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Ground-state density-matrix algorithm for excited-state adiabatic surfaces: application to polyenes

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Abstract

A low-cost method for computing excited-state adiabatic surfaces, which totally avoids the calculation of the excited-state many-electron wavefunctions, and scales favorably with molecular size is proposed. The technique combines standard ground-state calculations with a time-dependent density-matrix calculation of vertical optical excitations, using the ground-state single-electron density matrix as an input. Several surfaces are generated simultaneously. The structure and vibrational frequencies of the 1B_u state of hexatriene and octatetraene are calculated using this method. The computed sign of the excited-state equilibrium displacements facilitates rapid analysis of resonance Raman measurements. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The adiabatic (Born–Oppenheimer) approach gives the following recipe for computing molecular properties. First, the electronic states are computed for a frozen nuclear configuration \mathbf{q} . This results in a set of adiabatic surfaces in the atomic configuration space, $E_v(\mathbf{q})$. Nuclear motion is then treated quantum-mechanically, with the adiabatic surfaces playing the role of effective potentials.

Well-developed quantum-chemistry techniques [1,2] yield highly accurate ground-state adiabatic surfaces, $E_0(\mathbf{q})$, at a reasonable computational cost. These methods provide reliable ground-state geometries and dynamical properties of large molecules, molecules in the condensed phase, large clusters, and

solids. Excited-state calculations constitute a much more complex task, since electronic correlations are typically much more pronounced in the excited states. In many cases the ground state can be represented by a single Slater determinant, built on the molecular orbitals. In contrast, the excited-state wavefunction needs to be expanded as a superposition of a large number of Slater determinants. Even though existing computational packages allow for such configuration interaction (CI) calculations, they are restricted to relatively small molecules and to a limited number of atomic configurations \mathbf{q} .

Excited-state adiabatic surfaces are of great interest since they determine photochemical reaction pathways [3–7]. The position of the adiabatic surface minimum gives the excited state geometry, while its curvature determines the excited-state vibrational frequencies that show up in the vibronic structure of linear absorption and fluorescence excitation spectra.

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The displacements of the excited-state equilibrium configuration and the difference between the ground- and excited-state vibrational modes (Dushinsky rotation) constitute a measure of the vibronic coupling strength. Within the Condon approximation, the vibronic structure of the linear absorption spectra and the resonant Raman scattering profile are completely determined by these displacements [8].

Valuable information about excited states can be obtained indirectly using time-dependent computational methods that target the linear response of the many-electron system. The coupled electronic oscillator (CEO) algorithm [9–11] calculates directly the relevant excited-state spectral properties, such as excitation energies and oscillator strengths, totally avoiding the computation of excited-state wavefunctions. It only requires a moderate computational effort to obtain the excited-state information for relatively large molecules [9–11], which is a notable advantage compared to CI calculations.

The CEO approach is based on the time-dependent Hartree–Fock (TDHF) approximation. The density-matrix spectral-moments algorithm (DSMA) [9] is a numerically efficient scheme for solving the CEO equations and computing optical spectra [10]. The excitation frequencies are obtained as the eigenvalues of the Liouville operator:

$$\hat{L}(\mathbf{q}) \xi_\nu(\mathbf{q}) = \Omega_\nu(\mathbf{q}) \xi_\nu(\mathbf{q}). \quad (1)$$

All quantities in this expression depend on nuclear coordinates. Solution of Eq. (1) at various nuclear configurations \mathbf{q} yields the variation of the excitation energy Ω_ν corresponding to the $0 \rightarrow \nu$ electronic transition with \mathbf{q} . $\hat{L}(\mathbf{q})$ is an effective Liouville operator and ξ_ν is the transition density matrix (electronic mode) for the optical transition between the ground-state $|0\rangle$ and electronically excited-state $|\nu\rangle$ [12]. Its matrix elements are $(\xi_\nu)_{mn} = \langle \nu | c_m^\dagger c_n | 0 \rangle$, where m and n label basis functions. The diagonal elements $(\xi_\nu)_{mm}$ represent the net charge induced on the m th atomic orbital by an external field, whereas off-diagonal elements represent the joint amplitude of finding an electron on orbital m and a hole on orbital n . Transition density matrices ξ_ν and frequencies Ω_ν carry all information necessary for computing molecular spectroscopic properties and can be conveniently and efficiently calculated using Eq. (1).

In this Letter we demonstrate that adiabatic surface of the ν th excited-state $E_\nu(\mathbf{q})$ can be computed by combining a standard calculation of the ground-state surface $E_0(\mathbf{q})$ with a CEO calculation of $\Omega_\nu(\mathbf{q})$: $E_\nu(\mathbf{q}) = E_0(\mathbf{q}) + \Omega_\nu(\mathbf{q})$. (2)

The expensive explicit calculation of many-electron wavefunctions $\Psi_\nu(\mathbf{q})$ is totally avoided. The \mathbf{q} -dependent transition dipole moment can be calculated as $\mu^{0\nu}(\mathbf{q}) = \text{tr}\{\mu(\mathbf{q})\xi_\nu(\mathbf{q})\}$. In Section 2 we apply this procedure to compute the lowest excited-state parameters of short polyenes. The calculations compare well with ab-initio CI calculations and with experiment. Our results are summarized in Section 3.

2. Vibronic structure of short polyenes

We have applied Eqs. (1) and (2) to study the excited-state surfaces of *trans*-1-3-5-hexatriene (C_6H_8) and *trans-trans*-1-3-5-7-octatetraene (C_8H_{10}). The ground- and lowest excited-state vibrational normal modes in short polyenes have been extensively studied both experimentally [13–20] and theoretically [19,21,22], making these molecules particularly suitable for testing the method. The ground-state modes and dimensionless displacements of hexatriene have been obtained from Raman scattering experiments by Myers et al. [13–15]. The 1B_u excited-state vibronic modes were observed in the direct absorption spectra of jet-cooled hexatriene by Vaida et al. [16,17]. The lowest 1B_u excited-state modes of octatetraene have been studied experimentally (fluorescence excitation and fluorescence from supersonic jets) by Kohler et al. [19,20]. Ab-initio ground- and excited-state frequencies of hexatriene were computed using Gaussian package by Zerbetto and Zgierski [21]. We have repeated the results of Ref. [21] and performed similar calculations for octatetraene. These results serve as a reference for the CEO calculations.

In the vicinity of the equilibrium configuration \mathbf{q}_ν , the potential surfaces can be expanded to quadratic order in $\mathbf{q} - \mathbf{q}_\nu$ ($\nu = 0$ denotes the ground state):

$$E_\nu(\mathbf{q}) = \frac{1}{2} \sum_{a=1}^{3K-6} m_{\nu a} \omega_{\nu a}^2 Q_{\nu a}^2, \quad (3)$$

$$Q_{\nu a} = D_{\nu a}(\mathbf{q} - \mathbf{q}_\nu),$$

with frequencies $\omega_{\nu a}$, and normal modes $Q_{\nu a}$. Here the index a labels the $3K - 6$ ground-state vibrational normal modes, K being the number of atoms. The vectors $D_{\nu a}$ are the rows of the transformation matrix, which can vary for different ν (Dushinsky rotation).

We have focused on the fundamental transition ${}^1A_g \rightarrow {}^1B_u$ and calculated the adiabatic surface of the 1B_u excited state. To obtain the excited-state surface parameters we have adopted the following procedure. (i) The Hartree–Fock (HF) optimized ground-state geometry and the ground-state vibronic modes were computed using GAUSSIAN-94 [1]. The 6-31 + G basis set was used in order to take into account the diffusive character of the excited state [21,23]. For hexatriene it was possible to increase the basis further to 6-311 + + G** with no noticeable change in the results. The ground-state ab-initio optimized geometry and vibrational normal modes were used as an input to all subsequent calculations. (ii) The ZINDO code [24–26] was used next to generate the INDO/S spectroscopic Hamiltonian and to compute the HF ground-state electronic density matrices, which are the input to the CEO algorithm. (iii) Finally, the CEO normal modes ξ_ν and frequencies Ω_ν were obtained by solving Eq. (1) using the DSMA procedure [9], and the excited-state energy was obtained using Eq. (2) The procedure thus employs an ab-initio Hamiltonian to compute the ground-state adiabatic surface and the INDO/S Hamiltonian to calculate optical transition energies. The former is most suitable for ground-state calculations whereas the latter provides a good description of excited-state structure in various molecules [9,10].

Steps (ii) and (iii) were repeated for nuclear coordinates displaced by 0.02 Å along each of the ground-state normal modes. Steps (ii) and (iii) combined take 1.73 s computational time for hexatriene and 3.68 s for octatetraene on a Silicon Graphics workstation¹. For comparison, single-point calculations of the excited states of these molecules at CIS(6-31 + G) level on GAUSSIAN-94 take 2.5 and 17.5 min, respectively.

¹ Here and below, CPU timing results are obtained using a single MIPS R10000 175 MHz processor on a 256 Mb RAM SGI Octane workstation.

Two levels of computation were performed: with and without taking into account Dushinsky rotation, i.e. the deviation of the excited-state normal modes with respect to their ground-state counterparts. When Dushinsky rotation is negligible, as we found to be the case for almost all modes in both molecules (see below), only the diagonal second derivatives $\partial^2\Omega_\nu/\partial^2q_\alpha$ with respect to each vibronic mode are required. Computing all the first and the diagonal second derivatives takes 2 min for hexatriene and 3 min for octatetraene. Obtaining the Dushinsky rotational matrix requires computing all second derivatives $\partial^2\Omega_\nu/\partial q_\alpha \partial q_\beta$ of the excited-state energy with respect to the vibronic modes. Using direct numerical differentiation this takes 20 min for hexatriene and 75 min for octatetraene.

The 1B_u surfaces were calculated in the vicinity of the ground-state geometry, neglecting excited-state anharmonicity. The first and second derivatives allow to obtain the excited-state equilibrium geometry, assuming that the excited-state surface is harmonic. Table 1 lists the C–C bond lengths for the excited state geometry obtained in this way. The numerical

Table 1
C–C bond lengths in Å in the ground- and excited-state optimized geometry of *trans*-hexatriene and *trans-trans*-octatetraene. Ground-state geometry is obtained using GAUSSIAN-94 HF geometry optimization. Excited-state geometry is obtained using GAUSSIAN-94 CIS excited-state geometry optimization and using ground-state geometry and excited-state-surface CEO derivatives

Bond	Ground state	Excited state	
	HF (optimized)	CIS (optimized)	CEO (parabolic)
<i>trans</i> -Hexatriene (6-311 + + G**)			
C ₁ –C ₂	1.3245	1.3746	1.3625
C ₂ –C ₃	1.4632	1.3997	1.3982
C ₃ –C ₄	1.3292	1.4178	1.4017
<i>trans</i> -Hexatriene (6-31 + G)			
C ₁ –C ₂	1.3317	1.3800	1.3689
C ₂ –C ₃	1.4605	1.4019	1.3979
C ₃ –C ₄	1.3363	1.4216	1.4069
<i>trans-trans</i> -Octatetraene (6-31 + G)			
C ₁ –C ₂	1.3321	1.3640	1.3550
C ₂ –C ₃	1.4596	1.4141	1.4158
C ₃ –C ₄	1.3376	1.4034	1.3916
C ₄ –C ₅	1.4557	1.3940	1.3876

derivatives were computed for the ground-state HF optimized geometry (first column). Excellent agree-

ment was found with the bond lengths obtained using full single-CI geometry optimization. The re-

Table 2

Calculations for *trans*-hexatriene. $\omega_c^{(a)}$ and $\omega_c^{(b)}$ are the excited-state frequencies obtained without and with taking into account Dushinsky rotation effects, respectively. The values in parentheses give the excited- to ground-state CIS frequency ratios for comparison. An asterisk (*) denotes that the adiabatic surface curvature is negative along the mode. GAUSSIAN-94 results are obtained using 6-311 + + G** basis set for HF ground-state and CIS excited-state calculations. Geometries of both ground and excited states were separately optimized using the VeryTight option. Experimental dimensional displacements [13–15] are for hexatriene in vapor phase; experimental excited-state frequencies [16,17] were taken from the absorption in supersonic molecular beams.

Experiment			HF/6-311 + + G**	CEO		
ω_g, cm^{-1}	$ \Delta $	ω_c/ω_g	ω_g, cm^{-1}	Δ	$\omega_c^{(a)}/\omega_g$	$\omega_c^{(b)}/\omega_g$
<i>In-plane modes</i>						
<i>A_g</i>						
			3371	0	1	1 (1)
			3300	-0.03	1	1 (1)
			3292	-0.05	1	1 (1)
			3281	0.03	1	1 (1)
1634	1.32	1	1870	-1.60	1.03	1.03 (0.97)
1403	0.085		1769	0.07	0.95	0.95 (0.92)
1581	0.38		1545	-0.15	0.99	0.98 (0.96)
1290	0.49		1417	-0.49	1	1 (0.96)
1290	-		1438	-0.20	0.98	0.98 (0.95)
1192	0.82	1.03	1298	0.78	0.98	0.98 (0.98)
934	0.23	0.77	1009	0.29	0.98	0.98 (1)
444	0.23	1.06	468	0.25	0.94	0.96 (0.99)
354	0.55	0.87	376	-0.20	0.81	0.76 (0.95)
<i>B_u</i>						
			3371		1	1 (1)
			3303		1	1 (1)
			3292		1	1 (1)
			3281		1	1 (1)
			1829		0.88	0.91 (0.89)
			1578		0.99	0.98 (1)
			1427		0.98	0.97 (0.97)
			1381		0.99	0.98 (0.95)
			1216		0.98	0.97 (1.04)
			1035		0.98	0.98 (1.02)
			578		1.01	1.01 (0.99)
			158		0.60	0.47 (0.95)
<i>Out-of-plane modes</i>						
<i>A_u</i>						
			1142		0.89	0.93 (0.91)
			1075		0.83	0.92 (0.88)
			1049		0.81	0.68 (0.82)
			769		0.61	0.58 (0.63)
			266		0.88	0.63 (0.35)
			96		***	*** (0.31)
<i>B_g</i>						
			1116		0.91	0.94 (0.91)
			1058		0.93	0.93 (0.90)
			992		0.94	0.93 (0.87)
			665		0.89	0.83 (0.68)
			204		***	*** (0.92)

Table 3

Calculations for *trans-trans*-octatetraene. $\omega_e^{(a)}$ and $\omega_e^{(b)}$ are the excited-state frequencies obtained without and with taking into account Dushinsky rotation effects, respectively. The values in parentheses give the excited- to ground-state CIS frequency ratios for comparison. Stars denote that the adiabatic surface curvature is negative along the mode. GAUSSIAN-94 results are obtained using 6-31 + G basis set for HF ground-state and CIS excited-state calculations. Geometries of both ground and excited states were separately optimized using the VeryTight option. Experimental data [20] are for octatetraene in supersonic jet; mode assignment is based on $|\Delta|$ and ω_e ; dimensionless displacements are obtained from the experimental data using the effective masses of the normal modes given by GAUSSIAN-94: 4.89, 2.01, and 3.04 au for 1646, 1327, and 245 cm^{-1} modes, respectively.

Experiment		HF/6-31 + G		CEO		
ω_g, cm^{-1}	$ \Delta $	ω_e/ω_g	ω_g, cm^{-1}	Δ	$\omega_e^{(a)}/\omega_g$	$\omega_e^{(b)}/\omega_g$
<i>In-plane modes</i>						
<i>A_g</i>						
			3412	0	1	1 (1)
			3330	-0.01	1	1 (1)
			3322	-0.04	1	1 (1)
			3315	-0.03	1	1 (1)
			3311	0.02	1	1 (1)
1603	1.27	1.03	1874	-1.49	1.03	1.03 (0.98)
			1820	0.03	0.96	0.97 (0.94)
			1613	-0.08	0.99	0.99 (1)
			1478	0.03	0.99	0.99 (0.99)
			1467	-0.23	0.99	0.99 (0.97)
			1449	0.40	1	1 (0.96)
1170	0.97	1.06	1327	0.77	0.99	0.98 (1.04)
			1228	0.28	0.98	0.98 (1.07)
			1066	0.21	0.99	0.99 (1.01)
			597	0.13	1.02	1.02 (1)
			366	0.28	0.99	0.99 (1)
199	0.60	1.01	245	0.28	0.90	0.87 (0.98)
<i>B_u</i>						
			3412		1	1 (1)
			3331		1	1 (1)
			3326		1	1 (1)
			3318		1	1 (1)
			3312		1	1 (1)
			1865		0.87	0.93 (0.90)
			1773		0.97	0.93 (0.93)
			1592		0.99	0.99 (0.97)
			1482		0.99	0.99 (0.96)
			1455		0.98	0.98 (0.96)
			1399		0.99	0.97 (0.95)
			1268		0.98	0.97 (1)
			1034		0.98	0.98 (1.01)
			625		0.97	0.98 (0.99)
			430		0.88	0.86 (0.96)
			96		0.63	0.51 (0.96)
<i>Out-of-plane modes</i>						
<i>A_u</i>						
			1169		0.96	0.97 (0.96)
			1133		0.93	0.95 (0.94)
			1093		0.93	0.94 (0.93)
			997		0.99	0.96 (0.93)
			709		0.93	0.91 (0.84)
			228		0.74	0.80 (1.09)
			178		0.95	0.67 (0.73)
			61		***	*** (1.06)

Table 3 (continued)

Experiment		HF/6-31 + G		CEO		
ω_g, cm^{-1}	$ \Delta $	ω_c/ω_g	ω_g, cm^{-1}	Δ	$\omega_c^{(a)}/\omega_g$	$\omega_c^{(b)}/\omega_g$
<i>Out-of-plane modes</i>						
B_g						
			1158		0.97	0.98 (0.96)
			1112		0.94	0.96 (0.94)
			1074		0.83	0.96 (0.95)
			1067		0.95	0.80 (0.87)
			752		0.82	0.83 (0.80)
			369		0.86	0.77 (0.63)
			149		***	*** (1.03)

sulting dimensionless displacements $\Delta_{\nu_a} = (Q_{\nu_a} - Q_{0_a})\sqrt{\hbar/m\omega_{0_a}}$ and excited-state frequencies ω_{ν_a} for both molecules are presented in Tables 2 and 3. Δ_{ν_a} is given for the fully symmetric (A_g) modes only, since for other modes they vanish by symmetry. The experimental vibrational modes are assigned based on the values of Δ_{ν_a} and ω_{ν_a} . The ab-initio results for the excited-state frequencies are obtained for the CIS excited-state optimized geometry.

First, we note the remarkably good agreement with the experimental displacements Δ_{ν_a} obtained by fitting the Raman scattering profiles using the Condon approximation [13–15]. We found that the four modes of *trans*-hexatriene that are not resolved in the experiment have dimensionless displacements less than 0.05. The experimental data for *trans-trans*-octatetraene are taken from Ref. [20], where only three vibrational modes were resolved in the fluorescence from supersonic jet. It should be noted that the calculation also provides the signs of the displacements, which are not available from Raman experiment [13–15] and are necessary for establishing excited state geometries (see Table 1).

Vibrational frequency changes upon electronic excitation are small in both molecules. Noticeable mode rotation and frequency shift occur primarily for the out-of-plane modes. For these modes we observe reasonable correlation in frequency shifts between the CI and CEO calculations, except for the lowest-frequency modes. For both molecules and for each of the two out-of-plane symmetries, our calculations predict negative curvature of the excited state surface along one normal mode, suggesting the possibility of barrierless isomerization in the excited state. This

differs from CI calculations which suggest that the optimized excited-state *trans* geometry is stable [21] (see Tables 2 and 3)². The discrepancy could be attributed to the anharmonicity of the excited-state surface along these modes. In our model calculations we have assumed a harmonic excited-state surface so that its curvature does not change with nuclear configuration. This assumption is reasonable, as long as the geometry change is small, which may not be the case for low-frequency modes. We have studied the excited-state surface nonlocally by changing geometry along the isomerization coordinate and computing ground-state and excitation energies at every point. These results show that the excited-state surface along this coordinate is noticeably anharmonic, as is expected for molecules undergoing photoisomerization [27].

Although we observe reasonable ($\sim 5\%$) agreement with the ab-initio excited-state frequencies, experimental frequencies are overestimated by $\sim 20\%$. This is a well-known problem in quantum chemistry and a rescale factor 0.9 is usually applied to the ab-initio ground-state frequencies calculated at 6-31G level [28]. A different rescaling factor may be required for the excited states (the values in Tables 1 and 2 are not rescaled). Another possible reason is related to the isomerization, since an anharmonic

² Note that the TDHF and single-CI calculations are similar since they both deal with the same amount of information. The difference is that single CI neglects all states that have more than one electron-hole excitations, while TDHF treats each such excitation as a harmonic oscillator thus allowing for double, triple, etc., excitations in the harmonic ladder approximation.

motion along one of the coordinates may affect the observed frequencies of other modes.

3. Conclusion

We have proposed a low-cost algorithm for computing excited-state adiabatic surfaces of large molecules. The excited-state adiabatic surface $E_v(\mathbf{q})$ is obtained using Eq. (2) by adding the electronic excitation energies $\Omega_v(\mathbf{q})$ obtained from a time-dependent density matrix calculation to the ground-state adiabatic surface $E_0(\mathbf{q})$, which is an input to this calculation.

Calculations of the 1B_u excited-state surfaces of hexatriene and octatetraene show very good agreement with experimental dimensionless displacements. Comparison with ab-initio GAUSSIAN-94 excited-state geometry optimization for the same molecules shows that the CEO gives reasonable description of the excited-state vibronic frequencies, except for the lowest-energy out-of-plane modes, which are predicted to be unbound. Using the calculated dimensionless displacements and excited-state vibronic frequencies we have calculated the excited-state geometries of both molecules, assuming a harmonic excited-state surface. Excellent agreement with ab-initio optimized excited-state was obtained for the bond lengths in the excited-state optimized geometry.

We have used the HF ground state as an input to our calculations. This is, however, not essential and the method can be easily combined with other ground-state (e.g., density-functional) techniques. The lack of long-range electronic coherence may be used to reduce the number of density matrix elements from $\sim N^2$ to $\sim N \times N_c$ where the coherent size N_c denotes the number of orbitals of closely lying atoms [29]. We anticipate favorable linear N -scaling of computational effort with size, since typically $N_c \ll N$. This is analogous to similar developments in the ground state calculations [30–32].

The present technique is not limited to harmonic surfaces and could be applied to compute photochemical processes. We have recently applied it to perform an excited-state molecular dynamics simulation of a Schiff base cation upon optical excitation [33]. The technique is also most suitable for excited-

state molecular dynamics simulations where the surface is generated ‘on the fly’. The variation of the CEO modes $\xi_v(\mathbf{q})$ with \mathbf{q} can be computed using equations of motion. This requires the expansion of Eq. (1) with respect to small deviations in \mathbf{q} , and using an analytic derivative procedure as an alternative to the numerical differentiation used in this Letter [33]. Combination of such expansion with equations of motion should provide a Car–Parinello-type [34,35] algorithm for excited-state dynamical simulations.

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