

Five ways to the nonresonant dynamic Stark effect

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The dynamic Stark effect is the quasistatic shift in energy levels due to the application of optical fields. The effect is in many ways similar to the static Stark effect. However, the dynamic Stark effect can be applied on rapid time scales and with high energies, comparable to those of atoms and molecules themselves. The dynamic Stark effect due to nonresonant laser fields is used in a myriad of contemporary experiments to hold and align molecules, to shape potential energy surfaces, and to make rapid transient birefringence. Five approaches of increasing sophistication are used to describe the dynamic Stark effect. One application, molecular alignment, is summarized and a comparison is made between the dynamic Stark effect and Stokes light generation in a Raman scattering process. © 2011 American Association of Physics Teachers.

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I. INTRODUCTION

The Stark effect is the shift of energy levels due to the presence of an external electric field. It was discovered in 1913 by Stark¹ and is a mainstay of the undergraduate and graduate physics curriculum. Numerous textbooks such as Refs. 2–4 discuss the Stark effect due to a static field.

A similar effect occurs in the oscillating electric fields produced by lasers. If the field oscillates with a very low frequency, the level shifts adiabatically follow the static Stark shift formula. As the frequency is increased, and under appropriate conditions, the eigenstates do not follow the instantaneous electric field, but instead follow only the intensity envelope of the field. This quasistatic shift of the eigenstates in the presence of an oscillating field is known as the dynamic Stark effect (or AC Stark effect).

Modern ultrafast lasers⁵ are so rapid and intense that they can interact with many quantum systems on their intrinsic time and energy scales. As a result, the influence of these lasers (via the dynamic Stark effect) has become an increasingly important part of atomic, molecular, and optical physics. This level of influence would not be accessible with DC approaches. The effect is used in a diverse set of exciting new molecular experiments that hold and align molecules,⁶ shape potential energy surfaces,^{7,8} and use quantum superpositions to generate macroscopic time-dependent birefringences for modifying propagating pulses.^{9–11} The dynamic Stark effect is an increasingly important tool for controlling and measuring quantum systems.^{12,13} It is particularly useful for quantum control because the mechanism is nonresonant (requiring no highly specific wavelength sources) and because it can be nonperturbative (causing a large change in target systems).

The organization of the paper is as follows. Section II presents a brief discussion of the different forms of the Stark effect in a static or oscillating field. The rest of the paper discusses only the nonresonant form. Sections III–VI discuss various different approaches to deriving the dynamic Stark effect interaction. The results of these sections are almost equivalent, but each presents the effect in increasingly more detailed formalisms, revealing the limits of other approaches. To connect the dynamic Stark effect with a contemporary experiment that utilizes it, Sec. VIII discusses molecular

alignment with a laser. Section IX contrasts the dynamic Stark effect with conventional Raman scattering.

II. DIFFERENT FORMS OF THE STARK EFFECT

Depending on the field strengths, the frequencies involved, and the approximations used, there are many different limits of the Stark effect which all have unique physical characteristics. Here we are concerned only with the semiclassical nonresonant effect, with a particular emphasis on molecular applications, but we briefly contrast with some other forms.

A number of excellent atomic physics texts,^{14–16} nonlinear optics texts,¹⁷ and quantum optics texts^{18,19} discuss the Stark effect due to an oscillating field. There also are several papers that discuss the material.^{20–23}

In static electric fields, the energy of the n th state in terms of the unperturbed energy $E_n^{(0)}$ may be written as

$$E_n = E_n^{(0)} + \langle n|V|n\rangle + \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}} + \mathcal{O}(V^3), \quad (1)$$

where the interaction of the electric field is $V = -\boldsymbol{\mu} \cdot \mathbf{E}$, with $\boldsymbol{\mu}$ as the dipole moment and \mathbf{E} as the electric field. In first-order perturbation theory, there is no effect in nondegenerate systems with definite parity because the first-order matrix elements of the perturbation vanish (although this situation is not the case in degenerate systems). Therefore, Stark shifts usually refer to the second-order effect and the dynamic Stark effect considered here is the AC analog of the quadratic term.

There are some important differences between the dynamic Stark effect and its static namesake. In an oscillating field, the idea of static levels is not appropriate because there are no stationary states. However, under appropriate conditions, which we discuss in Sec. III, the idea of a quasistatic level becomes applicable and the levels behave as if they are in a static field, reacting only to the laser pulse envelope and not the instantaneous field (see Fig. 1). The field strengths achievable with a static electric field are much less than the field strengths achievable with ultrafast laser pulses. Ultrafast laser pulses can easily exceed atomic field strengths of 10^9 V/cm, opening the possibility of the dynamic Stark effect being highly nonperturbative and being so on femtosecond timescales.

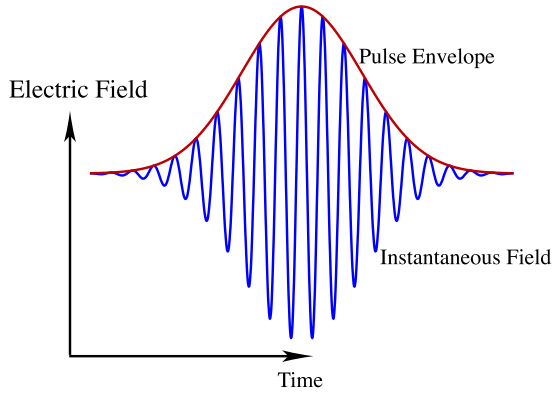


Fig. 1. The electric field of a laser pulse and its envelope. In the static Stark effect, the system responds to the instantaneous electric field. In the non-resonant dynamic Stark effect, the system responds only to the pulse envelope.

There are different cases with oscillating fields depending on the field strengths and frequencies. If the oscillation is very slow, the states adiabatically follow the instantaneous electric field. If the driving field is in or near resonance with a pair of quantum levels, population transfer will occur and the levels may be split as in the Rabi effect or Autler–Townes splitting.²² The resonance case is well discussed in textbooks. Our focus is on the nonresonant case, which is of special interest in molecular physics due to its generality.

Because the dynamic Stark effect can be nonperturbative and nonresonant, its effects are dramatic and flexible and are (within limits) independent of the wavelength of the applied field. As a result of these unique features, the dynamic Stark effect has been increasingly used in the modern laser laboratory.

III. CLASSICAL OSCILLATOR APPROACH

We consider the dynamic Stark effect from several elementary perspectives before discussing a more complete formalism. We first discuss a classical harmonic oscillator with resonant frequency ω_i , driven in a field $E(t) = \mathcal{E} \cos(\omega t)$. If there is more than one resonance ω_i , the result below will be summed over i . The interaction potential depends on the component of the electric field directed along the dipole moment and is written in full vector form in subsequent sections. For the scalar case the potential that the oscillator experiences is

$$V = \frac{1}{2}m\omega_i^2x^2 - qxE(t). \quad (2)$$

The charge of the system is q and x is the position of the charge from its equilibrium state. The dynamics of the system are given by Newton's second law, the periodic solution of which is

$$x(t) = \frac{q\mathcal{E}/m}{\omega_i^2 - \omega^2} \cos(\omega t). \quad (3)$$

The applied field moves the charge from its equilibrium position in phase (or out of phase, depending on the charge and frequency) with the electric field.

The displacement of the charge defines the induced dipole moment

$$\mu(t) \equiv qx(t). \quad (4)$$

The polarizability α is defined as the proportionality constant between the dipole moment and the electric field

$$\mu(t) = \alpha E(t) \quad (5)$$

and thus,

$$\alpha = \frac{q^2/m}{\omega_i^2 - \omega^2}. \quad (6)$$

The energy of the induced dipole is $\int \mu(E)dE = -\frac{1}{2}\mu(t)E(t)$ and its time average is

$$-\left\langle \frac{1}{2}\mu(t)E(t) \right\rangle = -\frac{1}{4}\alpha\mathcal{E}^2, \quad (7)$$

which implies that the average energy of the induced dipole decreases in the presence of an oscillating field. That is, the energy level shifts in the presence of the laser field. From this classical perspective, the quadratic term in the interaction energy rectifies the electric field and because the dipole interaction is negative, the time average reduces the system energy.

IV. REFRACTIVE INDEX APPROACH

Alternatively, consider the electromagnetic field energy^{4,24} density of a propagating wave in vacuum: $\epsilon_0 = \frac{1}{8\pi}\mathcal{E}^2$. In the presence of material with a refractive index n , the expression for the energy is modified to $\epsilon(n) = \frac{n}{8\pi}\mathcal{E}^2$. The increase in the energy density is due to the decrease in the phase velocity in materials with refractive index $n > 1$. Therefore, the energy of an incident field is “bunched up.” The bunching compresses the wavelength and therefore increases the energy density. The change in energy due to the presence of the matter is the difference from the vacuum case

$$\epsilon(n) - \epsilon_0 = \frac{1}{8\pi}(n-1)\mathcal{E}^2. \quad (8)$$

Energy must be conserved and hence the increase in the field energy must be offset by an equal and opposite decrease in the energy of the surrounding matter. Because the refractive index^{4,24} $n = \sqrt{1+4\pi\rho\alpha} \approx 1+2\pi\rho\alpha$ for low number densities ρ , the energy change per unit particle is then

$$-(\epsilon(n) - \epsilon_0)/\rho = -\frac{1}{4}\alpha\mathcal{E}^2. \quad (9)$$

Thus, the mean shift per particle is the same as that given by the classical oscillator formalism (7). Note that cgs units have been used.

V. INTERACTION POTENTIAL APPROACH

Another method for determining the dynamic Stark effect energy shift is a purely classical field approach. In this approach, there is no need to consider the constituents of the system and only classical electromagnetism is required.

We first consider a scalar electric field with a slowly varying envelope

$$E(t) = \mathcal{E}(t)\cos(\omega t). \quad (10)$$

If the system can respond instantaneously, the dipole moment can be expressed as a Taylor series in the electric field

$$\mu(E) = \mu_0 + \alpha E + \dots \quad (11)$$

Here, μ_0 is the field-free static dipole moment and α is the polarizability. Although simply a Taylor series coefficient at this point, as discussed in Sec. VII, α represents the average contribution to the dipole moment from all states not directly participating in the field-system interaction; that is, states that are not resonantly dipole coupled by the field. These states are often denoted as “nonessential.”

The energy of interaction of the dipole and the electric field is

$$V(t) = - \int_E \mu(E) dE = -\mu_0 E - \frac{1}{2} \alpha E^2 + \dots \quad (12)$$

We can then express the interaction explicitly using the oscillating field (10) and convert the cosine to the exponential representation

$$V = -\mu_0 E - \frac{1}{8} \alpha \mathcal{E}^2(t) (e^{i\omega t} + e^{-i\omega t})(e^{i\omega t} + e^{-i\omega t}) + \dots \quad (13)$$

Although this approach is purely classical, a photon interpretation is already apparent. The oscillating term $e^{-i\omega t}$ corresponds to absorption (as represented by the upward arrow \uparrow) and the $e^{i\omega t}$ term corresponds to emission (as represented by the downward arrow \downarrow).¹⁹ There are four terms formed from the product of the exponentials. Vertical two photon excitations ($\uparrow\uparrow$) arise from the term oscillating at $-2\omega t$ and the reverse ($\downarrow\downarrow$) arises from the term oscillating at $2\omega t$. Raman type excitations ($\uparrow\downarrow$, $\downarrow\uparrow$) arise from the quasistatic cross-terms, which are a product of two terms oscillating at ωt and $-\omega t$. The Raman excitations are quasistatic in the sense that only the envelope is time-dependent as there is no oscillating component.

If the system is unable to respond rapidly, we may neglect the high frequency components of the interaction oscillating at $\pm 2\omega t$ and consider the portion that responds only to the pulse envelope. This portion represents the dynamic Stark effect potential

$$V \approx -\mu_0 E(t) - \frac{1}{4} \alpha \mathcal{E}^2(t). \quad (14)$$

We see again that the dynamic Stark effect shift lowers the system energy by $-\frac{1}{4} \alpha \mathcal{E}^2(t)$.

This procedure can be generalized to three dimensions when the electric field $\mathbf{E}(t) = \frac{1}{2} (\mathcal{E}(t) e^{-i\omega t} + \text{complex conjugate (c.c.)})$ includes a phase in the complex envelope \mathcal{E} . The envelope is now a vector to permit arbitrarily polarized light. The dipole moment becomes a series expansion in three dimensions with

$$\boldsymbol{\mu}(\mathbf{E}) = \boldsymbol{\mu}_0 + \boldsymbol{\alpha} \mathbf{E} + \dots \quad (15)$$

The scalar polarizability has become a tensor $\boldsymbol{\alpha}$ with Cartesian components α^{ab} , where a and b can be x , y , or z . The Cartesian indices are written as superscripts for convenience later. The generalization of the interaction (14) can then be derived as

$$V \approx -\boldsymbol{\mu}_0 \cdot \mathbf{E}(t) - \frac{1}{4} \boldsymbol{\mathcal{E}}^*(t) \cdot \boldsymbol{\alpha} \cdot \boldsymbol{\mathcal{E}}(t). \quad (16)$$

Note that the complex conjugate $\boldsymbol{\mathcal{E}}^*$ is used.

To summarize, in the presence of a strong external field, the static dipole is augmented by a dipole induced by the applied field. The net result is that the interaction of the static

portion $-\boldsymbol{\mu}_0 \cdot \mathbf{E}(t)$ remains the same, but the induced portion adds a potential shift that is quadratic in the applied field envelope.

VI. OPERATOR REPLACEMENT APPROACH

In quantum mechanical calculations, we may approximate the dipole interaction $-\boldsymbol{\mu}E$ by replacing the operator $\boldsymbol{\mu}$ with its expectation value as calculated in first-order perturbation theory

$$\langle \boldsymbol{\mu} \rangle = \boldsymbol{\mu}_0 + \alpha E + \dots, \quad (17)$$

where $\boldsymbol{\mu}_0$ is the field-free dipole operator expectation value and the first-order coefficient (which is the polarizability) is defined as^{14,17}

$$\alpha(\omega) = \sum_m \left(\frac{\boldsymbol{\mu}_{gm} \boldsymbol{\mu}_{mg}}{\omega_{mg} - \omega} + \frac{\boldsymbol{\mu}_{mg} \boldsymbol{\mu}_{gm}}{\omega_{mg} + \omega} \right). \quad (18)$$

The index g represents the state in question and m is all other states. The derivation of Eq. (18) will be given in Sec. VII, but we can understand its application here. Much like the classical case, we take the interaction energy (12) for the induced dipole and time average over the rapidly oscillating terms in the quadratic portion and obtain

$$V \approx -\mu_0 E(t) - \frac{1}{4} \alpha \mathcal{E}^2(t). \quad (19)$$

As before, the dynamic Stark effect level shift follows the intensity of the optical field. This quantum mechanical approach is almost identical to the classical approach, except for the fact that the polarizability can be calculated from the material Hamiltonian. In comparison with the complete adiabatic elimination approach that we will discuss, this approximation is not always applicable because it replaces the operator $\boldsymbol{\mu}$ with a number and thus, for example, ignores any possibility of operating on the electronic portion of a molecular wave function. A more complete discussion of the dynamic Stark effect is given next.

VII. ADIABATIC ELIMINATION APPROACH

We consider a complete quantum mechanical approach for a general system and then specialize to the case of molecules. Our objective is to use an entirely quantum mechanical approach to derive the dynamic Stark effect potential V^{DSE} (although the applied field is classical). We will first derive the matrix elements of V^{DSE} and then determine the potential that generates those matrix elements.

A. General system

Quantum mechanical levels often separate themselves into manifolds of states. For example, molecules have electronic states on which sit nuclear levels (rotations and vibrations). If we are interested only in motion in a subset of all states, for example, all the nuclear states in a particular electronic level, it is convenient to ignore the uninteresting states and focus on the important ones. The method of essential states^{14,25} has been developed to treat this problem. In this method, we divide the system into essential and nonessential states. Often, essential corresponds to the ground molecular electronic state and nonessential corresponds to all electronically excited states. If we integrate out the motion in nonessential states, these states can be ignored, with the cost that

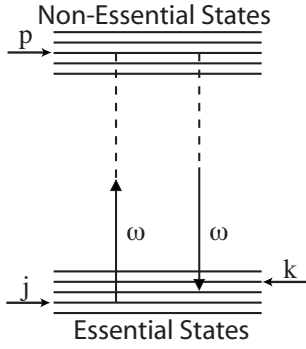


Fig. 2. The dynamics of interest occur in the essential states. Transitions between levels j and k within the essential states occur via far off-resonance nonessential state p . This sequence is a type of Raman transition.

their influence on the essential states is included by the introducing a new interaction. In our case, this new interaction is the dynamic Stark effect. Symbolically this method may be represented as

$$\underbrace{-\boldsymbol{\mu} \cdot \mathbf{E}}_{\text{all states}} \rightarrow \underbrace{-\boldsymbol{\mu} \cdot \mathbf{E} + V^{\text{DSE}}}_{\text{essential states}}, \quad (20)$$

which implies that when all states are considered in a calculation, only the dipole interaction is required, but when only a subset of essential states are considered, a new term V^{DSE} needs to be included. The influence of the nonessential states is equivalent to a new potential.

To develop the approach, the following convention for state indices is introduced. For sums over all states, we use the letters ℓ and m ; for sums over the essential states, we use the letters j and k ; and for sums over the nonessential states, we use the letter p (see Fig. 2). The interaction with a laser field of the form

$$\mathbf{E}(t) = \frac{1}{2} \boldsymbol{\mathcal{E}}(t) e^{-i\omega t} + \text{c.c.} \quad (21)$$

is given by $V(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t)$. The wave function can then be expanded in terms of the field-free basis

$$|\Psi(t)\rangle = \sum_{\ell} c_{\ell}(t) e^{-i\omega_{\ell} t} |\ell\rangle \quad (22)$$

and substitution into the time-dependent Schrödinger equation yields the equations of motion

$$i\hbar \dot{c}_{\ell} = \sum_m e^{-i\omega_m t} V_{\ell m}(t) c_m(t), \quad (23)$$

where

$$\omega_{m\ell} = \omega_m - \omega_{\ell} \quad (24)$$

and

$$V_{\ell m}(t) = \langle \ell | \boldsymbol{\mu} \cdot \mathbf{E}(t) | m \rangle. \quad (25)$$

The indices in Eq. (23) are over all states.

Let's consider the dynamics of one essential state c_k

$$i\hbar \dot{c}_k = \sum_j e^{-i\omega_{jk} t} V_{kj}(t) c_j(t) + \sum_p e^{-i\omega_{pk} t} V_{kp}(t) c_p(t). \quad (26)$$

The sum over all states has been split into a sum over the essential states j and a sum over the nonessential states p . Our goal is to solve for the nonessential state dynamics $c_p(t)$ and substitute it into Eq. (26). This substitution will remove

the explicit appearance of the nonessential states.

To solve for $c_p(t)$, assume that there is zero initial population in the nonessential states and there are no transitions within these states (the sum over all states is replaced by a sum over essential states j). Hence, the dynamics can be written from Eq. (23) as

$$c_p(t) = \frac{1}{i\hbar} \int_{-\infty}^t \sum_j e^{-i\omega_{jp} t'} V_{pj}(t') c_j(t') dt'. \quad (27)$$

Because the state coefficients $c_j(t)$ and the pulse envelope $\boldsymbol{\mathcal{E}}(t)$ are expected to vary slowly, we can approximate the integral in Eq. (27) by generating a Taylor series in the derivatives of the product $c_j(t)\boldsymbol{\mathcal{E}}(t)$. We do so by integrating by parts repeatedly to yield

$$c_p(t) = -\frac{1}{2\hbar} \sum_{s=0}^{\infty} \sum_j (-i)^s \left[\frac{e^{-i(\omega_{jp}-\omega)t}}{(\omega_{jp}-\omega)^{s+1}} \frac{d^s}{dt^s} [\boldsymbol{\mathcal{E}}(t) c_j(t)] \cdot \boldsymbol{\mu}_{pj} + \frac{e^{-i(\omega_{jp}+\omega)t}}{(\omega_{jp}+\omega)^{s+1}} \frac{d^s}{dt^s} [\boldsymbol{\mathcal{E}}^*(t) c_j(t)] \cdot \boldsymbol{\mu}_{pj} \right], \quad (28)$$

where $\boldsymbol{\mu}_{pj} = \langle p | \boldsymbol{\mu} | j \rangle$. If $c_j(t)\boldsymbol{\mathcal{E}}(t)$ varies slowly, only the $s=0$ term is required (no derivative). For rapidly varying envelopes, $s>0$ terms must be included or the series may not converge. Note that in the resonant rotating wave approximation,¹⁶ the counter-rotating terms (with detunings $\omega_{jp} + \omega$) are often dropped and only the resonant terms (with detunings $\omega_{jp} - \omega$) are retained. This approximation is appropriate near resonance, but cannot be performed when both terms may be comparable, as in the nonresonant case presented here.

Now that the dynamics of the nonessential states have been found, the solution may be substituted in the equation of motion for the essential states, thus eliminating the nonessential dynamics. Specifically, the $s=0$ term of Eq. (28) may be inserted into the second sum of Eq. (26). The rotating wave approximation is then invoked by neglecting the fast moving oscillations whose contributions are not cumulative. The result is that the dynamics for the essential states may be written as

$$i\hbar \dot{c}_k = \sum_j e^{-i\omega_{jk} t} V_{kj}^{\text{effective}}(t), \quad (29)$$

where the effective perturbation $V_{kj}^{\text{effective}}(t) = V_{kj}^{\text{dipole}}(t) + V_{kj}^{\text{DSE}}(t)$ is composed of a dipole contribution

$$V_{kj}^{\text{dipole}}(t) = -\boldsymbol{\mu}_{kj} \cdot \mathbf{E}(t) \quad (30)$$

and a quadratic contribution

$$V_{kj}^{\text{DSE}}(t) = -\frac{1}{4} \sum_p \left(\frac{\boldsymbol{\mu}_{kp} \cdot \boldsymbol{\mathcal{E}}^*(t) \boldsymbol{\mu}_{pj} \cdot \boldsymbol{\mathcal{E}}(t)}{\omega_{pj} + \omega} + \frac{\boldsymbol{\mu}_{kp} \cdot \boldsymbol{\mathcal{E}}(t) \boldsymbol{\mu}_{pj} \cdot \boldsymbol{\mathcal{E}}^*(t)}{\omega_{pj} - \omega} \right). \quad (31)$$

Note that when the dipole coupling dominates, the dynamics follow the instantaneous field $\mathbf{E}(t)$ and when the dynamic Stark effect coupling dominates, the dynamics follow only the field envelope $\boldsymbol{\mathcal{E}}(t)$. Equation (31) can be written as [see Eq. (16)]

$$V_{kj}^{\text{DSE}}(t) = -\frac{1}{4} \mathcal{E}^*(t) \cdot \alpha_{kj} \cdot \mathcal{E}(t), \quad (32)$$

where the individual components of the polarizability matrix elements are

$$\alpha_{kj}^{ab} = \sum_p \left(\frac{\mu_{kp}^a \mu_{pj}^b}{\omega_{pj} + \omega} + \frac{\mu_{kp}^b \mu_{pj}^a}{\omega_{pj} - \omega} \right), \quad (33)$$

with the indices a and b representing the Cartesian components x, y, z . We next determine the interaction that generates these matrix elements.

B. Molecules

The previous approach is applicable to any charged quantum system that can be separated into essential and nonessential states. The level subscript spans all degrees of freedom, nuclear and electronic. To proceed, we consider the molecular case and separate the index k into nuclear and electronic components (the Born–Oppenheimer and Placzek approximation²⁶)

$$k \rightarrow e, n. \quad (34)$$

In terms of wave functions, the vector $|k\rangle$ can be written as a product of nuclear and electronic vectors

$$|k\rangle \rightarrow |n(R)\rangle |e(r;R)\rangle, \quad (35)$$

where n is the nuclear quantum numbers of the rotational-vibrational wave function $|n(R)\rangle$ that exists on electronic state e (n implicitly depends on e). The nuclear coordinates are given by R . The electronic wave function $|e(r;R)\rangle$ depends on the electronic coordinate r and parametrically on the nuclear coordinates R . This assumption of nuclear and electronic separability allows the polarizability (33) to be written as

$$\alpha_{e_1 n_1, e_2 n_2}^{ab} = \sum_{e_3 n_3 \in N} \left(\frac{\mu_{e_1 n_1, e_3 n_3}^a \mu_{e_3 n_3, e_2 n_2}^b}{\omega_{e_3 n_3, e_2 n_2} + \omega} + \frac{\mu_{e_1 n_1, e_3 n_3}^b \mu_{e_3 n_3, e_2 n_2}^a}{\omega_{e_3 n_3, e_2 n_2} - \omega} \right). \quad (36)$$

N represents all nonessential states. We wish to determine the function that generates this matrix element. It is difficult to make this identification because we cannot simply remove the nuclear bra $\langle n_1|$ from the left side and the nuclear ket $|n_2\rangle$ from the right side because the denominators also depend on n_2 . We proceed by making some approximations that will allow us to make the identification. First, we focus on the simple case where only the essential dynamics in the ground state $e_1 = e_2$ are considered. Also, because the electronic response of the molecule dominates the interaction, the polarizability varies very little with the nuclear quantum numbers n_2 and n_3 and we can make the approximation that the energy differences $\omega_{e_3 n_3, e_1 n_2}$ do not depend strongly on the nuclear number and simply replace them with the average $\bar{\omega}_{e_3, e_1}$

$$\alpha_{e_1 n_1, e_1 n_2}^{ab} = \sum_{e_3 n_3 \in N} \left(\frac{\mu_{e_1 n_1, e_3 n_3}^a \mu_{e_3 n_3, e_1 n_2}^b}{\bar{\omega}_{e_3, e_1} + \omega} + \frac{\mu_{e_1 n_1, e_3 n_3}^b \mu_{e_3 n_3, e_1 n_2}^a}{\bar{\omega}_{e_3, e_1} - \omega} \right). \quad (37)$$

At this point, we may remove the nuclear bra $\langle n_1|$ from the left side and the nuclear ket $|n_2\rangle$. We can go one step further and note that in each electronic state e_3 , the nuclear functions form a complete basis ($1 = \sum_{n_3} |n_3\rangle \langle n_3|$). This closure relation can be inserted to replace the sum over n_3 with the identity. We can then write the dynamic Stark effect polarizability in state e_1 as

$$\alpha_{e_1}^{ab} = \sum_{e_3 \in N} \left(\frac{\mu_{e_1, e_3}^a \mu_{e_3, e_1}^b}{\bar{\omega}_{e_3, e_1} + \omega} + \frac{\mu_{e_1, e_3}^b \mu_{e_3, e_1}^a}{\bar{\omega}_{e_3, e_1} - \omega} \right), \quad (38)$$

where the repeated subscript e_1 has been dropped on the left hand side, indicating that only a single essential electronic state is being considered.

Now that we have identified a function whose matrix elements are given in Eq. (36), we can consider the dynamic Stark effect matrix elements from Eq. (32) and construct the corresponding potential

$$V^{\text{DSE}}(t) = -\frac{1}{4} \mathcal{E}^*(t) \cdot \alpha_{e_1} \cdot \mathcal{E}(t). \quad (39)$$

We recover the dynamic Stark effect interaction as in the previous approaches with the exception that the polarizability is slightly modified in the denominator (using average energy differences). For electronic ground state dynamics, it is appropriate in many cases to approximate Eq. (38) by the usual static polarizability because the nuclear level spacings are much smaller than the electronic energies spacings.

We conclude that when considering a subset of essential states in the presence of a strong, nonresonant, but nondestructive laser field, the dipole interaction is modified by the addition of a dynamic Stark effect potential V^{DSE} . This potential generates Raman type transitions (to be discussed in Sec. IX) and has the property that it follows the intensity envelope, not the instantaneous electric field. Contemporary lasers have enormous field strengths comparable to the forces that bind electrons and molecules (10^9 V/cm) and can vary on time scales on the order of femtoseconds. The implication of the dynamic Stark effect is that optical fields can be used to apply large and rapid level shifts to quantum states in a regime well beyond what is accessible with DC fields.

VIII. DYNAMIC STARK EFFECT FOR MOLECULAR ALIGNMENT

We briefly note the connection to an exciting recent application of the dynamic Stark effect: The use of lasers to align a collection of randomly distributed neutral molecules.⁶ Many molecules behave like field-free rotors and their Hamiltonian is given by

$$H_0 = \frac{L^2}{2I}, \quad (40)$$

where I is the moment of inertia and L is the angular momentum operator. The solutions are the spherical harmonics²⁻⁴ $Y_{lm}(\theta, \phi)$. Rotor molecules have no potential energy; their statics and dynamics are determined purely by

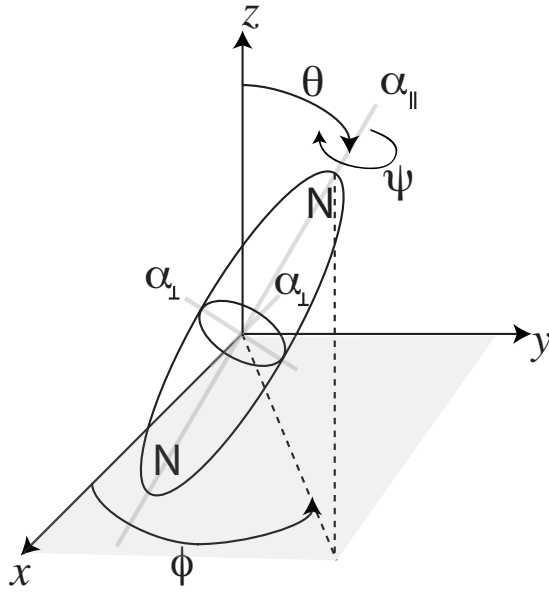


Fig. 3. An axially symmetric molecule, here shown as N_2 . The Euler angles θ and ϕ relate the principal axis of the molecule to the space-fixed frame. The principal axes of the molecule are shown in gray. The molecule is symmetric about the main principal axis and invariant with respect to Euler angle ψ . The polarizabilities parallel α_{\parallel} and perpendicular α_{\perp} to the main axis are shown. The application of a laser field linearly polarized along z creates a dynamic Stark effect potential that aligns the principal axis toward the z axis.

H_0 and the boundary conditions as the angles are swept through a full rotation. In the presence of the dynamic Stark

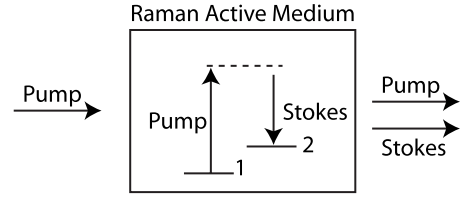


Fig. 4. A Raman process. An input pump field excites the medium and a Stokes field is generated. In the photon perspective, a pump photon is destroyed and a Stokes photon and material phonon are created. The energy difference between pump and Stokes is the energy difference between states 1 and 2. If the pump duration is short, it may have sufficient bandwidth to simultaneously overlap states 1 and 2, thus stimulating Stokes light. States 1 and 2 are analogous to states j and k , respectively, in Fig. 2. See the text for more details.

effect, a potential energy term is introduced of the form of Eq. (39) or equivalently Eq. (16). We can investigate the form of the quadratic interaction by considering an axially symmetric molecule such as N_2 (see Fig. 3). In the frame of the molecule (principal axis), the polarizability tensor is given by

$$\alpha^{\text{principal}} = \begin{bmatrix} \alpha_{\perp} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\parallel} \end{bmatrix}, \quad (41)$$

where α_{\parallel} is the polarizability parallel to the molecular axis and α_{\perp} is perpendicular. The relation between the polarizability in the principal frame and the space-fixed frame is

$$\alpha = R' \alpha^{\text{principal}} R, \quad (42)$$

where R is the Euler transformation matrix^{17,27}

$$R = \begin{bmatrix} -\cos \psi \sin \phi - \cos \theta \cos \phi \sin \psi & \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \sin \psi \sin \theta \\ \sin \psi \sin \phi - \cos \theta \cos \phi \cos \psi & -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & \cos \psi \sin \theta \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{bmatrix}. \quad (43)$$

The dynamic Stark effect interaction may be written using this relation to link the two frames

$$V^{\text{DSE}}(t) = -\frac{1}{4} \mathcal{E}^*(t) \cdot R' \alpha^{\text{principal}} R \cdot \mathcal{E}(t). \quad (44)$$

If the electric field vector is polarized along the z direction such that

$$\mathcal{E} = \mathcal{E}_0(t) \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad (45)$$

the interaction simplifies to

$$V^{\text{DSE}}(t) = -\frac{1}{4} |\mathcal{E}_0(t)|^2 (\alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta). \quad (46)$$

Therefore, molecules placed in a laser field experience a dynamic Stark effect shift, which is equivalent to adding or shaping a potential energy surface to create a well that varies as $\cos^2 \theta$. This potential well draws the principal axis of the

molecule toward the z coordinate axis and is the key mechanism for the laser alignment of molecules. Note that because the interaction pulls toward both $\theta=0, \pi$, the molecules do not orient themselves with respect to one end or the other.

Most experiments start with a thermal distribution of molecules. All the dynamics discussed here assume no dissipation, which means that while the molecules are in an aligning field, they do not have a chance to cool to the ground state, just as a ball rolling in the valley of a bowl does not come to rest without friction. If the aligning field is adiabatically applied, each state of the initial thermal ensemble is transferred slowly to an aligned state and the motion remains static, as in the initial thermal configuration. However, often the interest is in obtaining field-free alignment so that molecules are aligned and have their natural spectral characteristics (to avoid the Stark level shifts that occur when the field is applied). This objective has led to various approaches including dynamic Stark effect kicks and sudden changes in the applied field to generate transient alignment.⁶

IX. DYNAMIC STARK EFFECT AND RAMAN PROCESSES

It is interesting to investigate the relationship between the dynamic Stark effect interaction and the process of Stokes light generated during a Raman process. In a typical Raman process, a pump field with envelope \mathcal{E}_p travels through a medium and a new field is produced at a shorter Stokes wavelength \mathcal{E}_s (see Fig. 4). One photon of the pump field is destroyed and a shorter wavelength photon at the Stokes frequency is created, simultaneously exciting the system from state 1 to 2. The photon energy deficit is deposited in the system as a phonon excitation provided that the pump-Stokes energy difference ω_{pS} is resonant with the level spacing between states 1 and 2. If the Stokes field grows sufficiently large, it can reverse the process, producing anti-Stokes light at the longer pump wavelength.

The origin of the terms Stokes and anti-Stokes derives from studies of light emission which indicated that fluorescence [a term coined by Stokes in 1852 (Ref. 28)] always occurs at longer wavelengths than the excitation. According to Larmor,²⁹ this observation became known as the experimental Law of Stokes. The discovery of fluorescence at shorter wavelengths was at first surprising and termed anti-Stokes, in violation of the original law.³⁰

To illustrate these effects, the formalism of Secs. V or VII may be extended to include two fields, the pump p and Stokes S . The net result is the interaction

$$V = -\frac{1}{4}(\mathcal{E}_p^* \cdot \alpha \cdot \mathcal{E}_p + \mathcal{E}_S^* \cdot \alpha \cdot \mathcal{E}_S + \mathcal{E}_p^* \cdot \alpha \cdot \mathcal{E}_S e^{-i\omega_{pS}t} + \mathcal{E}_S^* \cdot \alpha \cdot \mathcal{E}_p e^{i\omega_{pS}t}), \quad (47)$$

which we write as $V = V_p + V_S + V_{pS} + V_{Sp}$, respectively. Each term corresponds to different processes. The inclusion of two fields results in the introduction of a beat frequency ω_{pS} in parts of the interaction. The first term V_p represents the dynamic Stark effect from a single pump. The term V_S represents the dynamic Stark effect due to the Stokes field, which, in the absence of large excitation, is usually small compared to that due to the pump and can be neglected. There is no oscillating component in these two interactions—they follow the pulse envelope—which means that they are not resonant with different states. The implication is that after the interaction, the state populations remain unchanged, as can be seen by considering first-order perturbation theory in V_p of Schrödinger's equation for a system starting in state 1 ($c_1(t) \approx 1$) and being excited to state 2. The following is strictly applicable only in the weak (perturbative) limit, although analogous aspects can be carried to stronger fields. The perturbative state amplitude at time t is given by the finite time Fourier transform via Eq. (23) (the time-dependent Fermi golden rule)

$$c_2(t) \approx \frac{1}{i\hbar} \int_{-\infty}^t e^{-i\omega_{12}t'} \langle 2 | V_p(t') | 1 \rangle dt'. \quad (48)$$

At finite times, while $V_p(t)$ is on, c_2 is nonzero as the population is excited due to apparent bandwidth introduced by truncating the integral at time t , instead of at infinity, which means the excitation is equivalent to a suddenly switched-off pulse. At long times, when the pulse is over, $c_2(t) \rightarrow_{t \rightarrow \infty} (2\pi/i\hbar) \delta(\omega_{12})$, the Fourier transform samples the full-time excitation and finds no resonant excitation that would

leave population in the excited state (provided ω_{12} is non-zero): The system does not discover that the excitation has no resonant bandwidth until the pulse is over.

The term V_{pS} oscillates with frequency $-\omega_{pS}$ and corresponds to Stokes light generation. If ω_{pS} is equal to the energy difference between states 1 and 2, the process is resonant and the excited population remains in state 2 after the interaction: the pump pulse excites the system and Stokes light is produced. The term V_{Sp} corresponds to the inverse processes. When there is population in state 2, the interaction can reverse the Stokes process and transfer population from state 2 to state 1. In this process, the Stokes field generates anti-Stokes light at the pump frequency.

In the absence of a classical Stokes field at the input, the function \mathcal{E}_S can be written as a quantum field that spontaneously starts the Raman processes. However, if the pump pulse envelope becomes very short, V_p may have sufficient bandwidth to simultaneously cover states 1 and 2 and the separation of fields into independent pump and Stokes is not unique. In this case, the interaction is termed *impulsive*.³¹ An interesting feature is that in this case, the pump has sufficient spectral content to cover both pump and Stokes frequencies. Thus, in the impulsive case, the Stokes field is stimulated from the pump itself, not the spontaneous field.

X. CONCLUSION

We have considered the effects of a nonresonant optical field on matter using a series of approaches of increasing sophistication. All approaches illustrate that in the presence of an external field, the system experiences a quasistatic dynamic Stark energy shift which is quadratic in the field envelope. Therefore, this shift follows the intensity, not the instantaneous electric field. A complete approach indicates that the dynamic Stark effect arises from the motion of states that do not participate directly in the dynamics of interest. The motion of these nonessential states is incorporated by the introduction of an induced dipole interaction.

The dynamic Stark effect can be used to align molecules. The applied laser field induces a dipole that interacts with the original field and draws it toward the electric field vector to reduce the energy. The dynamic Stark effect may be contrasted with conventional Raman scattering, where Stokes light is generated from a pump. When the pump is slowly varying (with respect to rotations) and too weak to significantly stimulate the Stokes light, the process is adiabatic with respect to the pulse envelope. Phonons (rotational excitations) are excited during the pump, but they do not persist afterward. If the pump intensity is increased, spontaneous Stokes generation may be initiated, leaving the system excited after the pump. Regardless of intensity, when the pulses are short enough, the interaction is impulsive. An impulsive interaction has sufficient bandwidth that frequencies at the Stokes wavelength are present in the pump which then stimulates the Raman process itself.

With the advent of modern ultrafast lasers that operate at high intensities and with incredibly fast time scales, exquisitely crafted light pulses can be used to influence quantum systems. Among the multitude of phenomenon that occur in strong fields, the dynamic Stark effect is becoming an increasingly important tool due to its generality and simplicity.

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