



Permanent dipole moments and energies of excited states from density functional theory compared with coupled cluster predictions: Case of *para*-nitroaniline



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ABSTRACT

Different ways to extract properties of excited states from time-dependent density functional theory (TD-DFT) calculations are compared to *ab initio* results obtained with the Equation of Motion Coupled Cluster approach. The recently proposed *a posteriori* Tamm–Dancoff approximation (ATDA) predicts the permanent dipole moments to be underestimated by 25% on average, close to the results of the relaxed density TD-DFT formalism, quadratic response formalism, and numerical energy derivatives, while the unrelaxed density approximation results are less accurate (40% overestimate). We also propose a correction for TD-DFT excitation energies, which are known to be problematic for charge transfer states. The static DFT energies evaluated on the relaxed densities of the excited states are found to be more accurate than TD-DFT excitation energies (RMSD is 0.7 eV vs. 1.1 eV, while maximum deviation is -1.0 eV vs. -2.0 eV). This validates ATDA for description of nonlinear optical properties of donor–acceptor molecules, exemplified by *para*-nitroaniline, and extends this method to improve the excitation energy predictions.

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1. Introduction

Theoretical description of excitations in conjugated molecules plays a critical role in understanding of these processes and may assist in the rational design of the new materials. *Para*-nitroaniline (PNA) is often used as a prototypical donor/acceptor (D/A) substituted conjugated molecule. Its structure is shown in Fig. 1.

PNA has a nonbonding electron pair localized on the amino group (which plays a role of π -donor) and a low-lying vacant antibonding orbital localized on the nitro group (π -electron acceptor). The π -conjugation through the phenyl ring allows for a partial transfer of electron density from the donor to acceptor groups in both ground and excited states. This electron mobility results in a number of properties important for organic electronics [1] and photonics [2] applications.

A photoinduced change in the permanent electric dipole moment reflects degree of charge transfer resulting from electronic excitation [3], and is necessary for understanding of many practi-

cally important systems, from isolated molecules in the gas phase and in solution to band structures of organic semiconductors and crystalline materials, to complex biological systems [4]. Knowledge of the excited state dipole moments of the higher PNA homologs is also important for a wide variety of light-induced charge transfer reactions [5].

Accurate numerical values of permanent dipole moments are also important, along with transition dipole moments, for prediction of nonlinear optical (NLO) properties using the Sum-Over-States (SOS) formalism [6]. A reliable estimation of hyperpolarizability typically requires higher theory levels that include electron correlation, while DFT tends to overestimate off-resonant hyperpolarizability values [7]. A quick fix is provided by increasing fraction of Hartree–Fock (HF) exchange in hybrid exchange–correlation functional [8–13]. In prediction of the resonant NLO properties, such as two-photon absorption (2PA) cross-sections, the results are somewhat improved when M05-*qx* functional with 35% HF exchange is used [14–16]. However, increase in fraction of HF exchange beyond 40% was shown to be disastrous: it leads to the overestimated state energies and underestimated transition dipoles [17].

Within DFT framework, prediction of dipole moments of excited states and related 2PA cross-sections of these states requires going

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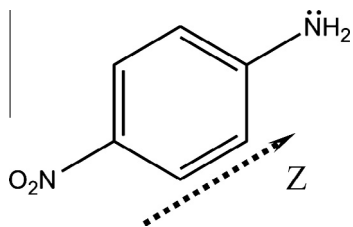


Fig. 1. Para-nitroaniline with z-axis direction.

beyond the linear response in Time-Dependent Density Functional Theory (TD-DFT) [18–22]. However, we have recently shown that *a posteriori* Tamm–Dancoff approximation (ATDA) to the second-order Coupled Electronic Oscillator (CEO) formalism, applied at the Density Functional Theory level can be used for accurate, yet computationally inexpensive predictions of transition dipole values [23,24]. That was demonstrated on linear polyenes, for which the permanent dipole moment vanishes due to their symmetry. Donor–acceptor substituted conjugated molecules, on the other hand, have large dipole moments in all the electronic states. They also feature charge transfer states, which are predicted to lie too low in energy by linear response TD-DFT [25].

Previously observed good agreement of ATDA predicted 2PA cross-sections with experimental values [26,27], may serve as indirect evidence for the accuracy of ATDA in state-to-state transition dipoles prediction. In this contribution we continue our systematic investigation of ATDA performance and directly analyze the predictions for permanent dipole moments of excited states. We employ benchmarking against the results obtained at a high-level wavefunction theory, and compare performance four TD-DFT formalisms. We also propose corrections to the excitation energies, based on relaxed electron density of the excited states. As a test case, we selected *para*-nitroaniline, and analyze the details of electronic structure for the twenty lowest valence excited states (five in each of four irreducible representations of the C_{2v} symmetry group) in the Franck–Condon geometry.

2. Theory

The permanent dipole moment $\mu_{\alpha,\alpha}$ for excited state Ω_α with excitation energy Ω_α is defined as a negative of a derivative of the total energy of this state E_α with respect to an external electric field \mathbf{F} , and can be expressed via the dipole moment of the ground state and the derivative of the excitation energy:

$$\mu_\alpha = -\frac{\partial E_\alpha}{\partial \mathbf{F}} = \mu_0 - \frac{\partial \Omega_\alpha}{\partial \mathbf{F}}. \quad (1)$$

The finite field method, where the latter derivative is calculated numerically, is based on this expression. When the derivative is evaluated analytically [28], it can be expressed via the dipole moment integrals in the molecular orbital basis:

$$\frac{\partial \Omega_\alpha}{\partial \mathbf{F}} = \sum_{pq} D_{pq}^\alpha \langle p | \boldsymbol{\mu} | q \rangle, \quad (2)$$

where D^α is the one-particle density matrix for the excited state [29]. The occupied–virtual and virtual–occupied blocks of this density matrix express the orbital relaxation due to the external field, and appear in the most methods. These blocks describe the effect of orbital relaxation, which has to be taken into account when the excited state energy is not stationary with respect to the MO coefficients for the methods that do not satisfy the Hellmann–Feynman theorem [30]. Nonetheless, these blocks are sometimes neglected, and this approximation is called unrelaxed electron density. It is worth noting that numerical differentiation of the state energy with

respect to the external electric field by Eq. (1) accounts for orbital relaxation in all the methods.

A Coupled Cluster expression for the wavefunction, truncated at single and double substitutions (CCSD) provides arguably the best accuracy-to-cost ratio among *ab initio* methods [31]. The excited states methodology within the Coupled Cluster approach is based on the Equation of Motion (EOM-CCSD) approach [32] or, equivalently, on the linear response theory [33]. Unlike complete active space based multireference methods, the EOM-CCSD approach does not use different treatment for π - and σ -electrons, and accounts for static and dynamic correlation on the equal footing. This motivated us to adopt the EOM-CCSD method as a benchmark *ab initio* method in the present study.

The CEO formalism solves the Heisenberg equation of motion for the electron density of the ground state, moving in frequency-dependent electric field. The CEO formalism can be applied to the ground state, described at various theory levels, including the DFT one [34]. When the terms, higher than linear in external field are neglected in the Heisenberg equation (linear response approximation, LR), the CEO approach is equivalent to the Time-Dependent DFT method [35]. Here the equation of motion is reduced to a non-Hermitian eigenvalue problem:

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \Omega \begin{bmatrix} X \\ Y \end{bmatrix}, \quad \xi = \begin{bmatrix} X \\ Y \end{bmatrix},$$

solution to which are the excitation energies Ω_α and transition density matrices ξ_α for the ground to excited state transitions. In the basis of occupied (i, j) and vacant (a, b) Kohn–Sham (KS) orbitals of σ, τ subsets ($\sigma, \tau = \alpha, \beta$), transition density is block-diagonal with occupied–vacant $X = (\xi)_{ia}$ and vacant–occupied $Y = (\xi)_{ai}$ blocks being non-zero. Matrices \mathbf{A} and \mathbf{B} are defined as

$$A_{ai\sigma,bj\tau} = \delta_{ab}\delta_{ij}\delta_{\sigma\tau}(\epsilon_a - \epsilon_i) + K_{ai\sigma,bj\tau}, \quad \text{and } B_{ai\sigma,bj\tau} = K_{ai\sigma,jb\tau} \quad (4)$$

For the hybrid DFT with c_{HF} fraction of HF exchange, the coupling matrix \mathbf{K} is expressed through the second derivatives of exchange–correlation functional w , Coulomb and exchange integrals as:

$$K_{ai\sigma,bj\tau} = (1 - c_{HF})(ia|w|jb) + (ia|jb) - c_{HF}\delta_{\sigma\tau}(ab|ij). \quad (5)$$

The matrix \mathbf{A} consists of interactions between two singly-excited configurations ($a \leftarrow i|H|b \leftarrow j$), also known as Configuration Interaction Singles (CIS) Hamiltonian. The matrix \mathbf{B} includes, by virtue of swapping indexes, the excitations from virtual to occupied MOs (deexcitations) of the form ($a \leftarrow i|H|j \leftarrow b$). Mathematically, they are equivalent to the matrix elements between the ground and doubly excited states [36].

Transition dipole moments between the ground and excited states are readily obtained in LR-DFT as the trace of the dipole moment operator acting on the transition density:

$$\mu_{0,\alpha} = \text{Tr}(\boldsymbol{\mu}\xi_\alpha), \quad (6)$$

while analytical expressions for the state-to state transition dipoles and the permanent dipoles of the excited states do not appear in the LR-formalism. However, the permanent dipole moments can be evaluated numerically, by performing two sets of LR-DFT calculations at different values of external electric field.

Sometimes an additional approximation is introduced in LR formalism. It is called Tamm–Dancoff approximation (TDA) [37,38], and consists in neglecting the deexcitation matrix \mathbf{B} in Eq. (3). The Eq. (3) is then simplified to the form

$$AX = \Omega X \quad (7)$$

and is also called CIS equation. Its solution yields excitation energies Ω_α and transition density matrices ξ_α . These excitation energies are typically higher than the ones obtained by solution of the full

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