2}$$

and the time-independent anharmonic part of the potential

$$H^{(1)}(\boldsymbol{r}) = \sum_{j,k,l} V_{jkl}\,x^j y^k z^l \tag{3}$$

with $V_{jkl} = 0$ for $j + k + l \le 2$. The shape of the potential is completely arbitrary, as long as the global minimum remains at $\boldsymbol{r} = \boldsymbol{0}$. Without loss of generality, however, the eigenfrequency matrix may always be chosen in the diagonal form

$$\Omega = \begin{pmatrix} \omega_x & 0 & 0 \\ 0 & \omega_y & 0 \\ 0 & 0 & \omega_z \end{pmatrix} \tag{4}$$

by aligning the coordinate system with the principal axes of the harmonic part of the potential. The expansion coefficients of the anharmonic part are obtained from

$$V_{jkl} = \frac{1}{j!\,k!\,l!}\left[\frac{\partial^{j+k+l}}{\partial x^j \partial y^k \partial z^l}V(\boldsymbol{r})\right]_{\boldsymbol{r}=\boldsymbol{0}}\,. \tag{5}$$

In general, if the coordinate system is determined in this way, the time-dependent external electric field contains projections

$$\boldsymbol{E}(t) = \sum_q E_q(t)\boldsymbol{e}_q \tag{6}$$

on all Cartesian unit vectors $\boldsymbol{e}_q$ with $q \in \{x,y,z\}$, which may be written as a sum of Fourier components in the form

$$E_q(t) = \sum_\omega \hat{E}_q(\omega)e^{-i\omega t}e^{\gamma t} = \sum_\omega \hat{E}_q(\omega)e^{-i(\omega+i\gamma)t}\,. \tag{7}$$

The sum runs over pairs of positive and negative frequencies. As the field components $E_q(t)$ are real, the Fourier coefficients must satisfy the relation $\hat{E}_q(-\omega) = \hat{E}_q^*(\omega)$. Furthermore, we have assumed that the field is switched on adiabatically with a parameter $\gamma > 0$. For more compact expressions, we use the shorthand notation $\tilde{\omega} = \omega + i\gamma$.

The adiabatic switching of external electric fields is a ubiquitous mathematical device in ab initio electronic-structure calculations because it connects the dynamics of driven quantum systems with the stationary initial ground state and thus facilitates the use of time-dependent perturbation theory. For example, it underlies the Adler–Wiser formula [32,33] for the polarizability and dielectric function that is exploited in nearly all implementations of linear-response time-dependent density-functional theory for solids [34]. Furthermore, the nonzero imaginary part of $\omega + i\gamma$ gives rise to a complex frequency-dependent dielectric function, which reflects the absorption and damping due to electron scattering. In this sense, the switching parameter γ plays a very similar role as the damping constant or the inverse scattering time $1/\tau$ in the Lorentz model and leads to a broadening of the peaks in the spectral function. Instead of the limit $\gamma \to 0$, practical applications typically use a finite, not even necessarily small value, both for numerical reasons and to simulate the effect of additional scattering channels, such as electron–phonon scattering, that are not explicitly included. The temporal modulation of the electric field may instead be controlled by an appropriate Fourier series. For a consistent construction of nonlinear susceptibilities by means of generalized Miller formulae, a proper treatment of the imaginary parts of the complex frequencies will turn out to be crucial, as seen in the following.

The applied external electric field induces a dynamic polarization

$$\boldsymbol{P}(t) = -Ne_0 \int \Psi^*(\boldsymbol{r},t)\boldsymbol{r}\Psi(\boldsymbol{r},t)\, d^3r\,, \tag{8}$$

which equals the total electric dipole moment of N electrons with the charge $-e_0$. It can be expanded by orders of the external field with the nth-order components [1]

$$P_\alpha^{(n)}(t) = \varepsilon_0 \sum_{\omega_1,\ldots,\omega_n} \sum_{\alpha_1,\ldots,\alpha_n} \chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1 + \ldots + \tilde{\omega}_n; \tilde{\omega}_1, \ldots, \tilde{\omega}_n)\hat{E}_{\alpha_1}(\omega_1)\ldots\hat{E}_{\alpha_n}(\omega_n)e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)t}\,. \tag{9}$$

The first-order susceptibility $\chi^{(1)}_{\alpha\alpha_1}$ is called linear because the contribution to the polarization is directly proportional to the electric field, whereas all higher-order susceptibilities are called nonlinear. If there is no ambiguity, then we will use the short-hand notation $\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1 + \ldots + \tilde{\omega}_n)$ instead of $\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1 + \ldots + \tilde{\omega}_n; \tilde{\omega}_1, \ldots, \tilde{\omega}_n)$ for simplicity.

In the following, we will solve the time-dependent Schrödinger Equation (1) analytically for a weakly anharmonic but otherwise arbitrary potential using time-dependent perturbation theory up to the first order in the anharmonicity. The results demonstrate that all nonlinear susceptibilities up to arbitrary order in the electric field can be expressed exactly in terms of the linear susceptibility in a generalization of Miller's rule.

3. Results and Discussion

For a weak anharmonicity, the Schrödinger Equation (1) can be solved by perturbation theory. In contrast to standard approaches, where the unperturbed system is assumed to be in a stationary initial state and the external electric field is regarded as a small time-dependent perturbation, we take the driven harmonic oscillator with the Hamiltonian (2) as our starting point, while the time-independent anharmonic part of the potential (3) acts as a perturbation. It is this reversal of roles that allows us to include the full external electric field in a nonperturbative manner and subsequently analyze the nonlinear response up to arbitrary order. The wavefunction is thus expanded by orders of the anharmonicity as

$$\Psi(\boldsymbol{r},t) = \sum_{n\geq 0} \Psi^{(n)}(\boldsymbol{r},t)\,. \tag{10}$$

After inserting this expansion into (1), the terms of each order n form a hierarchy of differential equations, which can be solved in sequence.

3.1. Zeroth Order: Three-Dimensional Driven Harmonic Oscillator

The Schrödinger equation of a driven harmonic oscillator in three dimensions, with no anharmonic deformation of the potential, is given by

$$i\hbar\partial_t \Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r},t) = H^{(0)}(\boldsymbol{r},t)\Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r},t)\,. \tag{11}$$

As the axes were chosen in such a way that the eigenfrequency matrix (4) becomes diagonal, the Hamiltonian $H^{(0)}(\boldsymbol{r},t)$ decomposes into a sum of three decoupled operators that describe the independent one-dimensional motion along each of the Cartesian coordinates q. As a consequence, the wavefunction can be factored into components

$$\Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r},t) = \prod_q \psi_{n_q}^{(0)}(q,t)\,, \tag{12}$$

each of which obeys the time-dependent Schrödinger equation for a driven one-dimensional harmonic oscillator

$$i\hbar\partial_t \psi_{n_q}^{(0)}(q,t) = \left(-\frac{\hbar^2}{2m}\partial_q^2 + \frac{m\omega_q^2}{2}q^2 + e_0 E_q(t) q\right)\psi_{n_q}^{(0)}(q,t)\,. \tag{13}$$

The exact analytic solution, first derived by Schrödinger [35], is discussed in detail in [27]. The resulting coherent states can be written as

$$\psi_{n_q}^{(0)}(q,t) = \varphi_{n_q}(q - q_0(t))e^{i[-E_{n_q}t + m(q-q_0(t))\dot{q}_0(t) + \int_{-\infty}^{t} L(q_0(t'),\dot{q}_0(t'),t')\,dt']/\hbar} \tag{14}$$

in terms of the normalized stationary eigenfunctions of the quantum harmonic oscillator

$$\varphi_{n_q}(q) = \left(\frac{m\omega_q}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^{n_q} n_q!}} H_{n_q}\left(\sqrt{\frac{m\omega_q}{\hbar}}\, q\right) e^{-m\omega_q q^2/(2\hbar)} \tag{15}$$

and the corresponding energy eigenvalues $E_{n_q} = \hbar\omega_q(n_q + 1/2)$ with $n_q \in \mathbb{N}_0$. The symbol H_{n_q} denotes the Hermite polynomial of order n_q. Furthermore,

$$q_0(t) = \sum_{\omega} \hat{q}_0(\omega) e^{-i\tilde{\omega}t} \tag{16}$$

is the corresponding classical trajectory, i.e., the solution of Newton's equation of motion for a classical particle with the same one-dimensional harmonic potential and time-dependent electric field. The Fourier coefficients are easily obtained as

$$\hat{q}_0(\omega) = -\frac{e_0}{m}\left(\frac{1}{\omega_q^2 - \tilde{\omega}^2}\right)\hat{E}_q(\omega)\,. \tag{17}$$

The last ingredient is the classical Lagrangian for the driven harmonic oscillator

$$L\big(q_0(t), \dot{q}_0(t), t\big) = \frac{m}{2}\dot{q}_0(t)^2 - \frac{m\omega_q^2}{2}q_0(t)^2 - e_0 E_q(t) q_0(t)\,. \tag{18}$$

As the trajectory is known, the integral over the Lagrangian in (14) could be evaluated explicitly, but this is in fact not necessary, because the phase factor cancels out later and does not contribute to the physical observables.

The quantum-mechanical expectation value of the position operator is given by

$$\langle \boldsymbol{r}_0(t)\rangle = \int \Psi_{\boldsymbol{n}}^{(0)*}(\boldsymbol{r},t)\boldsymbol{r}\Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r},t)\, d^3r\,. \tag{19}$$

By inserting (12) as well as the explicit form (14) of the coherent states and exploiting the normalization of the individual components of the wavefunction, this yields

$$\langle q_0(t)\rangle = \int_{-\infty}^{\infty} \varphi_{n_q}(q-q_0(t))q\varphi_{n_q}(q-q_0(t))\, dq = q_0(t)\,. \tag{20}$$

In the absence of anharmonic perturbations, the quantum-mechanical expectation value $\langle q_0(t)\rangle$ is thus identical to the classical trajectory $q_0(t)$. The corresponding contribution to the induced polarization is linear in the electric field and equals $\hat{P}_q^{(1)}(\omega) = -Ne_0\hat{q}_0(\omega)$. By comparing to the definition $\hat{P}_q^{(1)}(\omega) = \varepsilon_0\chi_{qq}^{(1)}(\tilde{\omega})\hat{E}_q(\omega)$, which follows from (9) with $n = 1$, we eventually obtain the explicit expression for the linear susceptibility

$$\chi_{qq}^{(1)}(\tilde{\omega}) = \frac{Ne_0^2}{\varepsilon_0 m}\left(\frac{1}{\omega_q^2 - \tilde{\omega}^2}\right). \tag{21}$$

3.2. First Order: Anharmonic Perturbation of the Potential

The first-order terms of the Schrödinger Equation (1) satisfy the relation

$$\Big(i\hbar\partial_t - H^{(0)}(\boldsymbol{r},t)\Big)\Psi_{\boldsymbol{n}}^{(1)}(\boldsymbol{r},t) = H^{(1)}(\boldsymbol{r})\Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r},t)\,. \tag{22}$$

The first-order correction to the wavefunction is obtained from time-dependent perturbation theory as

$$\Psi_{\boldsymbol{n}}^{(1)}(\boldsymbol{r},t) = \frac{1}{i\hbar}\sum_{\boldsymbol{n}'}\Psi_{\boldsymbol{n}'}^{(0)}(\boldsymbol{r},t)\int\int \Psi_{\boldsymbol{n}'}^{(0)*}(\boldsymbol{r}',t)H^{(1)}(\boldsymbol{r}')\Psi_{\boldsymbol{n}}^{(0)}(\boldsymbol{r}',t)\, d^3r'\, dt\,, \tag{23}$$

which exploits the fact that the eigenfunctions of the driven harmonic oscillator at a fixed time t, even in the presence of an external electric field, form a complete orthonormal set, satisfying the orthonormality relation

$$\begin{aligned}\int \Psi_{\boldsymbol{n}}^{(0)*}(\boldsymbol{r},t)\Psi_{\boldsymbol{n}'}^{(0)}(\boldsymbol{r},t)\, d^3r &= \prod_q \int_{-\infty}^{+\infty} \psi_{n_q}^{(0)*}(q,t)\psi_{n_q'}^{(0)}(q,t)\, dq \\ &= \prod_q e^{i(E_{n_q}-E_{n_q'})t/\hbar}\int_{-\infty}^{+\infty} \varphi_{n_q}(q-q_0(t))\varphi_{n_q'}(q-q_0(t))\, dq \\ &= \prod_q \delta_{n_q,n_q'}\end{aligned} \tag{24}$$

and the completeness relation

$$\begin{aligned}\sum_{\boldsymbol{n}} \Psi^{(0)}_{\boldsymbol{n}}(\boldsymbol{r},t)\Psi^{(0)*}_{\boldsymbol{n}}(\boldsymbol{r}',t) &= \prod_q e^{im(q-q')\dot{q}_0(t)/\hbar} \sum_{n_q} \varphi_{n_q}(q-q_0(t))\varphi_{n_q}(q'-q_0(t)) \\ &= \prod_q \delta(q-q')\,.\end{aligned} \tag{25}$$

The first-order contribution to the electron displacement, the expectation value of the position operator, is given by

$$\langle \boldsymbol{r}_1(t)\rangle = \int \Psi^{(0)*}_{\boldsymbol{n}}(\boldsymbol{r},t)\boldsymbol{r}\Psi^{(1)}_{\boldsymbol{n}}(\boldsymbol{r},t)\, d^3r + \text{c.c.}\,, \tag{26}$$

where c.c. denotes the complex conjugate. In the following, we focus on the x component of the position vector; the expressions for the other vector elements can be obtained from a straightforward permutation of symbols. By inserting the first-order wavefunction (23), the expectation value can be written as

$$\langle x_1(t)\rangle = \frac{1}{i\hbar}\sum_{\boldsymbol{n}'} \int \Psi^{(0)*}_{\boldsymbol{n}}(\boldsymbol{r},t)x\Psi^{(0)}_{\boldsymbol{n}'}(\boldsymbol{r},t)\, d^3r \int\!\!\int \Psi^{(0)*}_{\boldsymbol{n}'}(\boldsymbol{r}',t)H^{(1)}(\boldsymbol{r}')\Psi^{(0)}_{\boldsymbol{n}}(\boldsymbol{r}',t)\, d^3r'\, dt + \text{c.c.} \tag{27}$$

Using the factored form (12) and the orthonormality of the wavefunctions, the summation simplifies to one over n'_x, with $n'_q = n_q$ for all $q \neq x$. This leads to

$$\begin{aligned}\langle x_1(t)\rangle &= \frac{1}{i\hbar}\sum_{n'_x} \int_{-\infty}^{+\infty} \psi^{(0)*}_{n_x}(x,t)x\psi^{(0)}_{n'_x}(x,t)\, dx \\ &\times \int\!\!\int \psi^{(0)*}_{n'_x}(x',t)\left(\prod_{q\neq x}\psi^{(0)*}_{n_q}(q',t)\right)H^{(1)}(\boldsymbol{r}')\psi^{(0)}_{n_x}(x',t)\left(\prod_{q\neq x}\psi^{(0)}_{n_q}(q',t)\right) d^3r'\, dt + \text{c.c.}\end{aligned} \tag{28}$$

The previously derived solution for the wavefunctions of the driven harmonic oscillator (14) is then substituted. After applying the change of variables $x = \tilde{x} + x_0(t)$ and $\boldsymbol{r}' = \tilde{\boldsymbol{r}}' + \boldsymbol{r}_0(t)$, we obtain

$$\begin{aligned}\langle x_1(t)\rangle &= \frac{1}{i\hbar}\sum_{n'_x} e^{i(n_x-n'_x)\omega_x t}\int_{-\infty}^{+\infty} \varphi_{n_x}(\tilde{x})(\tilde{x}+x_0(t))\varphi_{n'_x}(\tilde{x})\, d\tilde{x} \int e^{i(n'_x-n_x)\omega_x t} \\ &\times \int \varphi_{n'_x}(\tilde{x}')\varphi_{n_y}(\tilde{y}')\varphi_{n_z}(\tilde{z}')H^{(1)}(\tilde{\boldsymbol{r}}'+\boldsymbol{r}_0(t))\varphi_{n_x}(\tilde{x}')\varphi_{n_y}(\tilde{y}')\varphi_{n_z}(\tilde{z}')\, d^3\tilde{r}'\, dt + \text{c.c.}\end{aligned} \tag{29}$$

For $n'_x = n_x$, all integrals become real. In conjunction with the prefactor $1/(i\hbar)$, this results in a purely imaginary contribution to the sum, which is canceled by its complex conjugate. Therefore this term may be omitted.

The first integral in Equation (29) can be evaluated by introducing the matrix elements

$$\Omega_{n_q,n'_q}(j) := \int_{-\infty}^{+\infty} \varphi_{n_q}(q)q^j\varphi_{n'_q}(q)\, dq\,, \tag{30}$$

whose explicit solutions are provided in Appendix A.1. We note that $-e_0\Omega_{n_q,n'_q}(1)$ are the dipole transition matrix elements of the harmonic oscillator. With this definition, the integral yields

$$\begin{aligned}\int_{-\infty}^{+\infty} \varphi_{n_x}(\tilde{x})(\tilde{x}+x_0(t))\varphi_{n'_x}(\tilde{x})\, d\tilde{x} &= \Omega_{n_x,n'_x}(1) + x_0(t)\Omega_{n_x,n'_x}(0) \\ &= \left(\frac{\hbar}{2m\omega_x}\right)^{1/2}\left(\sqrt{n_x+1}\,\delta_{n_x+1,n'_x} + \sqrt{n_x}\,\delta_{n_x-1,n'_x}\right) + x_0(t)\delta_{n_x,n'_x}\,.\end{aligned} \tag{31}$$

As $n_x' = n_x$ may be omitted in Equation (29), only the two terms with $n_x' = n_x + 1$ or $n_x' = n_x - 1$ contribute to the sum. The expectation value of the position operator can thus be written as $\langle x_1(t) \rangle = W^+ - W^-$ with

$$\begin{aligned} W^{\pm} = {} & \pm \frac{1}{i\hbar} \Omega_{n_x, n_x \pm 1}(1) e^{\mp i \omega_x t} \int e^{\pm i \omega_x t} \\ & \times \int \varphi_{n_x \pm 1}(\tilde{x}') \varphi_{n_y}(\tilde{y}') \varphi_{n_z}(\tilde{z}') H^{(1)}\left(\tilde{\mathbf{r}}' + \mathbf{r}_0(t)\right) \varphi_{n_x}(\tilde{x}') \varphi_{n_y}(\tilde{y}') \varphi_{n_z}(\tilde{z}')\, d^3\tilde{r}' dt + \text{c.c.} \end{aligned} \tag{32}$$

Inserting the explicit form of the anharmonic potential (3), the spatial integrals become

$$\sum_{j,k,l} V_{jkl} \int \varphi_{n_x \pm 1}(\tilde{x}') \varphi_{n_x}(\tilde{x}') \varphi_{n_y}(\tilde{y}')^2 \varphi_{n_z}(\tilde{z}')^2 \left(\tilde{x}' + x_0(t)\right)^j \left(\tilde{y}' + y_0(t)\right)^k \left(\tilde{z}' + z_0(t)\right)^l d^3\tilde{r}' \,. \tag{33}$$

After decomposing the volume integral into a product of one-dimensional integrals over each Cartesian coordinate and applying the binomial theorem, this can be written as

$$\begin{aligned} & \sum_{j,k,l} V_{jkl} \sum_{j'=0}^{j} \binom{j}{j'} \int_{-\infty}^{+\infty} \varphi_{n_x \pm 1}(\tilde{x}') \tilde{x}'^{j-j'} x_0(t)^{j'} \varphi_{n_x}(\tilde{x}')\, d\tilde{x}' \\ & \times \sum_{k'=0}^{k} \binom{k}{k'} \int_{-\infty}^{+\infty} \varphi_{n_y}(\tilde{y}')^2 \tilde{y}'^{k-k'} y_0(t)^{k'}\, d\tilde{y}' \sum_{l'=0}^{l} \binom{l}{l'} \int_{-\infty}^{+\infty} \varphi_{n_z}(\tilde{z}')^2 \tilde{z}'^{l-l'} z_0(t)^{l'}\, d\tilde{z}' \,. \end{aligned} \tag{34}$$

As $x_0(t)$, $y_0(t)$, and $z_0(t)$ depend only on time, they can be factored out. The remaining spatial integrals can again be expressed in terms of the matrix elements $\Omega_{n_q, n_q'}(j)$ defined in (30) and assume the form

$$\sum_{j,k,l} V_{jkl} \sum_{j'=0}^{j} \sum_{k'=0}^{k} \sum_{l'=0}^{l} \binom{j}{j'} \binom{k}{k'} \binom{l}{l'} x_0(t)^{j'} y_0(t)^{k'} z_0(t)^{l'} \Omega_{n_x \pm 1, n_x}(j - j') \Omega_{n_y, n_y}(k - k') \Omega_{n_z, n_z}(l - l') \,. \tag{35}$$

When these are substituted back into Equation (32) and the time-independent matrix elements $\Omega_{n_q, n_q'}$ are factored out from the integral over t, we obtain

$$\begin{aligned} W^{\pm} = {} & -\frac{1}{\hbar} \Omega_{n_x, n_x \pm 1}(1) \sum_{j,k,l} V_{jkl} \sum_{j'=0}^{j} \sum_{k'=0}^{k} \sum_{l'=0}^{l} \binom{j}{j'} \binom{k}{k'} \binom{l}{l'} \Omega_{n_x \pm 1, n_x}(j - j') \\ & \times \Omega_{n_y, n_y}(k - k') \Omega_{n_z, n_z}(l - l') (\pm i) e^{\mp i \omega_x t} \int x_0(t)^{j'} y_0(t)^{k'} z_0(t)^{l'} e^{\pm i \omega_x t}\, dt + \text{c.c.} \end{aligned} \tag{36}$$

For brevity, we introduce the short-hand notation for the time integrals

$$O^{\pm}_{jkl}(t) = \pm i e^{\mp i \omega_x t} \int x_0(t)^j y_0(t)^k z_0(t)^l e^{\pm i \omega_x t}\, dt \,. \tag{37}$$

The evaluation of the integrals can be found in Appendix A.2. Using this short-hand notation and including the complex conjugate explicitly into the summation, we obtain

$$\begin{aligned} \langle x_1(t) \rangle = {} & -\frac{1}{\hbar} \sum_{j,k,l} V_{jkl} \sum_{j'=0}^{j} \sum_{k'=0}^{k} \sum_{l'=0}^{l} \binom{j}{j'} \binom{k}{k'} \binom{l}{l'} \left(O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t) \right) \\ & \times \left(\Omega_{n_x, n_x + 1}(1) \Omega_{n_x + 1, n_x}(j - j') - \Omega_{n_x, n_x - 1}(1) \Omega_{n_x - 1, n_x}(j - j') \right) \\ & \times \Omega_{n_y, n_y}(k - k') \Omega_{n_z, n_z}(l - l') \,. \end{aligned} \tag{38}$$

We note that the time dependence of the expectation value stems exclusively from $O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t)$. By interchanging the double summation, this can be rearranged to

$$\begin{aligned}\langle x_1(t)\rangle = -\frac{1}{\hbar}\sum_{j',k',l'}\Big(O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t)\Big)\sum_{j=j'}^{\infty}\sum_{k=k'}^{\infty}\sum_{l=l'}^{\infty}\binom{j}{j'}\binom{k}{k'}\binom{l}{l'}V_{jkl} \\ \times \big(\Omega_{n_x,n_x+1}(1)\Omega_{n_x+1,n_x}(j-j') - \Omega_{n_x,n_x-1}(1)\Omega_{n_x-1,n_x}(j-j')\big) \\ \times \Omega_{n_y,n_y}(k-k')\Omega_{n_z,n_z}(l-l')\,.\end{aligned} \tag{39}$$

Next, we apply an index shift that simplifies the arguments of the matrix elements Ω_{n_q,n'_q} by substituting j with $j+j'$, k with $k+k'$, and l with $l+l'$. This leads to

$$\begin{aligned}\langle x_1(t)\rangle = -\frac{1}{\hbar}\sum_{j',k',l'}\Big(O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t)\Big)\sum_{j,k,l}\binom{j+j'}{j'}\binom{k+k'}{k'}\binom{l+l'}{l'}V_{j+j',k+k',l+l'} \\ \times (\Omega_{n_x,n_x+1}(1)\Omega_{n_x+1,n_x}(j) - \Omega_{n_x,n_x-1}(1)\Omega_{n_x-1,n_x}(j))\Omega_{n_y,n_y}(k)\Omega_{n_z,n_z}(l)\,.\end{aligned} \tag{40}$$

As the time-dependent factors $O^{\pm}_{j'k'l'}(t)$ play the decisive role in the derivation of the generalized Miller formulae, we introduce the symbols

$$\begin{aligned}A^{x}_{j'k'l'} = \sum_{j,k,l}\binom{j+j'}{j'}\binom{k+k'}{k'}\binom{l+l'}{l'}V_{j+j',k+k',l+l'} \\ \times (\Omega_{n_x,n_x+1}(1)\Omega_{n_x+1,n_x}(j) - \Omega_{n_x,n_x-1}(1)\Omega_{n_x-1,n_x}(j))\Omega_{n_y,n_y}(k)\Omega_{n_z,n_z}(l)\end{aligned} \tag{41}$$

for the time-independent coefficients with analogous definitions for $A^{y}_{j'k'l'}$ and $A^{z}_{j'k'l'}$. In this way, the expectation value simplifies to

$$\langle x_1(t)\rangle = -\frac{1}{\hbar}\sum_{j',k',l'}A^{x}_{j'k'l'}\Big(O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t)\Big)\,. \tag{42}$$

By inserting the expression for $O^{+}_{j'k'l'}(t) + O^{-}_{j'k'l'}(t)$ from Appendix A.2, the expectation value eventually yields

$$\begin{aligned}\langle x_1(t)\rangle = -\frac{1}{\hbar}\sum_{j',k',l'}\sum_{\omega_1,\ldots,\omega_{j'+k'+l'}}\frac{2\omega_x A^{x}_{j'k'l'}}{\omega_x^2 - (\tilde{\omega}_1 + \ldots + \tilde{\omega}_{j'+k'+l'})^2}\hat{x}_0(\omega_1)\ldots\hat{x}_0(\omega_{j'}) \\ \times \hat{y}_0(\omega_{j'+1})\ldots\hat{y}_0(\omega_{j'+k'})\hat{z}_0(\omega_{j'+k'+1})\ldots\hat{z}_0(\omega_{j'+k'+l'})e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_{j'+k'+l'})t}\,,\end{aligned} \tag{43}$$

which describes the induced dynamics of the driven quantum anharmonic oscillator along the x axis exactly up to first order in the anharmonicity. Analogous relations are valid for the other components of $\langle \boldsymbol{r}_1(t)\rangle$.

3.3. Generalized Miller Formulae

Based on the derivation in the previous section, we proceed to extract the nonlinear susceptibility and formulate the generalized Miller formulae. In a first step, we express the Fourier coefficients of the classical trajectory (17) of the harmonic oscillator in terms of the linear susceptibilities (21) and the electric field according to

$$\hat{q}_0(\omega) = -\frac{\varepsilon_0}{Ne_0}\chi^{(1)}_{qq}(\tilde{\omega})\hat{E}_q(\omega)\,. \tag{44}$$

The expectation value of the position operator thus takes the form

$$\begin{aligned}\langle x_1(t)\rangle = &-\frac{2\omega_x}{\hbar}\sum_{j',k',l'}\sum_{\omega_1,\ldots,\omega_{j'+k'+l'}} A^x_{j'k'l'}\frac{\varepsilon_0 m}{Ne_0^2}\chi^{(1)}_{xx}(\tilde{\omega}_1+\ldots+\tilde{\omega}_{j'+k'+l'})\left(-\frac{\varepsilon_0}{Ne_0}\right)^{j'+k'+l'} \\ &\times\chi^{(1)}_{xx}(\tilde{\omega}_1)\ldots\chi^{(1)}_{xx}(\tilde{\omega}_{j'})\chi^{(1)}_{yy}(\tilde{\omega}_{j'+1})\ldots\chi^{(1)}_{yy}(\tilde{\omega}_{j'+k'})\chi^{(1)}_{zz}(\tilde{\omega}_{j'+k'+1})\ldots\chi^{(1)}_{zz}(\tilde{\omega}_{j'+k'+l'}) \\ &\times\hat{E}_x(\omega_1)\ldots\hat{E}_x(\omega_{j'})\hat{E}_y(\omega_{j'+1})\ldots\hat{E}_y(\omega_{j'+k'})\hat{E}_z(\omega_{j'+k'+1})\ldots\hat{E}_z(\omega_{j'+k'+l'})e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_{j'+k'+l'})t}\end{aligned} \tag{45}$$

with individual sums over the three counter variables j', k', and l'. In order to collect all terms of the same order $n = j' + k' + l'$, we insert an appropriate filter. For the polarization, defined as $P_q(t) = -Ne_0\langle q(t)\rangle$ in (8), we thus obtain the nonlinear components

$$\begin{aligned}P^{(n)}_x(t) =&\varepsilon_0\sum_{\omega_1,\ldots,\omega_n}\frac{2m\omega_x}{\hbar e_0}\left(-\frac{\varepsilon_0}{Ne_0}\right)^n\chi^{(1)}_{xx}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)\sum_{j',k',l'}\delta_{n,j'+k'+l'}A^x_{j'k'l'} \\ &\times\chi^{(1)}_{xx}(\tilde{\omega}_1)\ldots\chi^{(1)}_{xx}(\tilde{\omega}_{j'})\chi^{(1)}_{yy}(\tilde{\omega}_{j'+1})\ldots\chi^{(1)}_{yy}(\tilde{\omega}_{j'+k'})\chi^{(1)}_{zz}(\tilde{\omega}_{j'+k'+1})\ldots\chi^{(1)}_{zz}(\tilde{\omega}_{j'+k'+l'}) \\ &\times\hat{E}_x(\omega_1)\ldots\hat{E}_x(\omega_{j'})\hat{E}_y(\omega_{j'+1})\ldots\hat{E}_y(\omega_{j'+k'})\hat{E}_z(\omega_{j'+k'+1})\ldots\hat{E}_z(\omega_{j'+k'+l'})e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)t}\,.\end{aligned} \tag{46}$$

This expression is already very similar to the definition of the optical susceptibilities in (9), but instead of a sum over $\alpha_1, \ldots, \alpha_n$, the indices of the Cartesian axes appear in a fixed order. For any given tuple of j', k', and l', there are $(j' + k' + l')!/(j'!\,k'!\,l'!)$ distinct index permutations that contribute equally to the polarization, as may be confirmed by changing the multiplication order and relabeling the summation variables appropriately. Therefore, we can insert additional summations over $\alpha_1, \ldots, \alpha_n$ if we simultaneously divide by the number of permutations for each distinct set. In this way, we eventually arrive at

$$\begin{aligned}P^{(n)}_x(t) =&\varepsilon_0\sum_{\omega_1,\ldots,\omega_n}\sum_{\alpha_1,\ldots,\alpha_n}\frac{2m\omega_x}{\hbar e_0}\left(-\frac{\varepsilon_0}{Ne_0}\right)^n\chi^{(1)}_{xx}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)\chi^{(1)}_{\alpha_1\alpha_1}(\tilde{\omega}_1)\ldots\chi^{(1)}_{\alpha_n\alpha_n}(\tilde{\omega}_n) \\ &\times\sum_{j',k',l'}\delta_{n,j'+k'+l'}\frac{j'!\,k'!\,l'!}{n!}A^x_{j'k'l'}\hat{E}_{\alpha_1}(\omega_1)\ldots\hat{E}_{\alpha_n}(\omega_n)e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)t}\end{aligned} \tag{47}$$

and equivalent expressions for the other vector elements of the polarization.

By comparison with (9), the susceptibility tensor elements are now identified as

$$\begin{aligned}\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n;\tilde{\omega}_1,\ldots,\tilde{\omega}_n) &= \frac{2m\omega_\alpha}{\hbar e_0}\left(-\frac{\varepsilon_0}{Ne_0}\right)^n\chi^{(1)}_{\alpha\alpha}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n) \\ &\times\chi^{(1)}_{\alpha_1\alpha_1}(\tilde{\omega}_1)\ldots\chi^{(1)}_{\alpha_n\alpha_n}(\tilde{\omega}_n)\sum_{j',k',l'}\delta_{n,j'+k'+l'}\frac{j'!\,k'!\,l'!}{n!}A^\alpha_{j'k'l'}\,.\end{aligned} \tag{48}$$

As in Miller's original formula for second-harmonic generation, these generalized Miller formulae express all higher-order tensor elements of the nonlinear susceptibility as products of linear susceptibilities with a material-specific but frequency-independent prefactor.

In practical applications, this prefactor or even the shape of the confining potential are often not explicitly known, as in a recent study where Miller's rule was invoked to analyze the polaronic enhancement of second-harmonic generation in lithium niobate [36]. In such situations, it is convenient to eliminate the prefactor by considering the ratio

$$\frac{\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n;\tilde{\omega}_1,\ldots,\tilde{\omega}_n)}{\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}'_1+\ldots+\tilde{\omega}'_n;\tilde{\omega}'_1,\ldots,\tilde{\omega}'_n)} = \frac{\chi^{(1)}_{\alpha\alpha}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n)\chi^{(1)}_{\alpha_1\alpha_1}(\tilde{\omega}_1)\ldots\chi^{(1)}_{\alpha_n\alpha_n}(\tilde{\omega}_n)}{\chi^{(1)}_{\alpha\alpha}(\tilde{\omega}'_1+\ldots+\tilde{\omega}'_n)\chi^{(1)}_{\alpha_1\alpha_1}(\tilde{\omega}'_1)\ldots\chi^{(1)}_{\alpha_n\alpha_n}(\tilde{\omega}'_n)}\,. \tag{49}$$

This relation allows a full evaluation of the frequency-dependent nonlinear susceptibility $\chi^{(n)}_{\alpha\alpha_1\ldots\alpha_n}(\tilde{\omega}_1+\ldots+\tilde{\omega}_n;\tilde{\omega}_1,\ldots,\tilde{\omega}_n)$ based only on knowledge of the linear susceptibility and a single data point for an nth-order process at a set of reference frequencies $\tilde{\omega}'_1,\ldots,\tilde{\omega}'_n$.

3.4. Practical Application

When applying the generalized Miller formulae as a screening tool for materials with desired nonlinear optical properties, it must be assumed that the linear susceptibilities $\chi^{(1)}_{\alpha\alpha}(\omega+i\gamma)$ are tabulated in a database as functions of the real irradiation frequency ω and have been measured or calculated with a fixed broadening γ. As a consequence, one requires a practical procedure for constructing the susceptibility $\chi^{(1)}_{\alpha\alpha}(\omega_1+\ldots+\omega_n+in\gamma)$ that enters (49) with an increased broadening parameter $n\gamma$. Indeed, as we show below, this can be achieved by evaluating the convolution

$$\chi^{(1)}_{\alpha\alpha}(\omega+in\gamma)=\frac{1}{2\pi i}\int_{-\infty}^{+\infty}\chi^{(1)}_{\alpha\alpha}(\omega'+i\gamma)\frac{1}{\omega'-(\omega+i(n-1)\gamma)}\,d\omega'\,. \tag{50}$$

In order to prove this identity, we first rewrite the linear susceptibility

$$\chi^{(1)}_{\alpha\alpha}(\omega+i\gamma)=\frac{Ne_0^2}{\varepsilon_0 m}\frac{1}{\omega_\alpha^2-(\omega+i\gamma)^2}\,, \tag{51}$$

using a partial fraction decomposition as

$$\chi^{(1)}_{\alpha\alpha}(\omega+i\gamma)=\frac{Ne_0^2}{\varepsilon_0 m}\frac{1}{2\omega_\alpha}\left(\frac{1}{\omega+(\omega_\alpha+i\gamma)}-\frac{1}{\omega-(\omega_\alpha-i\gamma)}\right). \tag{52}$$

This expression can be regarded as an analytic function of ω with simple poles in the lower half of the complex frequency plane. The convolution (50) is then equivalent to the contour integral

$$\chi^{(1)}_{\alpha\alpha}(\omega+in\gamma)=\frac{Ne_0^2}{\varepsilon_0 m}\frac{1}{2\omega_\alpha}\frac{1}{2\pi i}\oint\left(\frac{1}{\omega'+(\omega_\alpha+i\gamma)}-\frac{1}{\omega'-(\omega_\alpha-i\gamma)}\right)\frac{1}{\omega'-(\omega+i(n-1)\gamma)}\,d\omega'\,, \tag{53}$$

where the path along the real axis is closed by a semicircle over the upper or lower complex half-plane. According to the residue theorem, the contour integration yields

$$\begin{aligned}\chi^{(1)}_{\alpha\alpha}(\omega+in\gamma)&=\frac{Ne_0^2}{\varepsilon_0 m}\frac{1}{2\omega_\alpha}\left(\frac{1}{(\omega+i(n-1)\gamma)+(\omega_\alpha+i\gamma)}-\frac{1}{(\omega+i(n-1)\gamma)-(\omega_\alpha-i\gamma)}\right)\\&=\frac{Ne_0^2}{\varepsilon_0 m}\frac{1}{2\omega_\alpha}\left(\frac{1}{\omega+(\omega_\alpha+in\gamma)}-\frac{1}{\omega-(\omega_\alpha-in\gamma)}\right),\end{aligned} \tag{54}$$

which is indeed equivalent to (52) with $n\gamma$ instead of γ. Based on the knowledge of the linear susceptibility with a fixed broadening γ, the convolution (50) thus allows a numerical construction of the linear susceptibility at any frequency ω with the broadening $n\gamma$.

3.5. Numerical Example

In order to illustrate the practical application of the generalized Miller formulae, we explain the construction of the susceptibility for fifth-harmonic generation

$$\chi^{(5)}_{xx\ldots x}(5\tilde{\omega};\tilde{\omega},\ldots,\tilde{\omega})=\frac{2m\omega_x}{\hbar e_0}\left(-\frac{\varepsilon_0}{Ne_0}\right)^5 A^x_{500}\chi^{(1)}_{xx}(5\tilde{\omega})\chi^{(1)}_{xx}(\tilde{\omega})^5 \tag{55}$$

for an incident field along the x direction as an example. In the upper panel of Figure 1, we display the real and the imaginary part of the linear susceptibility $\chi^{(1)}_{xx}(\omega+i\gamma)$, given by (21). The resonance at the eigenfrequency ω_x of the harmonic part of the potential is clearly visible. As the imaginary part is a Lorentzian curve whose width is proportional to γ and whose height is inversely proportional to γ, this parameter value merely determines the broadening of the peaks but does not change the results in a qualitative way; for the results in Figure 1, we have chosen $\gamma = \omega_x/4$. In the same panel, we also show the function $\chi^{(1)}_{xx}(5\omega + i5\gamma)$ obtained from the convolution (50), whose resonance is much broader and located at $\omega_x/5$. In both cases, the linear susceptibility is displayed in units of $Ne_0^2/(\varepsilon_0 m\omega_x^2)$. In the lower panel, we plot the calculated fifth-order susceptibility in units of $2Ne_0^6 A^x_{500}/(\hbar m^5\omega_x^{11})$. According to (55), each data point of $\chi^{(5)}_{xxxxxx}(5\tilde{\omega})$ in the lower panel is constructed as a product involving one point from each of the blue and red curves of the upper panel. As a consequence, the main spectral features are observed near the resonance frequencies of the two underlying linear susceptibilities.

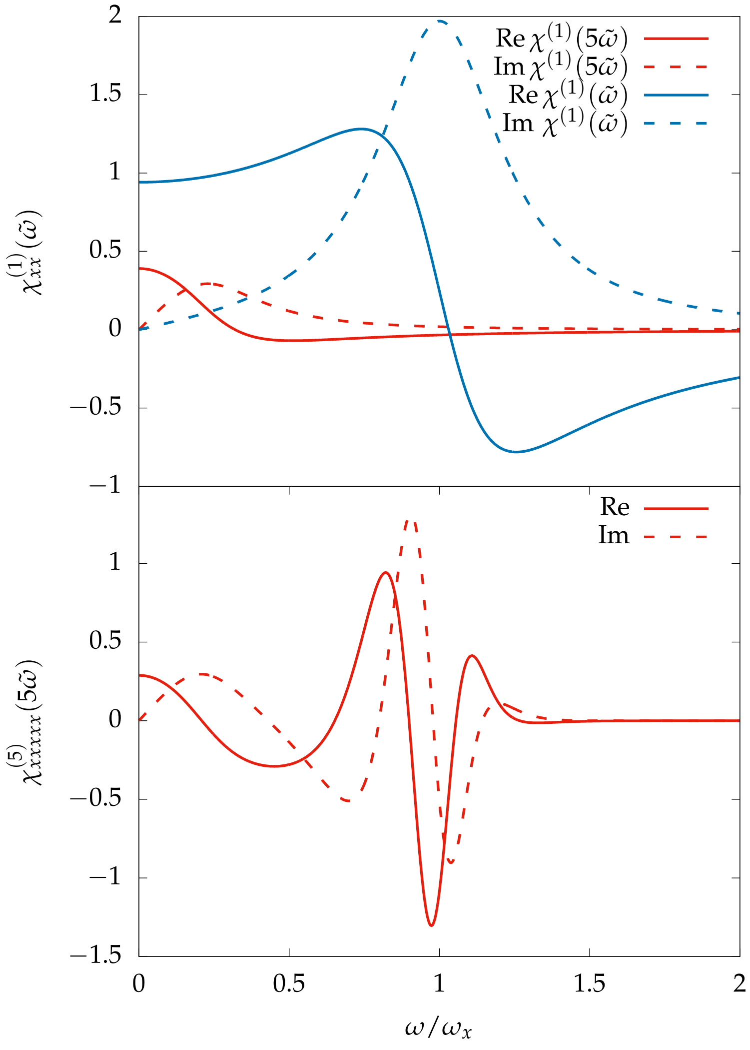

Figure 1. Frequency dependence of the susceptibility $\chi^{(5)}_{xxxxxx}(5\tilde{\omega})$ for fifth-harmonic generation, calculated from the generalized Miller formulae.

4. Conclusions

In this work, we presented an analytic solution of the time-dependent Schrödinger equation for a three-dimensional quantum oscillator with an arbitrary, weakly anharmonic potential driven by an external electric field. While the anharmonicity is treated within first-order perturbation theory, we include the full electric field in a nonperturbative manner. Therefore, the results remain valid for strong fields and allow us to derive explicit expressions for the induced dynamic polarization up to arbitrary order in the electric field. As the central result of this paper, we proved that all components of the nonlinear optical susceptibilites can be written exactly as products of the linear susceptibility. These generalized Miller formulae thus facilitate a highly efficient numerical evaluation of any nonlinear optical coefficients. Although analogous expressions were already known for the classical Lorentz model [28], this constitutes the first rigorous proof for quantum systems and justifies their application in actual materials investigations where the electron dynamics are governed by quantum mechanics. There are also notable differences: In the classical Lorentz model, the peak broadening arises from the velocity-dependent damping and is an intrinsic property of the material; therefore, all linear susceptibilities in the generalized Miller formulae must be evaluated with the same broadening parameter but different real frequency arguments. In contrast, for quantum anharmonic oscillators the broadening stems from the adiabatic switching of the external electric field, which can formally be described by complex frequencies $\tilde{\omega} = \omega + i\gamma$, and one of the linear susceptibilities in (49) must be evaluated at the sum of the *complex* frequencies. A failure to take the modified broadening properly into account may lead to significant deviations, and a comparison with accurate experimental or theoretical results for the nonlinear optical coefficients may then falsely suggest a violation of the generalized Miller formulae [27].

The generalized Miller formulae hold particular promise in data-driven materials science, where specific optical coefficients, such as high-harmonic generation or multi-wave mixing for given frequencies, are often not contained in databases due to the vast number of nonlinear phenomena and must instead be generated on the fly. In such situations, the generalized Miller formulae may be invoked to predict nonlinear optical susceptibilities quickly and with modest computational resources, using only readily available measured or computed data for the linear susceptibility as an input. We illustrated the practical procedure by means of a numerical example, fifth-harmonic generation by a monochromatic electric field, in Figure 1 above. In particular, we showed how the linear susceptibility for complex frequencies with an imaginary part $n\gamma$, which is required to evaluate the generalized Miller Formula (49) for an nth-order process, can easily be obtained numerically from a convolution with a suitable broadening function. In combination with a database of frequency-dependent linear susceptibilities, the generalized Miller formulae can thus be exploited to generate arbitrary nonlinear optical coefficients efficiently in high-throughput screening and computational materials discovery.

As an example for practical applications, Gjerding et al. [37] compared the second-order susceptibility $\chi^{(2)}(2\tilde{\omega})$ with the product $\chi^{(1)}(2\tilde{\omega})\chi^{(1)}(\tilde{\omega})^2$ in the static limit $\omega \to 0$ for 67 transition-metal dichalcogenides with the chemical formula MX_2, where M denotes a transition-metal cation and X is a chalcogen anion. This class of two-dimensional crystals is known to possess high nonlinear optical coefficients with a pronounced directional anisotropy. As demonstrated in [37], the products of the linear susceptibilities are indeed approximately proportional to the true nonlinear susceptibilities, and the proportionality factor is only weakly material dependent. In such situations, Miller's rule can be exploited to efficiently derive the nonlinear coefficients based on available data for the linear coefficients, in this case from the Computational 2D Materials Database (C2MD), and screen for materials with the desired properties. The generalized Miller formulae derived in this work facilitate the same approach for higher-order nonlinear processes.

While the generalized Miller formulae derived here are exact for weakly anharmonic potentials, it should be noted that the results for systems with a strong anharmonicity, as may be encountered in actual materials, will only be approximate. Therefore, further benchmarking of the quantitative accuracy in such cases remains highly desirable, as do investigations of additional effects on the electron dynamics, such as the mutual Coulomb repulsion in interacting many-electron systems.

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Appendix A

Appendix A.1. Matrix Elements $\Omega_{n_q,n'_q}(j)$

The matrix elements $\Omega_{n_q,n'_q}(j)$ defined in (30) can be written as

$$\Omega_{n_q,n'_q}(j) = \left(\frac{\hbar}{m\omega_q}\right)^{j/2} \frac{1}{\sqrt{2^{n_q+n'_q} n_q!\, n'_q!\, \pi}} \int_{-\infty}^{+\infty} H_{n_q}(z) z^j H_{n'_q}(z) e^{-z^2}\, dz \tag{A1}$$

by inserting the time-independent eigenfunctions of the harmonic oscillator (15) and substituting $z = \sqrt{m\omega_q/\hbar}\, q$. For $j = 0$, the result

$$\Omega_{n_q,n'_q}(0) = \frac{1}{\sqrt{2^{n_q+n'_q} n_q!\, n'_q!\, \pi}} \int_{-\infty}^{+\infty} H_{n_q}(z) H_{n'_q}(z) e^{-z^2}\, dz = \delta_{n_q,n'_q}\,. \tag{A2}$$

follows directly from the orthogonality of the Hermite polynomials. For $j > 0$, the identity

$$zH_{n_q}(z) = \frac{1}{2} H_{n_q+1}(z) + n_q H_{n_q-1}(z) \tag{A3}$$

leads to the recursion formula

$$\Omega_{n_q,n'_q}(j) = \left(\frac{\hbar}{2m\omega_q}\right)^{1/2} \left(\sqrt{n_q+1}\, \Omega_{n_q+1,n'_q}(j-1) + \sqrt{n_q}\, \Omega_{n_q-1,n'_q}(j-1)\right), \tag{A4}$$

which can be iterated as necessary. In particular, the matrix elements for $j = 1$ that enter (31) are given by

$$\Omega_{n_q,n'_q}(1) = \left(\frac{\hbar}{2m\omega_q}\right)^{1/2} \left(\sqrt{n_q+1}\, \delta_{n_q+1,n'_q} + \sqrt{n_q}\, \delta_{n_q-1,n'_q}\right). \tag{A5}$$

Appendix A.2. Integrals $O^{\pm}_{jkl}(t)$

The integrals $O^{+}_{jkl}(t)$ and O^{-}_{jkl} defined in (37) are complex conjugates of each other. With the Fourier representations (16) of the classical trajectory of the harmonic oscillator in each Cartesian coordinate, they can be written as

$$O^{\pm}_{jkl}(t) = \pm i e^{\mp i\omega_x t} \int \left(\sum_{\omega} \hat{x}_0(\omega) e^{-i\tilde{\omega} t}\right)^j \left(\sum_{\omega} \hat{y}_0(\omega) e^{-i\tilde{\omega} t}\right)^k \left(\sum_{\omega} \hat{z}_0(\omega) e^{-i\tilde{\omega} t}\right)^l e^{\pm i\omega_x t}\, dt\,. \tag{A6}$$

By introducing distinct frequency variables for each sum, this can be rearranged to

$$
\begin{aligned}
O^{\pm}_{jkl}(t) = \pm\, i e^{\mp i\omega_x t} \sum_{\omega_1,\ldots,\omega_{j+k+l}} & \hat{x}_0(\omega_1)\ldots\hat{x}_0(\omega_j)\hat{y}_0(\omega_{j+1})\ldots\hat{y}_0(\omega_{j+k}) \\
& \times \hat{z}_0(\omega_{j+k+1})\ldots\hat{z}_0(\omega_{j+k+l}) \int e^{\pm i[\omega_x \mp (\tilde{\omega}_1+\ldots+\tilde{\omega}_{j+k+l})]t}\, dt\,.
\end{aligned}
\tag{A7}
$$

The remaining integration over t is elementary and yields

$$
\begin{aligned}
O^{\pm}_{jkl}(t) = \sum_{\omega_1,\ldots,\omega_{j+k+l}} & \hat{x}_0(\omega_1)\ldots\hat{x}_0(\omega_j)\hat{y}_0(\omega_{j+1})\ldots\hat{y}_0(\omega_{j+k}) \\
& \times \hat{z}_0(\omega_{j+k+1})\ldots\hat{z}_0(\omega_{j+k+l}) \frac{e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_{j+k+l})t}}{\omega_x \mp (\tilde{\omega}_1+\ldots+\tilde{\omega}_{j+k+l})}\,.
\end{aligned}
\tag{A8}
$$

Finally, the evaluation of the expectation values in (42) only involves the real-valued sum $O^{+}_{jkl}(t) + O^{-}_{jkl}$, which simplifies to

$$
\begin{aligned}
O^{+}_{jkl}(t) + O^{-}_{jkl} = \sum_{\omega_1,\ldots,\omega_{j+k+l}} & \hat{x}_0(\omega_1)\ldots\hat{x}_0(\omega_j)\hat{y}_0(\omega_{j+1})\ldots\hat{y}_0(\omega_{j+k}) \\
& \times \hat{z}_0(\omega_{j+k+1})\ldots\hat{z}_0(\omega_{j+k+l}) \frac{2\omega_x e^{-i(\tilde{\omega}_1+\ldots+\tilde{\omega}_{j+k+l})t}}{\omega_x^2 - (\tilde{\omega}_1+\ldots+\tilde{\omega}_{j+k+l})^2}\,.
\end{aligned}
\tag{A9}
$$

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