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Assessment of the Δ SCF-DFT approach for electronic excitations in organic dyes

Tim Kowalczyk*, Shane R. Yost*, Troy Van Voorhis**

*These authors contributed equally to this work, **To whom correspondence should be addressed

E-mail: tvan@mit.edu

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

Abstract

This article assesses the accuracy of the Δ SCF method for computing low-lying HOMO \rightarrow LUMO transitions in organic dye molecules. For a test set of vertical excitation energies of 16 chromophores, surprisingly similar accuracy is observed for time-dependent density functional theory (TDDFT) and for Δ SCF density functional theory. In light of this performance, we reconsider the *ad hoc* Δ SCF prescription and demonstrate that it formally obtains the exact stationary density within the adiabatic approximation, partially justifying its use. The relative merits and future prospects of Δ SCF for simulating individual excited states are discussed.

I. Introduction

Small conjugated organic dyes have found widespread use: from lasers, paints and inks to more exotic technologies such as dye-sensitized solar cells¹⁻³ organic light-emitting devices⁴⁻⁷, organic transistors⁸, and organic solar cells^{9, 10}. The performance of these materials relies heavily on the careful tuning of their electronic properties. Consequently, there is growing interest in the development and application of computational methods for characterizing electronic excitations in condensed-phase organic materials^{11, 12}.

Among the earliest approaches to this challenge were semi-empirical molecular orbital methods such as CNDO¹³ and PPP¹⁴. As computational resources expanded, *ab initio* methods such as TDHF and CIS became feasible for molecules of moderate size¹⁵. None of these methods are expected to give quantitative results, but often they are sufficient to predict trends. More recently, methods like CASSCF¹⁶ and EOM-CC¹⁷ have been developed, which promise quantitative results for excited states. Unfortunately, at present, these are too expensive for routine use on organic dyes that typically have 50-100 atoms. A modern method that offers a good compromise between accuracy and efficiency is

time dependent density functional theory (TDDFT)^{15, 18, 19}.

TDDFT within the adiabatic approximation^{20, 21} has been the workhorse method for computing excitation energies in organic molecules over the last decade. TDDFT excitation energies with commonly employed exchange-correlation functionals are usually accurate to within 0.3 eV for localized valence excitations in organic molecules²². However, TDDFT is less reliable for excitations with long-range character, such as Rydberg^{23, 24} and charge transfer excitations^{25, 26}, as well as excitations in large conjugated molecules²⁷⁻²⁹. Recently developed long-range corrected functionals have addressed these issues with promising success³⁰⁻³³. Several time-*independent* alternatives for computing excitation energies within a DFT framework have been proposed³⁴⁻³⁶, but many of these methods pose significant implementation challenges³⁷ or are too computationally expensive compared to TDDFT.

The Δ SCF-DFT (or simply Δ SCF) method, one of the earliest such time-independent methods³⁸, is straightforward to implement and offers low computational cost. This method is also known in the literature as excited state DFT³⁹ or constrained DFT⁴⁰ (not to be mistaken for the method of the same name⁴¹ in which constraints are applied to the density). The Δ SCF procedure employs non-Aufbau occupations of the Kohn-Sham orbitals to converge the SCF equations to an excited state that might have other states of the same symmetry beneath it. Because SCF algorithms are geared towards energy minimization, they can sometimes cause a collapse to these lower-energy states during the SCF iterations. Techniques such as the maximum overlap method⁴² have been developed to address these convergence issues, thereby rendering the Δ SCF method an efficient potential alternative to TDDFT for excited state geometry optimizations and molecular dynamics. Analytical excited state Hessians, which are needed to obtain infrared or vibrationally resolved electronic spectra, are also readily accessible from the Δ SCF approach, in contrast to the current situation for TDDFT. Δ SCF was recently identified as the fourth-order correction to a constrained variational approach to TDDFT⁴³, but here we focus on

its use as a stand-alone method.

Although Δ SCF has gained some traction recently as a DFT-based alternative to TDDFT for excited states^{24, 42, 44-46}, the performance and range of validity of the method remain poorly understood. This paper addresses this gap in understanding in two ways: first, by comparing excitation energies computed by TDDFT and Δ SCF with experimental values for a representative set of conjugated organic molecules; and second, by providing new insight into the approximations that are made when computing excitation energies from Δ SCF.

The rest of the paper is arranged as follows. First, we construct a set of organic dye molecules that we use as a benchmark test set. Next, we present TDDFT and Δ SCF excitation energies and discuss the performance of the two methods relative to experiment. We find that the two approaches are quite comparable, which we find surprising given the lack of formal justification for Δ SCF. We therefore spend some time in the discussion examining the theoretical underpinnings of TDDFT and Δ SCF in order to determine if there might not be a deeper reason for the success of Δ SCF. Finally, we conclude our analysis and suggest some potential future directions.

II. Test set

It is of course impossible to construct a single test set that characterizes the quality of a given functional for excited states. The wide variety of behaviors of different functionals for Rydberg states²³, charge transfer states²⁶, excited states of conjugated organic molecules^{26, 28-30, 47}, and core excitations^{42, 48} suggests a more modest goal: to design a test set that assesses a functional's utility *for a given purpose*. Because of our interest in organic electronics, we are most keenly interested in testing TDDFT and Δ SCF for the low-lying singlet excited states of common dye molecules. Other test sets consisting of small conjugated organic molecules have been constructed to assess the performance of TDDFT, with typical errors of roughly 0.2-0.3 eV for the best-performing functionals^{33, 49, 50}. Our

chosen test set is tabulated in Figure 1. In each case the E_{ex} is the energy of the lowest maximum in the experimental absorption spectrum.

There were a number of criteria that we used to select the molecules in the test set. First, they were required to have significant absorption in the visible. This typically requires extensive π conjugation over most of the molecule resulting in low-lying $\pi \rightarrow \pi^*$ transitions. Further, as can be seen in Figure 1, all of the excitations are predominantly HOMO \rightarrow LUMO. This restriction is not essential, but leads to more robust Δ SCF convergence than, say, HOMO \rightarrow LUMO+1 would. The single-reference character of the excited states helps us circumvent the general problem that some excited states require a multireference approach. We make no restriction on the degree of charge transfer present in the excited state. However, in order to mitigate solvatochromic effects, we selected molecules for which experimental absorption spectra are available in gas phase, thin film, or nonpolar solvent. Ideally, all of the experimental results would be in gas phase, but this restriction would only leave us with five molecules in our test set, which would be insufficient. We therefore must accept some degree of inequivalence between the experimental observable (absorption maximum in a weak environment) and the calculated quantity (vertical excitation in the gas phase). We should note that methods exist to attempt to correct theoretical gas phase excitation energies for dielectric⁵¹ and vibrational⁵² effects to obtain solvent-corrected 0-0 excitation energies, but such shifts will in any case be smaller than the errors due to the approximate nature of the density functional.

Despite the fact that all of the molecules satisfy the criteria given above, our test set includes molecules covering a wide range of current applications. Some molecules are found in biological systems (1, 8, 9, 13, 14), others are used for organic electronics (2, 3, 4, 15, 16), and some as synthetic organic dyes (5, 6, 7, 10, 11, 12). Thus we have made an effort to select a structurally diverse set of molecules that can answer the question: how accurate are Δ SCF and TDDFT for organic dyes?

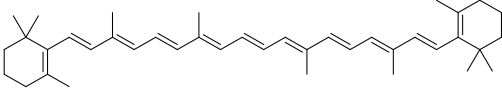
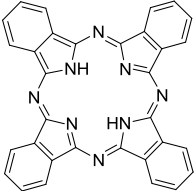
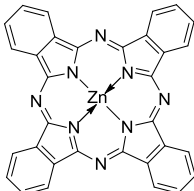
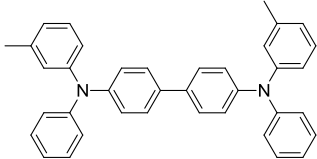
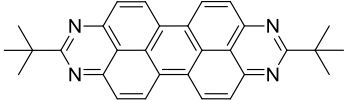
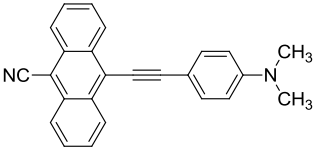
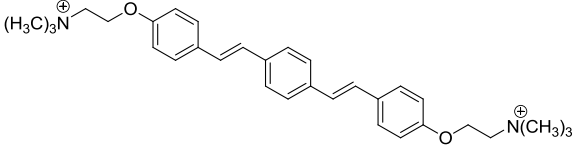
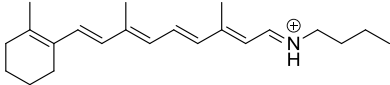
| dye | Structure | environment | E_{ex} (eV) | % H \rightarrow L | Ref. |
|-----|-------------------------------------------------------------------------------------|-------------|----------------------|---------------------|------|
| 1 |  | pentanes | 2.50 | 100.0 | 53 |
| 2 |  | gas phase | 1.82 | 95.3 | 54 |
| 3 |  | gas phase | 1.88 | 91.9 | 54 |
| 4 |  | thin film | 3.46 | 97.5 | 55 |
| 5 |  | toluene | 2.87 | 95.7 | 56 |
| 6 |  | thin film | 2.59 | 99.5 | 57 |
| 7 |  | thin film | 3.55 | 99.6 | 58 |
| 8 |  | gas phase | 2.01 | 95.2 | 59 |

Figure 1a. Test set, molecules **1** through **8**: chemical structure, absorption maximum measured in the specified environment, and TD-B3LYP HOMO \rightarrow LUMO character of the lowest singlet excited state.

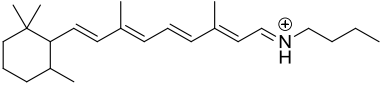
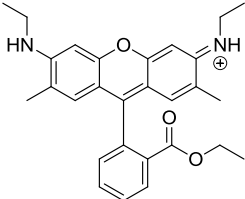
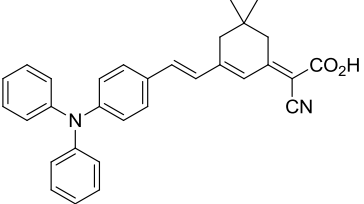
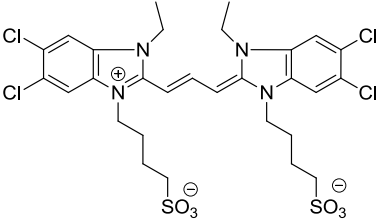
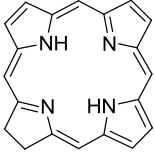
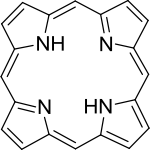
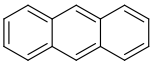
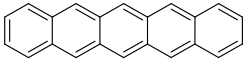
| dye | Structure | environment | E_{ex} (eV) | % H \rightarrow L | ref. |
|-----|-------------------------------------------------------------------------------------|------------------|----------------------|---------------------|------|
| 9 |  | gas phase | 2.36 | 99.7 | 59 |
| 10 |  | thin film | 2.26 | 98.0 | 60 |
| 11 |  | thin film | 2.58 | 98.6 | 61 |
| 12 |  | thin film | 2.11 | 74.6 | 62 |
| 13 |  | benzene | 1.94 | 72.1 | 63 |
| 14 |  | gas phase | 2.01 | 57.0 | 64 |
| 15 |  | trichlorobenzene | 3.21 | 98.0 | 65 |
| 16 |  | trichlorobenzene | 2.06 | 100.0 | 65 |

Figure 1b. Test set, molecules **9** through **16**: chemical structure, absorption maximum measured in the specified environment, and TD-B3LYP HOMO \rightarrow LUMO character of the lowest singlet excited state.

III. Computational methods

All geometries were optimized at the B3LYP/6-31G* level in the gas phase. TDDFT and Δ SCF excitation energies were computed in the 6-311+G* basis set with an array of exchange-correlation functionals. An SRSC pseudopotential was employed for Zn⁶⁶. The functionals were chosen because of their widespread use, and the hybrid functionals intentionally represent a wide variation in the fraction of exact (Hartree-Fock) exchange. The Δ SCF calculations include two additional M06 functionals⁶⁷ for which TDDFT excitation energies were unavailable. An additional functional consists of 60% PBE exchange and 40% Hartree-Fock exchange with PBE correlation and will be denoted PBE4.

The Δ SCF procedure was carried out as follows. Starting with the molecular orbital coefficients of the ground state as an initial guess, the Kohn-Sham equations were solved using a modified SCF procedure in which the lowest $N - 1$ orbitals and the $(N + 1)^{\text{th}}$ orbital were occupied at each update of the density matrix. The shifting of orbital energies during this procedure occasionally caused the density to collapse to the ground state. In these cases, the maximum overlap method⁴² provided a way to retain the target configuration through convergence.

The non-Aufbau electronic state obtained from this procedure is not a spin eigenfunction. To obtain the energy of the singlet excited state, we use the common spin purification formula³⁸

$$E_S = 2E_{\uparrow\downarrow} - E_{\uparrow\uparrow}$$

Both the spin-mixed ($\uparrow\downarrow$) and spin-pure energies are of interest, so we include both in our analysis. All computations were performed with a modified version of the Q-Chem 3.2 software package⁶⁸.

IV. Results

Deviations of computed TDDFT and Δ SCF vertical excitation energies from experiment are presented in Table 1, with a more detailed description of the PBE0 results in Table 2. Typical mean absolute errors (MAE) in TDDFT excitation energies are 0.3 eV, with B3LYP and PBE0 outperforming their counterparts with greater or lesser exact exchange. The magnitude of these deviations is in line with that observed in previous TDDFT benchmarking studies^{22,69}.

For Δ SCF with spin purification, the results parallel the TDDFT results quite closely for all functionals: B3LYP and PBE0 perform best, with similar MAE and RMSD to those of the corresponding functionals in the TDDFT approach. This similarity suggests an argument in favor of applying the spin purification procedure. In keeping with Becke's assertion that the fraction of exact exchange reflects the independent-particle character of the system⁷⁰, the appropriate fraction of exact exchange in Kohn-Sham DFT should be characteristic of the system, not of the method (TDDFT, Δ SCF, or another approach) chosen to compute excitation energies. Of course, it is also convenient from a practical standpoint that TDDFT and spin-purified Δ SCF perform similarly for the same functionals.

The energy of the mixed state in Δ SCF systematically underestimates experimental energies when the employed functional possesses a conventional fraction of exact exchange (20-30%). Functionals with twice as much exact exchange (BH&H and M06-2X) give mixed states that are more accurate, performing comparably to the best functionals for TDDFT excitation energies. The satisfactory performance of spin-contaminated Δ SCF with a larger fraction of exact exchange can be interpreted as a convenient cancellation of errors. The energy of the mixed state underestimates the singlet energy by half the singlet-triplet splitting. The addition of surplus exact exchange systematically increases the singlet-triplet gap. Therefore, the energy of the mixed state tends to increase with increasing exact exchange. At least on average, one can thus raise the fraction of exact exchange such that the energy of the mixed state with surplus exact exchange matches the energy of the

pure singlet with the original functional. Functionals with roughly 50% exact exchange achieve this cancellation in our test set.

| Functional | Mean Error | | | MAE | | | RMSD | | |
|-------------------|------------|-----------------------------------|----------------------------------|-------|-----------------------------------|----------------------------------|-------|-----------------------------------|----------------------------------|
| | TDDFT | $\Delta\text{SCF}_{\text{mixed}}$ | $\Delta\text{SCF}_{\text{pure}}$ | TDDFT | $\Delta\text{SCF}_{\text{mixed}}$ | $\Delta\text{SCF}_{\text{pure}}$ | TDDFT | $\Delta\text{SCF}_{\text{mixed}}$ | $\Delta\text{SCF}_{\text{pure}}$ |
| PBE | -0.23 | -0.72 | -0.56 | 0.39 | 0.72 | 0.58 | 0.46 | 0.81 | 0.66 |
| B3LYP | 0.08 | -0.47 | -0.16 | 0.27 | 0.49 | 0.25 | 0.32 | 0.57 | 0.32 |
| PBE0 | 0.15 | -0.42 | -0.05 | 0.27 | 0.45 | 0.21 | 0.32 | 0.52 | 0.28 |
| LR- ω PBE0 | 0.23 | -0.26 | 0.24 | 0.27 | 0.32 | 0.26 | 0.33 | 0.38 | 0.32 |
| PBE4 | 0.28 | -0.26 | 0.26 | 0.31 | 0.33 | 0.30 | 0.38 | 0.38 | 0.37 |
| BH&H | 0.33 | -0.14 | 0.45 | 0.35 | 0.27 | 0.45 | 0.42 | 0.31 | 0.50 |
| M06-2X | | -0.08 | 0.41 | | 0.27 | 0.42 | | 0.30 | 0.48 |
| M06-HF | | 0.52 | 1.47 | | 0.52 | 1.47 | | 0.74 | 1.69 |

Table 1: Test set statistics for the three different excited state methods. All values are in eV.

The functional LR- ω PBE0 ($\omega = 0.1 \text{ bohr}^{-1}$, $c_{\text{HF}} = 0.25$) was included in our study to assess the performance of long-range corrected density functionals. Given that these functionals are optimized (in part) to give accurate TDDFT vertical excitation energies³¹, it is somewhat surprising to note that LR- ω PBE0 performs best neither for TDDFT nor ΔSCF . We suspect this arises from the fact that these excited states are bright, which selects against the charge transfer excitations (which tend to be dark) for which LR- ω PBE0 would outperform all other functionals.

It is important to note that, while ΔSCF and TDDFT have statistically similar accuracy for the singlet states, it does not follow that ΔSCF and TDDFT predict similar results for a given molecule. For example, as illustrated in Table 2, the ΔSCF and TDDFT vertical excitation energies with PBE0 can often differ by as much as 0.6 eV for the same molecule. These fluctuations cancel out, on average, and the MAE of ΔSCF and TDDFT excitation energies differ by only 0.06 eV over the whole set. Further, the $\langle S^2 \rangle$ values from the figure clearly justify the use of spin purification for these states.

| Molecule | Exp. | TDDFT | $\Delta\text{SCF}_{\text{Mixed}}$ | Mixed $\langle S^2 \rangle$ | $\Delta\text{SCF}_{\text{Pure}}$ | Triplet $\langle S^2 \rangle$ |
|----------|------|-------|-----------------------------------|-----------------------------|----------------------------------|-------------------------------|
| 1 | 2.50 | 2.25 | 1.64 | 1.015 | 2.08 | 2.088 |
| 2 | 1.82 | 2.08 | 1.55 | 1.014 | 1.91 | 2.021 |

| | | | | | | |
|----|------|------|------|-------|------|-------|
| 3 | 1.88 | 2.08 | 1.54 | 1.029 | 1.96 | 2.047 |
| 4 | 3.46 | 3.40 | 3.16 | 1.017 | 3.37 | 2.017 |
| 5 | 2.87 | 2.96 | 2.34 | 1.009 | 2.84 | 2.067 |
| 6 | 2.59 | 2.51 | 2.01 | 1.009 | 2.47 | 2.027 |
| 7 | 3.55 | 3.15 | 2.61 | 1.008 | 3.00 | 2.034 |
| 8 | 2.01 | 2.42 | 1.41 | 1.062 | 1.72 | 2.023 |
| 9 | 2.36 | 2.71 | 1.68 | 1.048 | 2.05 | 2.020 |
| 10 | 2.26 | 2.89 | 2.08 | 1.056 | 2.28 | 2.014 |
| 11 | 2.58 | 2.49 | 2.05 | 1.024 | 2.38 | 2.022 |
| 12 | 2.11 | 2.75 | 2.06 | 1.055 | 2.16 | 2.009 |
| 13 | 1.94 | 2.29 | 1.93 | 1.046 | 2.21 | 2.015 |
| 14 | 2.01 | 2.30 | 2.26 | 1.019 | 2.63 | 2.050 |
| 15 | 3.21 | 3.29 | 2.71 | 1.008 | 3.32 | 2.024 |
| 16 | 2.06 | 1.96 | 1.49 | 1.009 | 2.02 | 2.037 |

Table 2: PBE0 energies and spin multiplicities for the test set. All energies are in eV.

V. Discussion and Analysis

Based on the results of the previous section, it would appear that Δ SCF and TDDFT predict vertical excitation energies of organic dyes with approximately equal accuracy, with Δ SCF being perhaps slightly better when the best functionals are used. If we combine this information with existing evidence that Δ SCF is effective for Rydberg states³⁹, core excitations^{42, 48}, solvent effects⁷¹, and double excitations⁷² we are led to the pragmatic conclusion that Δ SCF is a powerful tool for excited states. Is this just a coincidence? Or are there deeper reasons why Δ SCF is so effective? To answer these questions, we must unpack the approximations inherent to TDDFT and Δ SCF calculations.

A. Linear Response TDDFT

According to the Runge-Gross theorem¹⁸, there exists a one-to-one correspondence between the time dependent density, $\rho(x,t)$, and the time dependent potential, $v_{ext}(x,t)$. Thus, one can formulate an equation of motion that involves $\rho(x,t)$ alone, where x contains spacial and spin coordinates, $x \equiv (\mathbf{r}, \sigma)$:

$$\dot{\rho}(x,t) = F[\rho]$$

where F must be defined. In the Kohn-Sham (KS) formulation of TDDFT, the exact density is constructed out of a set of time-dependent orbitals,

$$\rho(x,t) = \sum_{i=1}^{occ} |\phi_i(x,t)|^2.$$

The KS orbitals, in turn, obey a Schrödinger equation

$$i\dot{\phi}_i(x,t) = \left(-\frac{1}{2}\nabla^2 + v_{ext}(x,t) + \int \frac{\rho(x',t)}{|\mathbf{r}-\mathbf{r}'|} dx' + v_{xc}[\rho](x,t) \right) \phi_i(x,t) \equiv \hat{H}_{KS} \phi_i(x,t)$$

where the external potential, v_{ext} , is augmented by the classical Coulomb potential and the unknown exchange correlation potential, $v_{xc}[\rho]$. According to the Runge-Gross theorem¹⁸, v_{xc} exists and is uniquely determined by the density. Thus, $v_{xc}(x,t)$ is a functional of $\rho(x,t)$, justifying the notation $v_{xc}[\rho]$. The major challenge in TDDFT is determining accurate approximations to the exchange correlation potential^{32, 73-79}.

Now, in principle $v_{xc}(x,t)$ can depend on $\rho(x',t')$ at any point \mathbf{r}' in space and any time t' in the past. In practice, it is very difficult to obtain approximations to $v_{xc}(x,t)$ that obey causality and possess all the proper time translation invariance properties^{80, 81}. As a result, nearly all existing approximations to $v_{xc}(x,t)$ are strictly local in time – $v_{xc}(x,t)$ depends only on the density of the system at time t . This approximation is known as the adiabatic approximation (AA). It greatly simplifies the construction of approximate potentials and from this point forward, our manipulations will assume the AA.

In order to obtain excitation energies from TDDFT, the most common route is to employ linear response (LR)^{21, 82}. Here, one first performs a traditional DFT calculation to obtain the ground state density. Next, one subjects the system to a small time-dependent external potential, $\delta v(x,t)$, that induces a small change in the density, $\delta\rho(x,t)$, and a corresponding small change in the exchange correlation potential, $\delta v_{xc}(x,t)$. One then uses the time-dependent KS equations to connect the different linear variations and computes excitation energies as the poles in the frequency dependent response function¹⁹. The resulting equations can be cast as a generalized eigenvalue problem:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}_M \\ \mathbf{Y}_M \end{pmatrix} = \omega_M \begin{pmatrix} \mathbf{X}_M \\ \mathbf{Y}_M \end{pmatrix}.$$

Here, \mathbf{X} and \mathbf{Y} are vectors of length (occupied)x(unoccupied) that represent the density response and the \mathbf{A} and \mathbf{B} matrices are given by

$$\begin{aligned} A_{ia;jb} &\equiv (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + B_{ia;jb} \\ B_{ia;jb} &\equiv \int \phi_i(x_1) \phi_j(x_2) \left(\frac{1}{r_{12}} + \frac{\delta v_{xc}(x_1)}{\delta \rho(x_2)} \right) \phi_a(x_1) \phi_b(x_2) dx_1 dx_2 \end{aligned}$$

where i,j (a,b) index occupied (unoccupied) orbitals. In principle, the eigenvalues, ω_M , are the exact (within the AA) transition energies between the ground electronic state and the various excited states: $\omega_M = E_i - E_0$. Meanwhile the eigenvectors, \mathbf{X}_M and \mathbf{Y}_M , contain information about the intensity of the transition.

B. Δ SCF Densities

Now, because quantum mechanics is linear, linear response in Hilbert space starting from any two different reference states will give equivalent transition energies. However, since most density functionals have a *non-linear* dependence on the density, the excitation energy obtained from LR-TDDFT depends on the reference state one chooses. Thus, for example, in certain cases it is advantageous to choose a reference state with a different spin multiplicity⁸³⁻⁸⁷.

Instead of sifting for excitations in the density response, an alternative approach is to search directly for the excited state density in TDDFT. Here, one recognizes that every eigenstate, Ψ_i , of the Hamiltonian is a stationary state. Hence, $\rho_i(x,t)$ is constant in time and

$$\dot{\rho}(x,t) = F[\rho] = 0. \quad \text{Eq. 1}$$

Within the KS formulation, the density is invariant if each KS orbital changes by a phase factor

$$\phi_j(x,t) = e^{-i\varepsilon_j t} \phi_j(x)$$

so that

$$i\dot{\phi}_j(x,t) = \varepsilon_j \phi_j(x,t)$$

$$\Rightarrow \hat{H}_{KS} \phi_j(x,t) = \varepsilon_j \phi_j(x,t)$$

Thus, the equations obeyed by stationary densities within TDDFT are *exactly the same as the SCF equations for traditional KS-DFT*. Viewed in this light, it is clear that Δ SCF states – which solve the traditional KS-DFT equations with non-Aufbau occupation of the orbitals – have a rigorous meaning in TDDFT: they correspond to stationary densities of the interacting system. Further, these stationary densities have a clear connection with the excited states of the molecule. This connection between TDDFT and Δ SCF comes tantalizingly close to rigorously justifying the use of Δ SCF-DFT for excited states: Δ SCF-DFT gives stationary densities that are exact within the AA.

Before moving on, we note how the AA is expected to influence **Eq. 1**. The above derivation is so concise that it almost seems as if no approximation has been made at all. However, we note that in **Eq. 1** the density is constant at all times. Thus, the system must have been *prepared* in the desired eigenstate. This assumption violates the terms of the Runge-Gross theorem, which only applies to different densities that originate from the same state (usually assumed to be the ground state at $t=-\infty$). Only within the AA can different initial densities be justified⁸⁸.

The Δ SCF scheme implied by **Eq. 1** is exact within the AA because the system has no memory of how it was prepared. If our functional has memory, **Eq. 1** states that $F[\rho_t(x,t)]=0$ when applied to a particular density, $\rho_t(x,t)$, that is constant in time. To put it another way, **Eq. 1** only depends on the zero frequency ($\omega=0$) part of F . In many ways, this is the ideal scenario within the AA. Any adiabatic functional is time-local and thus frequency independent. However, it is trivial for a frequency independent kernel to be correct at one frequency (i.e. $\omega=0$) and so one suspects that the AA could be well-suited to the Δ SCF approach of **Eq. 1**. In contrast, within linear response one relies on the ω -independent kernel being a good approximation to the true kernel at every excitation energy. It is clear that, except in special cases, the latter condition cannot hold and thus LR-TDDFT would seem more

limited by the AA.

C. Δ SCF Energy Expressions

Δ SCF gives us a rigorous route to obtain a stationary density in TDDFT. But how should we associate an energy with this density? Since there is no Hohenberg-Kohn theorem for excited states⁸⁹, there can be no single density functional that gives the correct energy for all excited states. Instead, one must tackle the problem of defining different functionals for different excited states^{34, 36} or else make the functional depend on more than just the density^{90, 91}. The simplest procedure is to evaluate the ground state energy expression using the Δ SCF orbitals

$$E^{ex} = E[\phi_i^{ex}(x)]. \quad \text{Eq. 2}$$

and this is the “mixed” Δ SCF energy used above. It should be noted that this energy expression is *not* a functional of the density, but rather an explicit functional of the orbitals. If we used the excited state density (rather than the orbitals), we would need to derive a corresponding set of KS orbitals to compute the kinetic energy, $T_s[\rho]$. By definition, these orbitals would be obtained by constrained search⁹², and the resulting orbitals would give a different energy than the excited state orbitals. The orbital dependence lends some measure of robustness to the Δ SCF predictions.

In practice, it is necessary to correct **Eq. 2** because **Eq. 1** is necessary but not sufficient: *not all stationary densities correspond to excited states* even though all excited states give stationary densities. To see this, suppose you have a state that is a linear combination of two eigenstates:

$$|\Psi\rangle \propto |\Psi_1\rangle + |\Psi_2\rangle.$$

Then the time evolving wavefunction is

$$|\Psi(t)\rangle \propto e^{-iE_1 t} |\Psi_1\rangle + e^{-iE_2 t} |\Psi_2\rangle$$

and the density is

$$\begin{aligned}\rho(\mathbf{r}) &\equiv \langle \Psi(t) | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi(t) \rangle \\ &\propto \langle \Psi_1 | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi_1 \rangle + \langle \Psi_2 | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi_2 \rangle + \\ &\quad e^{-i\Delta Et} \langle \Psi_1 | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi_2 \rangle + e^{i\Delta Et} \langle \Psi_2 | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi_1 \rangle\end{aligned}$$

where $\Delta E = E_1 - E_2$. If ΔE is not zero we do not have an eigenstate and in general the density is not stationary. However, suppose the transition density between the two excited states is zero everywhere. That is, suppose that

$$\rho_{12} \equiv \langle \Psi_1 | \delta(\mathbf{r} - \hat{\mathbf{r}}) | \Psi_2 \rangle = 0.$$

In this situation, the oscillating piece of the density is zero and the density is stationary even though the wavefunction is not an eigenstate. Thus it is in principle possible for **Eq. 1** to locate densities that do not correspond to eigenstates.

How does this affect Δ SCF in practice? Note that ρ_{12} is only zero if no one particle potential can drive the 1 \rightarrow 2 transition. The most common situation where this occurs is if the eigenstates have different total spin (e.g. the transition density for singlet-triplet transitions is always rigorously zero). Thus, any linear combination

$$|\Psi\rangle \propto c_S |\Psi_S\rangle + c_T |\Psi_T\rangle$$

of a singlet eigenstate (Ψ_S) and triplet eigenstate (Ψ_T) will have a stationary density and could lead to spurious Δ SCF solutions. In practice, this indeterminacy leads to spin contamination of the KS eigenstates in the following way. Suppose we have a singlet ground state and we're interested in the HOMO \rightarrow LUMO transition. The singlet and one of the triplet states require two determinants:

$$\begin{aligned}|\Psi_S\rangle &\propto \left| \dots \psi_{HOMO}^\uparrow \psi_{LUMO}^\downarrow \right\rangle - \left| \dots \psi_{HOMO}^\downarrow \psi_{LUMO}^\uparrow \right\rangle \\ |\Psi_T\rangle &\propto \left| \dots \psi_{HOMO}^\uparrow \psi_{LUMO}^\downarrow \right\rangle + \left| \dots \psi_{HOMO}^\downarrow \psi_{LUMO}^\uparrow \right\rangle\end{aligned}$$

but KS-DFT biases us toward states that are well-represented by a single determinant⁹³. Thus, rather than obtaining a pure singlet or a pure triplet we obtain a broken symmetry solution like

$$|\uparrow\downarrow\rangle = |\dots\psi_{HOMO}^{\uparrow}\psi_{LUMO}^{\downarrow}\rangle \propto |\Psi_S\rangle + |\Psi_T\rangle.$$

When employed in **Eq. 2**, this mixed spin state gives an energy somewhere between the singlet and triplet excitation energies. Thus, we are led to the purification formula

$$E_S = 2E_{\uparrow\downarrow} - E_{\uparrow\uparrow}.$$

This scheme has a long history in predicting exchange couplings^{94,95}, and the results above suggest that it predicts singlet HOMO→LUMO transitions in line with intuition. We thus see that the projection of excited state energies arises directly from the indeterminacy of the Δ SCF equations in the presence of spin degeneracy. We can also explicitly solve the case of three unpaired electrons to obtain two doublet energies

$$E_D^{\pm} = \frac{1}{2}(E_{\downarrow\uparrow\uparrow} + E_{\uparrow\downarrow\uparrow} + E_{\uparrow\uparrow\downarrow} - E_{\uparrow\uparrow\uparrow}) \\ \pm \sqrt{\frac{1}{2}(E_{\downarrow\uparrow\uparrow} - E_{\uparrow\uparrow\downarrow})^2 + \frac{1}{2}(E_{\uparrow\downarrow\uparrow} - E_{\uparrow\uparrow\downarrow})^2 + \frac{1}{2}(E_{\downarrow\uparrow\uparrow} - E_{\uparrow\downarrow\uparrow})^2}.$$

The projection scheme can be further generalized to an arbitrary number of unpaired electrons⁹⁶, although the resulting equations are overdetermined⁹⁷.

A more sophisticated scheme for dealing with spin would involve introducing a multideterminant reference state into the KS calculation. This is the idea behind the ROKS and REKS methods⁹⁸⁻¹⁰⁰. Techniques of this sort are certainly more elegant than *post facto* energy projection, but they also fundamentally change the equations being solved. We will thus postpone examination of these approaches to a later publication.

VI. Conclusions

We have revisited the approximations that define the Δ SCF approach to excited states in DFT. The performance of the method was assessed by comparing Δ SCF excitation energies for several organic dyes with TDDFT and experimental excitation energies. We found that deviations of spin-

purified Δ SCF excitation energies from experimental values are comparable to those of TDDFT for all functionals tested. Spin-contaminated Δ SCF energies were found to require more exact exchange to achieve similar accuracy. As a partial justification of these results, we demonstrated that Δ SCF densities are precisely the stationary densities of TDDFT within the adiabatic approximation, and the necessity of purifying the energies arises from the indeterminacy of the stationary equations with respect to different spin states.

While this study establishes some expectations regarding the range of applicability of the Δ SCF approach, there remain several unanswered questions to be explored in future work. We have shown that Δ SCF performs well for HOMO \rightarrow LUMO excitations, but it remains to be determined how it performs for higher energy excitations. It will also be interesting to compare and contrast the performance of a spin-adapted approach such as ROKS with the spin purification approach presented here.

Several possible extensions and applications of Δ SCF methodology also deserve attention. Δ SCF gradients are readily available from ground-state SCF codes. Therefore, if the excited state potential energy surface (PES) obtained from Δ SCF is reasonably parallel to the true Born-Oppenheimer PES, Δ SCF could provide an efficient alternative to TDDFT and other wavefunction based methods for geometry optimization and molecular dynamics on excited states¹⁰¹⁻¹⁰³. Furthermore, Δ SCF also provides an affordable route to the excited state Hessian, from which one could construct vibrationally resolved absorption and emission spectra^{104, 105}. It is also a simple matter to incorporate solvation effects in Δ SCF^{71, 106}. Together, these features could provide an affordable way to calculate full absorption and emission spectra in different environments for large molecules like the phthalocyanines. It will be intriguing to see if the robustness of Δ SCF for low-lying excited states extends across a wide enough range of excited state properties to make these simulations worthwhile.

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