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CEO/semiempirical calculations of UV–visible spectra in conjugated molecules

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Abstract

The collective electronic oscillators (CEO) approach based on the TDHF approximation is combined with INDO/S, MNDO, AM1, and PM3 semiempirical Hamiltonians. This technique is applied to compute and analyze the electronic structure of acceptor-substituted oligomers and conjugated polymers. Calculated excited-state energies and oscillator strengths agree well with the experimental data and with each other. In particular, the results using the Hamiltonians parameterized for ground-state calculations such as AM1 and PM3 agree well with the INDO/S results. In addition, a two-dimensional analysis of the corresponding transition density matrices provides an efficient way for tracing the origin of various optical transitions by identifying the underlying changes in charge densities and bond-orders. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Accurate calculations of molecular vertical excitation energies and polarizabilities are essential for the modeling of spectroscopic probes, addressing structure–function relations and predicting structures with desired optical properties [1]. Generating a qualitatively acceptable description of excited states is a much more challenging task than the analogous ground-state calculations. The reason is that the ground-state electronic wave function is usually well approximated by a single Slater determinant, whereas much more complicated configuration interaction (CI) representations are often needed for the excited states [2]. The large computational demand associated with the CI calculations places severe limitations on the size of the systems whose excited states can be studied [3].

Alternatives to CI approaches such as time-dependent density functional theory (DFT) [4–6] are now available within the standard quantum chemistry packages (e.g., GAUSSIAN [7]). While we are still accumulating experience with these techniques, it appears that they produce quite reasonable spectra, especially when used with the new generation of gradient-corrected or hybrid functionals. They are much more accurate, for example, than the analogous random-phase approximation (RPA) applied to an ab initio Hartree–Fock wave function. However, while applicable to larger systems than traditional CI calculations, they are still fairly computationally expensive. To our knowledge, the largest system studied with these techniques to date is the C_{70} cluster [4].

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In this Letter, we focus on these RPA techniques used in conjunction with the semiempirical approaches developed to target larger system sizes [8–12]. These approaches are based on simplified Hamiltonians parameterized using high-level ab initio calculations and (or) experimental data. The semiempirical approximations usually limit the basis set to a minimum valence basis of Slater-type orbitals. Coulomb and exchange terms in the two-electron interaction are approximated and many are ignored completely. Typically, only one- and two-center Coulomb interactions are retained, and the exchange interactions are usually limited to those on a single atom. These approximations make semiempirical techniques fast and efficient yet reasonably accurate for computation of molecular properties.

The semiempirical Hamiltonians which have evolved over the years differ both in the types of two-electron integrals retained in the model, and the manner in which the relevant parameters are determined. In particular, models developed by Dewar and Stewart [9–12] adjusted their parameters to reproduce the ground-state geometry, heats of formation and other properties at Hartree–Fock level. This approach assumes that electron correlation effects can be incorporated in the empirically determined parameters. To study the excited states, Zerner [13,14] combined the intermediate neglect of differential overlap (INDO) model of Pople and co-workers [8] with a CI approximation to generate excited states. The CI expansion was limited to single excitations from the ground-state determinant, an approach dubbed the CI singles (CIS) approximation. The original INDO parameters did not work well, but Zerner found that the model could be reparameterized to reproduce the vertical excitation energies of small organic molecules and transition metal compounds [13,14]. This method was christened the INDO/S (INDO/spectroscopy) approach and has proven to be an extremely valuable technique [15]. Reproducing the excitation energies came at a price, however, as the INDO/S method does very poorly for ground-state geometries. In applications, typically either the experimental geometry or a semiempirical approach developed for the ground state is used to determine the geometry of the molecule, and is followed by an INDO/S calculation to generate the excited states.

Recently, the INDO/S Hamiltonian and parameterization have been used with the collective electronic oscillators (CEO) approach [16] to generate excitation energies. As opposed to a CI expansion, this method is based on the time-dependent Hartree–Fock (TDHF) approximation or RPA [17,18] and requires only the ground-state density matrix. It has been successfully used in calculations of the optical properties of a variety of conjugated chromophores such as porphyrins, dendrimers, donor/acceptor polymers, biological light-harvesting complexes, etc. [16,19,20]. By focusing only on the spectroscopically relevant observables, the CEO approach enables calculations on excited electronic states of molecules with hundreds of heavy atoms. In addition, the CEO approach allows the electronic excitations to be interpreted in terms of the underlying electron–hole motion by analyzing the relevant transition densities.

In this Letter, we wish to examine the applicability of the CEO technique combined with semiempirical Hamiltonians other than INDO/S. Our motivation is that we would like to treat both the ground state and its excitations within the same model Hamiltonian. As was mentioned earlier, the INDO/S parameterization does not work well for ground-state properties such as the equilibrium geometry. On the other hand, the models of choice for the ground state (Austin model 1 (AM1) [9], parametric model 3 (PM3) [10], modified intermediate neglect of diatomic overlap (MNDO) [11] and older modified intermediate neglect of differential overlap 3 (MINDO/3) [12]) have not been systematically studied as regards their applicability to excited states, presumably because of the success of INDO/S and the availability of the ZINDO molecular orbital package [15]. An example where a unified treatment would be particularly useful is in the generation of excited-state potential energy surfaces by adding an excitation energy to a ground-state energy [21]. This is particularly awkward if one Hamiltonian must be used to generate the ground-state surface and another to determine the excitation energy. Here, we examine this question by comparing the results of the CEO/

AM1 and CEO/PM3 combinations with the CEO/INDO/S model and also with the experiment. For our initial study, we choose a series of substituted carotenoids and the conjugated oligomers of various sizes. They have quite interesting optical properties and show promise in device applications [1,22,23]. We will not discuss the details of their excited-states or electronic structure as they have been analyzed earlier [16]. For our purposes, they represent a reasonably diverse set of test cases which are large enough to lie in the realm of semiempirical techniques.

Section 2 briefly describes the computational method. In Section 3, we compare the electronic spectra of carotenoids and oligomers computed with different semiempirical techniques. Finally we discuss the trends that emerge and summarize our results in Section 4.

2. Computational method

The family of acceptor-substituted betacarotene studied is shown in Fig. 1. We have also built a series of conjugated oligomers with varying lengths up to ~50 Å chain length. We consider oligomers of polyacetylene (PA), polydiacetylene (PDA), polytriacetylene (PTA), poly-phenylene-vinylene (PPV), poly-*p*-phenylene (PPP), polythiophene (PTh), polypyrrole (PPy), polyfuran (PF), and polyaniline (PAn) with the structures given in the insets of Figs. 2 and 3. Gaussian-98 [7] was used to optimize the geometry of each molecule with the AM1 semiempirical Hamiltonian [9], which provides reasonable ground-state geometries.

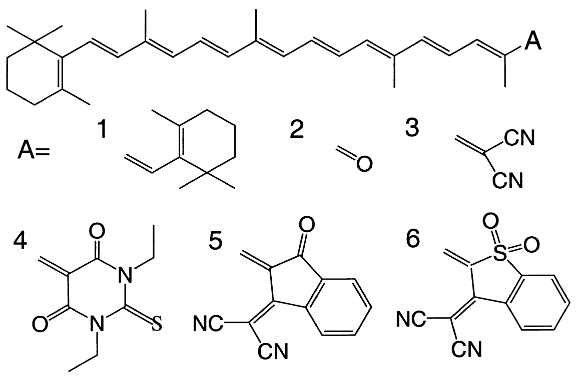

Fig. 1. Six acceptor-substituted carotenoids studied in [22,23] listed in order of increasing acceptor strength.

INDO/S, AM1, PM3, MNDO, and MINDO/3 semiempirical Hamiltonians were generated next for each optimal molecular structure using either ZINDO (INDO/S) [13,14] or the MOPAC-93 (AM1, PM3, MNDO, and MINDO/3) code [24]. The CEO code, described in detail elsewhere [16], was used to generate the Hartree–Fock ground-state density matrices which then serve as input to the subsequent CEO calculation to compute the lowest excited-state frequencies and their oscillator strength for each semiempirical approach. Complementary transition density matrices (denoted by the *electronic normal modes*, ξ_ν) connecting the molecular optical response with the underlying electronic motions have also been calculated. Each mode is a matrix representing the electronic transition between the ground state $|g\rangle$ and an electronically excited state $|\nu\rangle$. Its matrix elements are given by

$$(\xi_\nu)_{mn} = \langle \nu | c_m^+ c_n | g \rangle, \tag{2.1}$$

where c_m^+ (c_m) are the creation (annihilation) operators of an electron at the *m*th atomic orbital, and $|g\rangle$ ($|\nu\rangle$) is the ground (excited) state many-electron wave function. Transition dipole moments $\mu_\nu = \mathrm{Tr}(\mu\xi_\nu)$ were then calculated using the dipole moment operator $\mu = \sum_{nm} \mu_{nm} c_m^+ c_n$. Then $f_\nu = 2\Omega_\nu \mu_\nu^2$ is the oscillator strength of the g to ν transition, and Ω_ν is the excited-state energy.

The electronic modes are computed as eigenmodes of the linearized TDHF equations of motion for the density matrix in the presence of an external electric field. The eigenfrequencies Ω_ν of these equations provide the optical transition energies [16]. The TDHF approach coincides with the RPA for the linear optical response of many-electron systems (see [17], Chapter 8.5). The electronic modes are identical to the transition densities of the RPA eigenvalue equation. The numerical effort involved in computing these eigenvalues and eigenvectors is greatly reduced by using the oblique Lanczos algorithm [25]. These computations take into account the full active space (i.e., all the occupied and virtual orbitals) automatically.

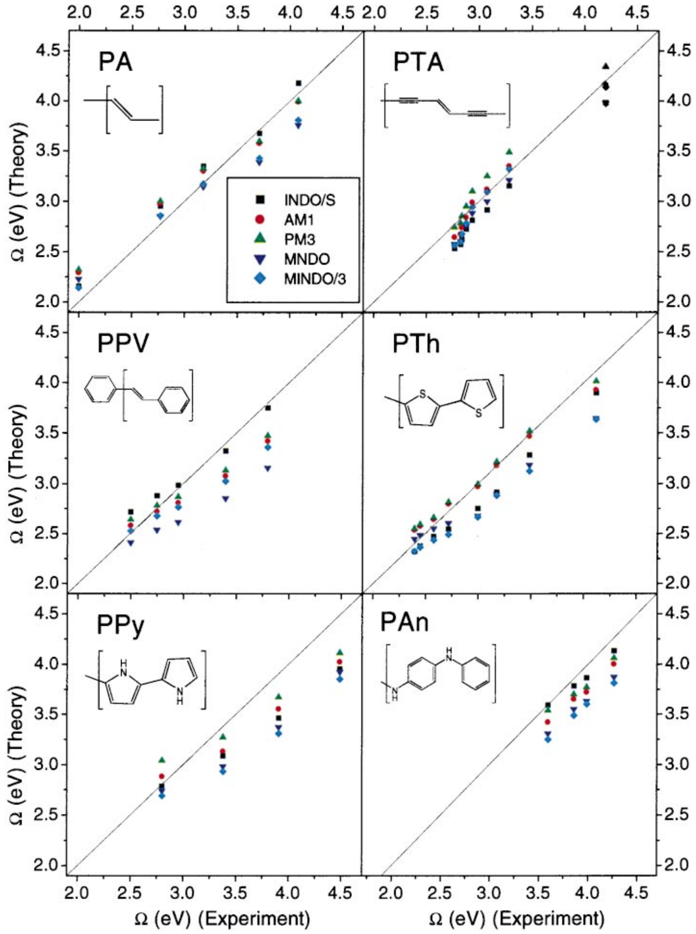

Fig. 2. Comparison of theoretically lowest transition energies (band-gap absorption maximum), computed with INDO/S, AM1, PM3, MNDO, and MINDO/3 Hamiltonians combined with CEO, with the experimental data for conjugated oligomers with structures shown in the insets. Computations used the CEO code in the full active space. An exact agreement of theory and experiment gives points lying at the diagonal of the plots, whereas blue- (red-) shifted computed values vs. experimental data result in points lying higher (lower) than the diagonal.

Compared to the CIS approximation, the RPA includes all the single excitations of CIS plus some additional higher-order electronic correlations as discussed in [17,18,26]. In addition, the RPA is inherently size-consistent which is not necessarily true for CI approaches [18].

Each semiempirical Hamiltonian assigns a single *s*-type basis function to hydrogen atoms and four basis functions (s, p_x, p_y, p_z) to heavy atoms (parameterization of transition metals with nine basis functions has been achieved for INDO/S [14] and is being developed for AM1 and PM3 [24]). Qualitatively, only the p orbitals perpendicular to the molecular plane (which are not sp^n hybridized forming the molecular σ-bonding skeleton) are responsible for the lowest delocalized optical excitations in conjugated molecules.

3. Vertical excitation energies and oscillator strengths

3.1. Acceptor-substituted carotenoids

Fig. 1 shows six acceptor-substituted carotenoids synthesized in a search for molecules with

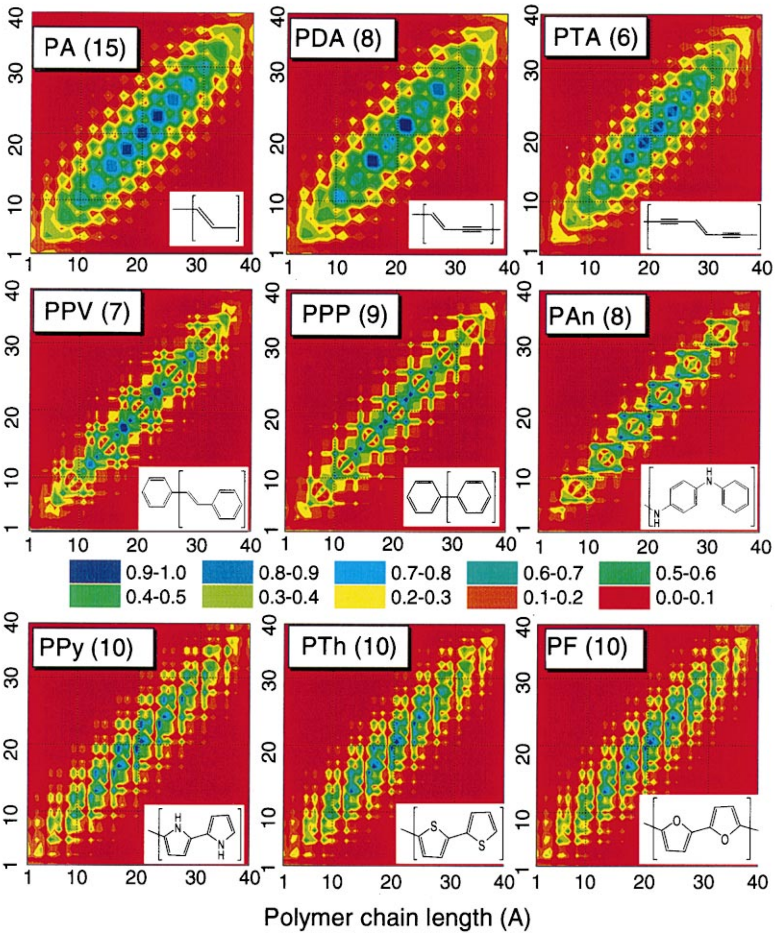

Fig. 3. Contour plots of the electronic modes computed with CEO using the AM1 Hamiltonian corresponding to the band-gap transition in conjugated oligomers of approximately the same length (40 Å). Molecular structures are shown in the insets. The axis labels represent the oligomer length in Å. The color map given in the middle row goes from red (the smallest matrix elements) to blue (the largest matrix elements).

large optical nonlinearities [22,23]. A detailed analysis of the physical phenomena emerging upon substitution in these and other molecules using the CEO approach was conducted in [16]. The optical absorption spectrum of the unsubstituted beta-carotene (molecule 1) is dominated by a single absorption peak. With increasing acceptor strength (molecules 2–6) this peak is red-shifted and a second weaker peak appears in compounds 5 and 6. The nonlinear polarizabilities of these molecules showed a dramatic growth with increasing acceptor strength. We refer the reader to [16,22] for a more detailed electronic spectrum analysis. Table 1 reports the vertical excitation energies and their oscillator strengths corresponding to peaks appearing in the absorption spectra using several different semiempirical approaches, including INDO/S, coupled with the CEO method [16]. In addition, we used the ZINDO code [15] to calculate these transition energies with the INDO/S parameterization combined with the CIS technique using the entire orbital space. This allows us to compare CIS with CEO using the *same* Hamiltonian.

Compared to experiment, the RPA–INDO/S approach is the most accurate and demonstrates

Table 1
Vertical excitation energies (in eV) of acceptor-substituted carotenoids studied in [22,23][a]

Mol. #	Experiment (RPA)	INDO/S (CIS)	INDO/S (RPA)	AM1 (RPA)	PM3 (RPA)	MNDO (RPA)	MINDO/3 (RPA)
1	2.5	2.47 (3.5)	2.62 (3.5)	2.52 (2.9)	2.56 (2.9)	2.46 (2.6)	2.40 (2.9)
2	2.6	2.56 (3.1)	2.67 (3.2)	2.60 (2.6)	2.64 (2.5)	2.54 (2.4)	2.48 (2.6)
3	2.3	2.37 (3.4)	2.48 (3.3)	2.48 (2.9)	2.51 (2.9)	2.44 (2.6)	2.39 (3.0)
4	2.1	2.33 (3.7)	2.39 (3.5)	2.44 (3.1)	2.46 (3.3)	2.39 (3.1)	2.33 (3.4)
5a	1.9	1.88 (3.0)	1.92 (2.7)	2.08 (2.5)	2.11 (2.3)	2.09 (2.3)	2.16 (2.8)
5b	3.0	2.72 (1.2)	2.75 (1.3)	2.73 (0.9)	2.75 (0.9)	2.68 (0.8)	2.68 (0.7)
6a	1.8	1.71 (3.1)	1.82 (2.9)	1.90 (2.5)	1.94 (2.5)	1.91 (2.3)	2.00 (2.8)
6b	2.9	2.94 (1.2)	3.10 (0.9)	2.71 (0.7)	2.79 (0.8)	2.67 (0.7)	2.61 (0.6)
σ		0.1	0.14	0.16	0.17	0.17	0.2

[a] The oscillator strengths are given in parentheses. Compounds 5 and 6 have two absorption peaks (denoted a and b) emerging due to substitution [16]. Computations are conducted using CEO (RPA), ZINDO (CIS) codes in the entire orbital space. The bottom line shows the average deviation σ (eV) of computed energies from experiment for a given method.

excellent agreement, especially for unsubstituted molecules or compounds substituted with weak acceptor molecules (1–3). For the more polar compounds 4–6, the agreement is less striking since intermolecular dipolar interactions in films (which are left unaccounted for in our computations) stabilize excited states in the experiment. The CIS–INDO/S results are very similar to those of the RPA–INDO/S, being blue-shifted by ~0.1 eV. The oscillator strengths in these two approaches are also very similar. Computational studies based on the INDO/S approximation reported in the literature claim that, compared to experiment, RPA provides better oscillator strength than CIS [26].

It is very striking to notice that AM1, PM3, and MNDO parameterization fits for the ground state also reproduce the excited-state energies at the RPA level extremely well (see Table 1). AM1 energies are blue-shifted compared to those of MNDO, and PM3 results are blue-shifted even further. The oscillator strengths computed with these methods are all very similar and generally smaller than calculated with RPA–INDO/S and follow all trends of the latter approach. The MINDO/3 technique also demonstrates a reasonable comparison with the experiment. The bottom line in Table 1 shows the average deviation of calculated energies from their experimental values for these methods. All the semiempirical approaches reproduce the experimental values within ~0.2 eV accuracy.

3.2. Conjugated oligomers

The comparison of computed excitation energies of conjugated oligomers with the experiment constitutes a tedious task. There exists a great diversity of experimental conditions: in the gas phase, in solution with various solvents, in the solid state. Furthermore, intermolecular interactions and solvents can play an important role in the stabilization of excited states. In addition, the literature reports energies either at the maximum absorption peak or at the onset of absorption. In calculations, we used the AM1 optimization for the ground-state geometries for all molecules, and computed vertical excitation energies for each of them. In addition to this approximation, there will be errors associated with the various environments, liquid vs. solid-state vs. gas-phase.

We will compare results, obtained from different semiempirical parameterizations coupled with the CEO approach, with experiment tracking both the absolute values and spectroscopic trends in absorption even though some deviations of the theory from experiment are expected. Each conjugated oligomer of any polymer type has a strongly allowed low-lying singlet state of $1B_u$ symmetry showing up in linear absorption (band-gap transition). In Fig. 2, we plot the $1B_u$ transition frequencies of oligomers with various sizes computed for each semiempirical parameterization vs. experimental results reported in the literature for PA [27], PTA, [28] PPV [29], PTh [30,31], PPy [32–35], and PAn [36]. Each panel represents the oligomer shown in the inset, whereas groups of points correspond to the oligomers of different sizes. Points lying higher (lower) than the diagonal of the plot indicate that the computed value is blue- (red-) shifted compared to experiment. Excitation energies of different oligomers are well separated since band-gap transition energy-shifts to the red with increasing chain length and gradually saturates to a constant for long chains [19,20]. This trend can be understood by analogy with the particle-in-a-box model. Fig. 2 suggests that overall the INDO/S results provide the best agreement with the experiment. AM1 and PM3 values are very similar with a small shift of PM3 energies to the blue. Compared with INDO/S, AM1 and PM3 results are shifted either to the blue (PTA, PTh, and PPy) or to the red (PA, PPV, PAn) and no universal trends could be discerned. MNDO and MINDO/3 give energies generally red-shifted compared to that of INDO/S.

Finally, we have examined the density matrices corresponding to band-gap transitions of different oligomers with similar chain lengths (~40 Å) to establish a connection between the optical response and the underlying photo-induced real-space dynamics of charges. These matrices represent the collective motions of electrons and holes and carry substantially less information than the complete many-electron eigenstates, but more than that required for calculating the molecular polarizabilities and spectroscopic observables. The diagonal elements $(\xi_\nu)_{nn}$ represent the net charge induced on the nth atomic orbital by an external optical field with frequency Ω_ν, whereas $(\xi_\nu)_{mn}$ $n \neq m$ is the dynamical bond-order (coherence) representing the joint amplitude of finding an electron on orbital m and a hole on orbital n [19].

The transition densities are plotted in Fig. 3 using the contraction described in [20]. The axes of each color panel show the coordinates of heavy atoms along the chain axis. All these plots are structurally similar: the electron–hole created upon optical excitation is delocalized over the whole chain (diagonal in the plot) and tends to be in the middle of the molecule. However, the exciton size (maximal distance between electron and hole) shown, as the largest off-diagonal extent of the nonzero matrix area, is different from polymer to polymer. PA, PDA, and PTA have the largest exciton size of about ~20 Å (top row). This is reduced to ~15 Å for PPV and PPP and to ~10 Å for PAn (middle row). PPy, PTh, and PF, which have double bond conjugation paths similar to PA, again have large electron–hole delocalization of ~20 Å (bottom row). In particular, large exciton size corresponds to the increased onset of band-gap saturation for longer chains [1,19].

4. Conclusion

We have computed UV–visible spectra of a family of acceptor substituted carotenoids and several conjugated oligomers with various sizes. Our approach combines different semiempirical Hamiltonians (INDO/S [8], AM1 [9], PM3 [10], MNDO [11], MINDO/3 [12]) with the CEO [16] technique which utilizes the TDHF approximation for the many-electron wave function [18]. Computational results were compared where possible against the existing experimental data. Vertical excitation energies computed with the INDO/S semiempirical parameterization show the best agreement with experiment because INDO/S was primarily designed for this purpose. However, this approximation is not adequate for the ground state. On the other hand, UV–visible spectra computed with AM1, PM3, and MNDO approaches show a reasonable agreement with the experiment and reproduce the basic trends. Also, these semiempirical Hamiltonians are more reliable for molecular ground-state properties at the Hartree–Fock level since they were parameterized for this purpose.

We conclude that computing observables which depend on both ground and excited-state molecular properties, such as adiabatic excited-state potential surfaces [21], within a single semiempirical framework is possible by combining AM1, PM3, or MNDO semiempirical parameterizations and the Hartree–Fock approximation for the ground state with the CEO technique for excited states. The CEO method maps optical spectra directly to the motions of electrons and holes in real space by generating the optically driven reduced single electron density matrix. This makes possible two-dimensional real-space analysis of relative motion of electron–hole pairs for any electronic transition. In turn, this is very useful for the interpretation of optical properties in conjugated molecules and constitutes an important advantage of the theoretical approach when combined with any semiempirical Hamiltonian.

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