SEMICLASSICAL EFFECTIVE HAMILTONIAN FOR COUPLED ELECTRONIC AND NUCLEAR OPTICAL RESPONSE

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1. INTRODUCTION

The theoretical treatment of the optical properties of organic molecules with delocalized electronic states, such as conjugated polymers, is complicated by strong Coulomb interaction between electrons [1,2] and by polaronic effects reflecting strong electron-phonon interactions [3]. Both effects are enhanced by low dimensionality [4,5]. The problem is complicated even for the purely electronic system, where the coupling to nuclear degrees of freedom is neglected. This finite many-electron problem can be treated using approximate many-body techniques [6]. These methods can be classified into two types, depending on the way they treat the perturbation induced by the optical field. The first is based on a variational and perturbative treatment of the ground state in the presence of the electric field (for example, the Coupled-Perturbed Hartree-Fock (CPHF) procedure [7]). The second type uses time-dependent perturbation theory, which relates the optical response to the properties of excited states e.g. the Configuration-Interaction / Sum-over-States (CI/SOS) method [2]). Another example of the latter methods is the Time-Dependent Hartree Fock (TDHF) [8.9] which works well for both the linear and the non-linear response of conjugated polymers [10]. For linear response the TDHF is equivalent to the Random Phase Approximation (RPA). In this approach one solves equations of motion for the elements of the reduced single-electron density matrix, which represents a set of parameters that characterize the electronic system. As demonstrated in [11], the solutions of the TDHF equations can be viewed as "classical trajectories" in the phase space of the generalized coherent states [12] represented by single Slater determinants. In that sense the TDHF provides a classical-like description of the quantum many-electron system [11]. The terms "classical" and "quantum" used here do not refer to the conventional expansion in \hbar but rather describe the strength of electronic correlations. "Classical" means a system with no correlations, so that its wavefunction can be

represented by a single Slater determinant.

Infrared spectra, vibronic structure of optical spectra, and Raman scattering depend on the combined effect of nuclear motions and electronic correlations. Theoretical investigation of these spectroscopies usually require calculation of excited state adiabatic surfaces. This task is computationally expensive and possible only for small molecules [13]. When the optical field is off-resonant with respect to the electronic transitions, both vibrational and electronic degrees of freedom can be treated classically. A straightforward generalization of the TDHF theory then yields a system of coupled classical equations of motion in the joint phase space of electronic and vibronic degrees of freedom. This approach, however, fails to reproduce the vibrational structure of electronically resonant spectroscopy. For these applications a semiclassical procedure needs to be developed which treats the electronic motions classically whereas the vibrational degrees of freedom are accounted for quantum-mechanically. This can be achieved by deriving a semiempirical effective quantum model where the electronic degrees are represented by a set of weakly coupled harmonic oscillators and whose electronic optical response reproduces the TDHF approximation for the original system.

We propose a new semiclassical method for computing the vibronic structure of the optical response. By treating electronic degrees of freedom in the TDHF approximation and including vibrational degrees of freedom explicitly within the Born-Oppenheimer approximation, we derive an effective Hamiltonian that describes the coupled electronic and nuclear motions. In this paper we derive the harmonic part of the effective Hamiltonian and apply it to compute the linear absorption and fluorescence spectra of small polyenes.

2. SEMICLASSICAL OSCILLATOR REPRESENTATION OF THE ELECTRON-PHONON SYSTEM

We start with the Pariser-Parr-Pople (PPP) Hamiltonian [14] which describes the system of π -electrons in conjugated molecules:

$$\widehat{H} = \sum_{\bar{m}\bar{n}} \bar{t}_{\bar{m}\bar{n}}(\widehat{R}) \widehat{c}^{\dagger}_{\bar{m}} \widehat{c}_{\bar{n}} + \sum_{\bar{m}\bar{n}\bar{k}\bar{l}} \bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}(\widehat{R}) \widehat{c}^{\dagger}_{\bar{m}} \widehat{c}^{\dagger}_{\bar{n}} \widehat{c}_{\bar{k}} \widehat{c}_{\bar{l}} + \widehat{H}_{\text{nucl}}.$$
(1)

Here $\hat{c}(\hat{c}^{\dagger})$ are the fermionic annihilation (creation) operators. Indices with overbars $\bar{m} = (m', m'')$ label the π -orbitals of carbon atoms (m') and the electron spin (m''). $\bar{t}_{\bar{m}\bar{n}} = \delta_{m''n''} t_{m'n'}$ is the hopping matrix and $\bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}} = \delta_{\bar{m}\bar{l}}\delta_{\bar{n}\bar{k}}V_{m'n'}$ represents Coulomb interaction between electrons. The dependence of all matrix elements on the nuclear coordinates \hat{R} describes the adiabatic interaction with the vibrational degrees of freedom, the last term represents the vibrational Hamiltonian. The total Hamiltonian of the system interacting with the classical external optical field $E(\mathbf{r}, \tau)$ through the polarization operator $\mathcal{P}(\mathbf{r})$ is [11]

$$\widehat{H}_{T}(\tau) = \widehat{H} - \int d\mathbf{r} \ E(\mathbf{r},\tau) \mathcal{P}(\mathbf{r}), \qquad \mathcal{P}(\mathbf{r}) \equiv \sum_{\bar{m}\bar{n}} \mu_{\bar{m}\bar{n}}(\mathbf{r},\widehat{R}) \hat{c}_{\bar{m}}^{\dagger} \hat{c}_{\bar{n}} - \mu'(\mathbf{r},\widehat{R}).$$
(2)

 μ and μ' in Eq. (2) represent the electronic and the nuclear dipole densities, respectively. Our first goal is to derive an effective classical Hamiltonian which is a classical

function of a set of parameters (the elements of the single-electron density matrix ρ as well as the nuclear coordinates R and momenta P). This function defined on a closed manifold always has a minimum, which corresponds to the stationary point $(R^{(0)},\bar{\rho})$ of the classical dynamics for $\rho(t)$ and R(t). We next introduce canonical variables that describe the classical dynamics of the system around this stationary point. Finally, we quantize the resulting Hamiltonian to arrive at an effective quantum Hamiltonian that describes the coupled electronic and vibrational degrees of freedom.

To achieve this goal we employ the scheme of [11] which is based on generalized coherent states [12]. We define the classical phase space of the system \mathcal{M} as the space of coherent states; \mathcal{M} has a form of the direct product $\mathcal{M} = \mathcal{M}_0 \times \mathcal{M}_1$ where \mathcal{M}_0 is the phase space of nuclear coordinates R and their conjugate momenta P. \mathcal{M}_1 is the set of single Slater determinants represented by the Grassman manifold [11] $\mathcal{M}_1 = G(M, N, C)$, where M is the number of electrons and N is the number of singleelectron basis functions. \mathcal{M}_1 can be viewed as the space of $N \times N$ hermitian complex matrices $\hat{\rho}$ with $\hat{\rho}^2 = \hat{\rho}$ and rank $(\hat{\rho}) = M$. Therefore, a point in \mathcal{M} is characterized by $(P, R, \hat{\rho})$. The Poisson bracket on \mathcal{M}_0 is canonical, the Poisson bracket on \mathcal{M}_1 is defined in [11]. The classical Hamiltonian is a function on the space \mathcal{M} of coherent states; according to [11] its value on a coherent state η is defined as the expectation value of \hat{H} on η . Following [11], we introduce a basis set $\hat{\sigma}_m$ of functions on \mathcal{M}_1 defined as $\hat{\sigma}_m(\hat{\rho}) \equiv \text{Tr}(\hat{\sigma}_m \hat{\rho})$. The classical Hamiltonian then becomes:

$$\widehat{H}(P,R) = \sum_{m} t_m(R)\widehat{\sigma}_m + \sum_{mn} V_{mn}(R)\widehat{\sigma}_m\widehat{\sigma}_n + \widehat{H}_{\text{nucl}}(P,R),$$
(3)

with

$$\mathcal{P}(\mathbf{r}) = \sum_{m} \mu_m(\mathbf{r}, R) \hat{\sigma}_m - \mu^{(1)}(\mathbf{r}, R).$$
(4)

In Eq. (3) $\hat{H}(P,R)$ for each value of P and R is treated as a function on \mathcal{M}_1 . Expressions for the parameters t_m, V_{mn} , and μ_m in terms of the original parameters $\bar{t}_{\bar{m}}, \bar{V}_{\bar{m}\bar{n}\bar{k}\bar{l}}$, on $\mu_{\bar{m}\bar{n}}$ are given in [11]. Minimization of \hat{H} [Eq. (3)] on the phase space \mathcal{M} is equivalent to solving the stationary Hartree-Fock (HF) equation together with geometry optimization.

We next choose a system of local coordinates on \mathcal{M} in the vicinity of the stationary point. We use R and P as canonical coordinates on \mathcal{M}_0 . The coordinates on \mathcal{M}_1 are the matrix elements of $\hat{\rho}$. The full set of matrix elements is, however, overcomplete due to the constraint $\hat{\rho}^2 = \hat{\rho}$. To define a complete set of canonical coordinates we use the decomposition of the density matrix $\hat{\rho} = \bar{\rho} + \hat{\xi} + T(\hat{\xi})$ [11] into the particle-hole part $\hat{\xi}$ and the remainder $T(\hat{\xi})$ that contains no particle-hole matrix elements and constitutes a function of ξ .

Expanding $\hat{\xi}$ in the eigenmodes $\hat{\xi}_{\alpha}, \hat{\xi}_{\alpha}^{\dagger}$ of the Liouville operator $L, L\hat{\xi}_{\alpha} = \Omega_{\alpha}\xi_{\alpha}, L\hat{\xi}_{\alpha}^{\dagger} = -\Omega_{\alpha}\hat{\xi}_{\alpha}$, we obtain the variables which are canonical to first order in $\hat{\xi}$. Expressions for the electronic Hamiltonian in terms of these variables as well as the Liouville operator L which determines the linearized TDHF equation were given in [11]. These can be transformed to canonical variables order by order in $\hat{\xi}$. Denoting the canonical variables \hat{B}_{α} and $\hat{B}_{\alpha}^{\dagger}$, and neglecting some unimportant constant

terms, we can recast the Hamiltonian in a form $\hat{H} = \hat{H}_e + \hat{H}_{ph} + \hat{H}_{int}$, where \hat{H}_e is the electronic Hamiltonian, written in terms of excitonic canonical variables

$$\hat{H}_e \equiv \sum_{\alpha} \Omega_{\alpha} \hat{B}^{\dagger}_{\alpha} \hat{B}_{\alpha} + \sum_{mn}^{m+n>2} \sum_{\alpha_1 \dots \alpha_m} \sum_{\beta_1 \dots \beta_n} A_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} \hat{B}^{\dagger}_{\alpha_1 \dots} \hat{B}^{\dagger}_{\alpha_m} \hat{B}_{\beta_1 \dots} \hat{B}_{\beta_n}, \quad (5)$$

 H_{ph} is the vibrational Hamiltonian,

$$\widehat{H}_{ph} \equiv \widehat{H}_{nucl} + \operatorname{Tr}\left\{\widehat{t}(R^{(0)} + q)\overline{\rho}\right\} + \operatorname{Tr}\left\{\overline{\rho}V(R^{(0)} + q)\overline{\rho}\right\},\tag{6}$$

where $q \equiv R - R^{(0)}$ is the deviation of the nuclear positions R from their equilibrium values $R^{(0)}$. The nuclear Hamiltonian under the harmonic approximation can be expanded in the nuclear eigenmodes:

$$\widehat{H}_{\text{nucl}} = \sum_{j=1}^{3K-6} \frac{p_j^2}{2m_j} + \frac{m_j \omega_j^2 q_j^2}{2}.$$
(7)

Here K is the number of nuclei, and q_j , p_j , and m_j represent the coordinate, the momentum, and the mass of the *j*-th nuclear mode, respectively. \hat{H}_{int} represents the interaction between electron-hole pairs and the vibrational modes.

$$\widehat{H}_{int} \equiv \sum_{mn}^{m+n>1} \sum_{\alpha_1\dots\alpha_m} \sum_{\beta_1\dots\beta_n} A^{(1)}_{\alpha_1\dots\alpha_m,\beta_1\dots\beta_n}(q) \widehat{B}^{\dagger}_{\alpha_1\dots} \widehat{B}^{\dagger}_{\alpha_m} \widehat{B}_{\beta_1\dots} \widehat{B}_{\beta_n} \tag{8}$$

In Eqs. (5)—(8) we have used the notation introduced in [11]. $\hat{t}(R)$ is a vector in a single-electron Liouville space, whereas V(R) is an operator in the same space (i.e., a superoperator).

$$\hat{t}(R) \equiv \sum_{m} t_m(R)\hat{\sigma}_m , \qquad V(R)\hat{\eta} \equiv \sum_{mn} V_{mn} \text{Tr}(\hat{\sigma}_n \hat{\eta})\hat{\sigma}_m.$$
(9)

Expressions for the coefficients A and $A^{(1)}$ will be given below. The Poisson bracket has the canonical form $\{p_i, q_j\} = \delta_{ij}, \{\widehat{B}_{\alpha}, \widehat{B}_{\beta}^{\dagger}\} = i\delta_{\alpha\beta}$, and the polarization operator is given by

$$P(\mathbf{r}) \equiv \sum_{mn} \mu_{\alpha_1 \dots \alpha_m, \beta_1 \dots \beta_n} (\mathbf{r}, R^{(0)} + q) \widehat{B}^{\dagger}_{\alpha_1 \dots} \widehat{B}^{\dagger}_{\alpha_m} \widehat{B}_{\beta_1 \dots} \widehat{B}_{\beta_n}.$$
(10)

We have thus succeeded in rewriting the Hamiltonian of Eq. (3) using canonical vari*ables with classical commutation relations.

Within the classical approximation, the linear response is obtained by retaining the harmonic terms in \hat{B} and \hat{B}^{\dagger} in H_{eff}

$$\widehat{H}_{\text{eff}} = \sum_{\alpha} \Omega_{\alpha} \widehat{B}_{\alpha}^{\dagger} \widehat{B}_{\alpha} + \widehat{H}_{\text{ph}} + \sum_{\alpha\beta} A_{\alpha,\beta}^{(1)}(q) \widehat{B}_{\alpha}^{\dagger} \widehat{B}_{\beta}$$

$$+\sum_{\alpha_1\alpha_2} A^{(1)}_{\alpha_1\alpha_2,}(q) \widehat{B}^{\dagger}_{\alpha_1} \widehat{B}^{\dagger}_{\alpha_2} + \sum_{\beta_1\beta_2} A^{(1)}_{,\beta_1\beta_2}(q) \widehat{B}_{\beta_1} \widehat{B}_{\beta_2}, \qquad (11)$$

and linear terms in the expression for polarization:

$$P(\mathbf{r}) = \sum_{\alpha} \mu_{\alpha}(\mathbf{r}, q) (\widehat{B}_{\alpha} + \widehat{B}_{\alpha}^{\dagger}).$$
(12)

To derive the effective quantum Hamiltonian we quantize the simplified classical Hamiltonian given by Eqs. (11) and (12) by treating the variables \hat{p}_j , \hat{q}_j , $\hat{B}^{\dagger}_{\alpha}$, and \hat{B}_{α} in Eqs. (5) through (8) and (10) as operators with the commutation relations that follow from classical Poisson bracket: $[\hat{p}_i, \hat{q}_j] = -i\delta_{ij}$, $[\hat{B}_{\alpha}, \hat{B}^{\dagger}_{\beta}] = \delta_{\alpha\beta}$. Since the parameters of the effective Hamiltonian are not changed by the quantization procedure, they can be evaluated using the classical (TDHF) approach developed in [11], which yields

$$A_{\alpha,\beta}^{(1)}(q) \equiv \frac{1}{2} \operatorname{Tr} \left\{ \widehat{S}(q) [[\hat{\xi}_{\alpha}^{\dagger}, \bar{\rho}], \hat{\xi}_{\beta}] \right\} + \frac{1}{2} \operatorname{Tr} \left\{ \widehat{S}(q) [[\hat{\xi}_{\beta}, \bar{\rho}], \hat{\xi}_{\alpha}^{\dagger}] \right\} + \operatorname{Tr} \left\{ \hat{\xi}_{\alpha}^{\dagger} U(q, \hat{\xi}_{\beta}) \right\} + \operatorname{Tr} \left\{ \hat{\xi}_{\beta} U(q, \hat{\xi}_{\alpha}^{\dagger}) \right\},$$
(13)

$$A^{(1)}_{\alpha_1\alpha_2,}(q) \equiv \frac{1}{2} \operatorname{Tr}\left\{\widehat{S}(q)[[\hat{\xi}^{\dagger}_{\alpha_1},\bar{\rho}],\hat{\xi}^{\dagger}_{\alpha_2}]\right\} + \operatorname{Tr}\left\{\hat{\xi}^{\dagger}_{\alpha_1}U(q,\hat{\xi}^{\dagger}_{\alpha_2})\right\}$$
(14)

$$A^{(1)}_{,\beta_1\beta_2}(q) \equiv \frac{1}{2} \operatorname{Tr} \left\{ \widehat{S}(q) [[\hat{\xi}_{\beta_1}, \bar{\rho}] \hat{\xi}_{\beta_2}] \right\} + \operatorname{Tr} \left\{ \hat{\xi}_{\beta_1} U(q, \hat{\xi}_{\beta_2}) \right\}$$
(15)

$$\mu_{\alpha}(\mathbf{r},q) \equiv \operatorname{Tr}\left\{ [\bar{\rho},\mu(\mathbf{r},R^{(0)}+q)][\hat{\xi}_{\alpha},\bar{\rho}] \right\}.$$
(16)

We have introduced the notation

$$U(q,\hat{\eta}) \equiv V(R^{(0)} + q)\hat{\eta} - V(R^{(0)})\hat{\eta}, \qquad (17)$$

$$\widehat{S}(q) \equiv \widehat{t}(R^{(0)} + q) - \widehat{t}(R^{(0)}) + 2U(q,\bar{\rho}).$$
(18)

Eqs. (11) through (18) express the effective Hamiltonian and the polarization in terms of the parameters of the original Hamiltonian [Eq. (3)] and the normal modes ξ_{α} of the linearized TDHF equation. The effective Hamiltonian describes a system of harmonic oscillators representing excitons interacting with phonons. The effective Hamiltonian represents a quantum model which is obtained by quantizing the harmonic (with respect to electron-hole operators) part of the classical counterpart of the original Hamiltonian. Neglecting the anharmonic terms for the linear response is justified on the classical level only, this implies that the formally completely quantum effective model constitutes a classical approximation with respect to the electronic degrees of freedom. The formal aspects of the semiclassical approximation as well as a systematic procedure of deriving the effective Hamiltonian which reproduces optical nonlinearities is developed in [15]. The effective model still represents a complicated many-body system. However, its complexity is only related to exciton-phonon interactions; the many-body problem of electron correlations has been taken

care of within the TDHF technique, which results in the formation of excitons. Direct exciton-exciton interaction will show up in nonlinear response functions only. Eq. (11) is an important result which allows us to develop various approximations for the system described by the effective Hamiltonian. First, provided the phonon energies and the exciton-phonon interaction are much smaller than the optical gap, the last two terms in the r.h.s. of Eq. (11) can be neglected. We can then retain only quadratic terms in the expansion of \hat{H}_{ph} , and linear terms in the expansion of $A_{\alpha,\beta}^{(1)}(q)$. Introducing the vibrational normal modes $q_{j\alpha}$ with frequencies ω_{α} and creation (annihilation) operators $\hat{b}^{\dagger}_{\alpha}(\hat{b}_{\alpha})$, we obtain the effective Hamiltonian

$$\widehat{H} = \sum_{\alpha} \Omega_{\alpha} \widehat{B}^{\dagger}_{\alpha} \widehat{B}_{\alpha} + \sum_{\beta} \omega_{\beta} \widehat{b}^{\dagger}_{\beta} \widehat{b}_{\beta} + \sum_{\mu\nu\beta} S_{\mu\nu,\beta} \widehat{B}^{\dagger}_{\mu} \widehat{B}_{\nu} (\widehat{b}_{\beta} + \widehat{b}^{\dagger}_{\beta}), \tag{19}$$

where
$$S_{\mu\nu,\beta} \equiv \sum_{j} \frac{\delta A^{(1)}_{\mu,\nu}(q)}{\delta q_{j}} q_{j\beta}.$$
 (20)

In order to treat higher-order response functions we need to retain higher-order terms in powers of B and B^{\dagger} in the effective Hamiltonian. To that end, we make use of the expansion of the classical Hamiltonian [Eqs. (5)—(8)]. The only remaining problem is how to order the B and B^{\dagger} operators in the expansion (since in the classical limit they commute). This problem can be solved in principle by starting with the canonical Poisson bracket and extending it to canonical boson commutation relations in the quantum case.

3. APPLICATION TO SMALL POLYENES

We have performed numerical simulations for trans-1,3,5-hexatriene and trans-1,3,5,7-octatetraene. Starting with *ab-initio* restricted Hartree-Fock 6-311++G^{**} calculation for the ground-state vibrational normal modes. We have used the PPP Hamiltonian Eq. (1) [10] which has been parametrized as follows: The size of basis set \tilde{K} is equal to the number of carbon atoms. The PPP Hamiltonian contains only the nearest-neighbor and the diagonal transfer integrals $t_{n'\pm 1,n'}(R) = \beta - \beta_1 \Delta r'_n$, $t_{n'n'} = \sum_{m'}^{'} V_{n'm'}(R)$, with Coulomb interaction given by Ohno's formula

$$V_{n'm'}(R) = \frac{U}{\sqrt{1 + (r_{n'm'}/a_0)^2}}.$$
(21)

Here $U = U_0/\epsilon$ is the on-site Hubbard repulsion, ϵ is the static dielectric constant, and r_{nm} is the distance between the *n*-th and *m*-th carbon atoms. Following [10] we use the following values of parameters $\beta_0 = -2.4$ eV, $\beta_1 = -3.0$ eVÅ⁻¹, $U_0 = 11.13$ eV, $\epsilon = 1.5$, $a_0 = 1.2935$ Å.

In Fig. 1 we show the dominant oscillator strengths f_{ν} in the linear response of hexatriene and octatetraene. The electronic and vibrational normal modes were used for calculating electronic-vibrational coupling matrix $S_{\mu\nu,\beta}$ in Eqs. (19) and (20). This can be recast in the following form which is suitable for numerical applications

$$S_{\mu\nu,\beta} = \operatorname{Tr}\left\{ \left(\frac{\delta t(R^{(0)} + q)}{2\delta q_{\beta}} q_{\beta} + \frac{\delta \bar{V}(R^{(0)} + q_{\beta})\bar{\rho}}{\delta q_{\beta}} q_{\beta} \right) \left(\left[[\hat{\xi}^{\dagger}_{\mu}, \bar{\rho}], \hat{\xi}_{\nu} \right] + \left[[\hat{\xi}_{\nu}, \bar{\rho}], \hat{\xi}^{\dagger}_{\mu} \right] \right) \right\}$$

$$+ \operatorname{Tr}\left\{\hat{\xi}^{\dagger}_{\mu}\frac{\delta\bar{V}(R^{(0)}+q_{\beta})\hat{\xi}_{\nu}}{\delta q_{\beta}}q_{\beta}\right\} + \operatorname{Tr}\left\{\hat{\xi}_{\nu}\frac{\delta\bar{V}(R^{(0)}+q_{\beta})\hat{\xi}^{\dagger}_{\mu}}{\delta q_{\beta}}q_{\beta}\right\}.$$
 (22)

Here

$$(\bar{V}(R)\eta)_{m'n'} = -\frac{1}{2} V_{m'n'}(R)\eta_{m'n'} + \delta_{m'n'} \sum_{l=1}^{\tilde{K}} V_{m'l'}(R)\eta_{l'l'}, \qquad (23)$$

where $\eta = \bar{\rho}, \hat{\xi}_{\nu}, \hat{\xi}_{\mu}^{\dagger}$. The derivatives in Eq. (22) were obtained numerically as finite differences. The dimensionality of the resulting *S* matrix is $\tilde{K}^2/2 \times \tilde{K}^2/2 \times (3K-6)$, where $\tilde{K}^2/2$ and 3K-6 are the numbers of electronic and vibronic normal modes. The diagonal elements $S_{\mu\mu,\beta}$ describe linear absorption spectrum with vibronic band positions $\Omega_{\mu} + n\omega_{\beta}$. Off-diagonal elements $S_{\mu\nu,\beta}$ determine the strength of the vibrationally-induced transition $\Omega_{\nu} + n\omega_{\beta}$ in the case when the transition Ω_{ν} is forbidden (e.g. for the states $\nu = A_q$ in polyenes).

Tables I and II list our numerical results for the coupling constants associated with the lowest allowed (B_u) and the lowest dark (A_g) optical transitions. Only modes that have non-zero couplings are shown. The diagonal coupling constants $S_{1B_u 1B_u,\beta}$ are displayed in Fig. 2 for hexatriene (upper panels) and octatetraene (lower panels). Fig. 3 shows off-diagonal couplings $S_{1B_u 2A_g,\beta}$. Table III gives comparison of our numerical results with experimental data on linear absorption obtained for jet-cooled hexatriene and octatetraene [16] respectively.

When the electronic and nuclear modes are well separated (i.e., $\omega_{\beta} \ll \Omega_{\alpha}$), we can set $S_{\mu\nu,\beta} = 0$ for $\mu \neq \nu$, and Eq. (19) describes a model of displaced oscillators which can be solved exactly [6,17]. To calculate the linear absorption lineshape we take into account only the first B_u mode and accept two-level model in the Condon approximation. Using the values of S_{1B1B} from Tables I and II and Eqs. (8.42a) and (8.42b) of [17] we have calculated vibronic structure for the $1B_u$ transition, shown in Fig. 4 (T=300K) and and Fid. 5 (T=3000K). The unrealistic temperature in Fig. 5 is chosen to clarify the Stoke's shift between the maxima of the absorption and fluorescence envelopes (solid and dashed lines). Upper and lower panels correspond to hexatriene and octatetraene respectively. A homogeneous broadening of 26 meV was used in calculations.

A more rigorous study of the excited-state surfaces of short polyenes that uses *ab-initio* ground-state surface calculations and INDO Hamiltonian for the excitation spectrum is reported in [18]. The theory can further be generalized to construct excited-state adiabatic surfaces of molecules using the ground-state surfaces as an input [18]. The generalization of the theory to nonlinear optical response is given in [15].

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TABLE I. K=6, Hexatriene

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cm^{-1}	S_{1B1B}	S_{HR}	S_{1B2A}	S_{HR}
158	0.215	0.000	-461.496	0.332
376	-31.231	0.002	-0.258	0.000
468	323.934	0.164	0.033	0.000
578	0.159	0.000	14.336	0.000
1009	197.514	0.061	0.003	0.000
1035	-0.007	0.000	162.183	0.041
1216	0.036	0.000	218.161	0.074
1298	394.855	0.243	0.041	0.000
1381	-0.027	0.000	-77.926	0.009
1416	122.672	0.023	-0.031	0.000
1427	-0.020	0.000	147.231	0.034
1438	51.420	0.004	0.003	0.000
1545	95.153	0.014	0.008	0.000
1578	-0.002	0.000	143.307	0.032
1769	-28.808	0.001	0.000	0.000
1829	-0.012	0.000	398.913	0.248
1870	627.494	0.614	-0.003	0.000
3281	0.002	0.000	20.810	0.001
3282	16.163	0.000	0.951	0.000
3292	-17.362	0.000	-0.947	0.000
3292	0.004	0.000	-14.666	0.000
3300	-6.809	0.000	0.004	0.000
3303	-0.003	0.000	17.605	0.000
3371	2.450	0.000	3.874	0.000
3371	-2.546	0.000	3.837	0.000

TABLE II. K = 8, Octatetraene

cm^{-1}	$S_{1B1B}/{\rm cm}^{-1}$	S_{HR}	$S_{1B2A}/{\rm cm}^{-1}$	S_{HR}
93	0.806	0.000	200.858	0.063
239	61.966	0.006	0.632	0.000
357	440.007	0.302	-0.253	0.000
418	-0.240	0.000	-52.317	0.004
577	-89.793	0.013	-0.422	0.000
605	-0.379	0.000	100.622	0.016
1008	0.079	0.000	168.747	0.044
1034	145.979	0.033	0.002	0.000
1204	156.834	0.038	-0.026	0.000
1231	0.140	0.000	189.527	0.056
1292	-421.076	0.277	-0.147	0.000
1351	-0.094	0.000	-149.681	0.035
1411	38.374	0.002	-0.111	0.000
1419	0.089	0.000	-118.546	0.022
1426	90.698	0.013	-0.065	0.000
1442	-5.135	0.000	-27.060	0.001
1442	-5.612	0.000	30.391	0.001
1554	0.003	0.000	80.849	0.010
1574	49.461	0.004	0.004	0.000
1760	0.004	0.000	38.509	0.002
1809	-12.127	0.000	-0.016	0.000
1854	0.031	0.000	-392.973	0.241
1864	-579.732	0.524	0.017	0.000
3281	7.558	0.000	-1.244	0.000
3281	-2.109	0.000	14.409	0.000
3288	0.545	0.000	0.002	0.000
3290	0.011	0.000	-11.584	0.000
3294	-14.026	0.000	0.011	0.000
3296	0.010	0.000	2.599	0.000
3301	2.185	0.000	0.011	0.000
3304	-0.004	0.000	6.713	0.000
3371	-2.598	0.000	-1.499	0.000
3371	0.968	0.000	-3.843	0.000

TABLE III. Comparison with experiment

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Exp			Theor		
height	cm^{-1}	Description	cm^{-1}	$S_{1Bu,1Bu}$	S_{HR}
Hexatri	ene:				
18	313	Skeletal bend	464	323.9	0.164
10	718	${ m CH}_2$ rock	1002	197.5	0.061
41	1224	C-C stretch	1289	394.9	0.243
81	1631	C=C stretch	1856	627.5	0.614
Octatrie	ene:				
11	197	Skeletal bend	237	62.0	0.006
5	348	Skeletal bend	355	440.0	0.302
2	547	Skeletal bend	573	-89.8	0.013
3	1006	${ m CH}_2$ rock	1026	146.0	0.033
7	1201	C-C stretch	1195	156.8	0.038
23	1235	C-C stretch	1283	-421.1	0.277
60	1645	C=C stretch	1850	-579.9	0.524



0 -1.0

4000

-0.5

0

FIG. 3.

FIG. 5.

0.0 Ω - Ω⁰_{eg} (eV) 1.0

0.5