Analytical Excited State Gradients for Time-dependent Density-functional Theory plus Tight-binding (TDDFT+TB)

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Understanding photoluminescent mechanisms has become essential for photocatalytic, biological, and electronic applications. Unfortunately, analyzing excited state potential energy surfaces (PES) in large systems is computationally expensive, and hence limited with electronic structure methods such as TDDFT. Inspired by the sTDDFT and sTDA methods, time dependent density functional theory plus tight binding (TDDFT+TB) has been shown to reproduce linear response TDDFT results much faster than TDDFT, particularly in large nanoparticles. For photochemical processes, however, methods must go beyond the calculation of excitation energies. Herein, this work outlines an analytical approach to the derivative of the vertical excitation energy in TDDFT+TB for more efficient excited state PES exploration. The gradient derivation is based on the Z-vector method, which utilizes an auxiliary Lagrangian to characterize the excitation energy. The gradient is obtained when the derivatives of the Fock matrix, the coupling matrix, and the overlap matrix are all plugged into the auxiliary Lagrangian, and the Lagrange multipliers are solved. This article outlines the derivation of the analytical gradient, discusses the implementation in Amsterdam Modelling Suite (AMS), and provides proof of concept by analyzing the emission energy and optimized excited state geometry calculated by TDDFT and TDDFT+TB for small organic molecules and nanoclusters.

I. INTRODUCTION

Elucidating photophysical and photochemical processes requires some knowledge of excited state potential energy surfaces (PES). PES describe the energy and behavior of a molecule at a particular geometry, and therefore are useful for obtaining physical insights such as equilibrium structures and reaction dynamics.[1] In particular, analytical gradients and Hessians are used to understand the topology and stationary points of the system. Stationary points, such as minima or first order saddle points, are critical in obtaining physical insights, and for excited state surfaces, these points lead to excited state structures, emission and excitation energies, and more. It can therefore be deduced that understanding stationary points in excited state PES leads to a range of applications in photochemistry, catalysis, biology, and electronics.[2–6] Photoluminescent (PL) mechanisms in small atomically precise nanoclusters, in particular, has gained large scientific interest as small nanoclusters have discrete energy gaps, promoting radiative relaxation, opposed to materials in which the lack of energy gap between bands makes PL improbable.[7,8] As clusters have tunable structure-property relationships with respect to different charge states, ligand structures, heteroatom dopants, and more,[9–11] understanding the stationary points in the excited state PES of nanoclusters leads to highly luminescent materials, thus advancing fields in bioimaging, electronics and more.

One of the most popular quantum mechanical methods used to understand optical and PL properties in molecules and nanoclusters is time-dependent density functional theory (TDDFT).[12–18] Unfortunately, the computational cost of TDDFT increases significantly when properties other than the energy are required, hindering the calculation of excited states on the level of theory and the system size. An example of this is $Au_{14}Cd(S\text{-}Adm)_{12}$, which exhibits a rare dual emission mechanism.[19] TDDFT calculations were used to decipher the two emissive points, but it took longer than 90 days to find and optimize both minima.[14] Targeting the computational bottleneck of TDDFT, methods such as time-dependent density functional tight binding (TDDFTB) have been used to obtain excited state properties.[20–22] Unfortunately, TDDFTB has shown large optical absorption red shifts (0.60 - 1.0 eV) in noble metal nanoclusters and nanowires as compared to TDDFT,[23,24] which can be traced back to limited parameterization and the minimal basis set of the method.[25] It is therefore critical to develop inexpensive methods that maintain the accuracy of TDDFT for excited state PES exploration.

Inspired by the sTDDFT and sTDA methods by Stefan Grimme, time dependent density functional theory plus tight binding (TDDFT+TB) was introduced in 2016.[25] TDDFT+TB has shown to reproduce linear response TDDFT results up to 100× faster than TDDFT in large plasmonic NCs, keeping electronic accuracy within 0.10 eV of TDDFT.[24] This method was created for pure exchange correlation (XC) functionals, whereas sTDDFT and sTDA can be used with hybrid functionals. This is not an issue, however, as lower classes of XC functionals are traditionally used to calculate excited state properties in large chemical systems due to the computational cost. TDDFT+TB uses a DFT ground state reference and targets the computationally expensive coupling matrix in TDDFT by applying a first order monopole approximation to the transition density in the linear response formulation.[25] Since the two-electron integrals are the computational bottleneck of classic TDDFT calculations, this approximation drastically improves the computational time. While TDDFT+TB has shown incredible accuracy with respect to TDDFT by maintaining the accurate DFT ground state geometry, the method has only been used to cal-

culate excitation energies. Herein, the purpose of this paper is three-fold. Initially, using the Z-vector method, the analytical excited state gradients of TDDFT+TB are derived. Second, the implementation of the gradients into ADF for excited state geometry optimizations will be discussed. Finally, the paper will provide proof of concept by comparing emission energy and optimized excited state geometries between TDDFT and TDDFT+TB in small organic molecules and nanoclusters.

II. THEORY

In order to obtain excited state properties other than energy, such as local minima and first order saddle points on excited state surfaces, the analytical excited state gradients must be derived. Following the Lagrangian based approach, introduced by Furche and Ahlrichs,[26] the TDDFT+TB analytical gradients are derived by taking the derivative of excitation energy with respect to a real perturbation. The full derivation can be split into four main parts: defining an energy functional that is equivalent to the vertical excitation energy of that system, setting up an energy functional that is stationary with respect to the molecular orbital coefficients, solving the Lagrange multipliers after the constraints have been defined, and taking the full derivative of each term in the energy functional to obtain the analytical gradient with respect to the position of the nuclear coordinates.

The notation used in this paper is as follows. A molecular orbital will be denoted by the indices a, b, c, ... if it is unoccupied in the ground electronic state, and i, j, k, ... if it is occupied in the ground electronic state. Further, p, q, r, s, ... denotes a general molecular orbital; the derivation will later be separated into cases in which the general MO is occupied or unoccupied. Atomic basis functions will be denoted by the indices μ, ν, κ, ... which belong to a specific atom denoted by the capital letters A, B, C, ...

A. Define an Energy Functional

The first step in calculating the derivative of the excitation energy with respect to the nuclear coordinates is to obtain an expression for the TDDFT+TB excitation energy. TDDFT+TB applies a first order monopole approximation to the transition density in the linear response formulation of TDDFT.[25] With this approximation, the two-electron integrals are no longer calculated, and $\phi_i(r)\phi_a(r) \approx \sum_A q_{ia,A}\zeta_A(r)$ where $\zeta_A(r)$ is a spherically symmetric function centered on atom A, and $q_{ia,A}$ is defined in equation (1)

$$q_{ia,A} = \sum_{\mu \in A} C'_{\mu i} C'_{\mu a} \tag{1}$$

where $\mathbf{C'} = \mathbf{S^{1/2}C}$, $\mathbf{C}$ is the molecular orbital coefficient matrix, and $\mathbf{S}$ is the overlap matrix. Using the variational approach, the vertical excitation energy of TDDFT+TB is expressed in equation (2), where the excited state energies (Ω) are stationary points of the functional

$$\begin{aligned} G[X,Y,\Omega] = \frac{1}{2}\left\langle \begin{matrix} X+Y \\ X-Y \end{matrix} \middle| \Lambda \middle| \begin{matrix} X+Y \\ X-Y \end{matrix} \right\rangle \\ - \frac{1}{2}\Omega\left(\left\langle \begin{matrix} X+Y \\ X-Y \end{matrix} \middle| \Delta \middle| \begin{matrix} X+Y \\ X-Y \end{matrix} \right\rangle - 2 \right) \end{aligned} \tag{2}$$

and

$$\Lambda = \begin{pmatrix} A+B & 0 \\ 0 & A-B \end{pmatrix} \text{ and } \Delta = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

X and Y are the transition density vectors of single particle transitions defined on the Hilbert space $N_{virt} \times N_{occ} \bigoplus N_{occ} \times N_{virt}$, where N_{occ} is the number of occupied molecular orbitals and N_{virt} is the number of virtual molecular orbitals. A and B are called rotational Hessians; they are positive definite matricies and the matrix representation is shown in equations (3) and (4), where ε_p corresponds to the energy of the molecular orbital, p.

$$(A+B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 4K^{S/T}_{iajb} \tag{3}$$

$$(A-B)_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} \tag{4}$$

The coupling matrix is written in equation (5) and (6) such that γ_{AB} is a function of the internuclear distance and a chemical hardness parameter, which signifies the coulombic interaction between two point charges, and W_A is the spin coupling constant, also referred to as magnetic Hubbard parameter.[25]

$$K^S_{iajb} = \sum_{AB} q_{ia,A}\gamma_{AB}q_{jb,B} \tag{5}$$

$$K^T_{iajb} = \sum_{A} q_{ia,A}W_A q_{jb,A} \tag{6}$$

It is important to deduce that the chemical hardness is not calculated with DFTB parameterization, but simply a semi-empirical algorithm relating hardness to atomic number as described by Ghosh and Islam.[27] The analytical gradients for TDDFT+TB are currently only implemented for systems with a singlet ground state and therefore all spin indices are dropped for simplicity.

B. Constrained Optimization Problem

If the derivative of equation (2) is simply taken as is, the calculation would be quite costly. The reason for this is that Λ depends on the molecular orbitals (MO) of the method. Recall that molecular orbitals are a combination of atomic contributions. This means that the derivation would require an implicit calculation of the derivative of the molecular orbital coefficients, which would add a cost increase by the number of nuclear degrees of freedom in a molecule.[26] It is possible to circumvent this issue by using a Lagrangian based method, often referred as the 'Z vector method' in quantum

chemistry.[28] This method has been used to derive the analytical gradients for several methods including TDDFT[26] and TDDFTB.[29] The Z vector method uses Lagrange multipliers to solve a constrained optimization problem. In other words, this method applies an equality constraint to the function of interest. For TDDFT+TB, the constraint restricts the molecular orbital transformations so that they are invariant with respect to an external perturbation. To do this, a new auxiliary functional is defined as seen in equation (7).

$$\begin{aligned} L[X,Y,\Omega,C,Z,W] &= G[X,Y,\Omega] \\ &+ \sum_{ia} Z_{ia}F_{ia} - \sum_{pq,p\leq q} W_{pq}(S_{pq}-\delta_{pq}) \end{aligned} \tag{7}$$

The functional, L, represents a fully variational expression for the excitation energy under any external perturbation. To remove the implicit dependence of the MO coefficients by restricting the transformation of the molecular orbital coefficients, Lagrange multipliers W and Z are introduced. To be more explicit, the following restriction criteria is imposed:

$$\frac{\partial L}{\partial Z_{ia}} = F_{ia} = 0 \tag{8}$$

$$\frac{\partial L}{\partial W_{pq}} = S_{pq} - \delta_{pq} = 0 \tag{9}$$

The MOs are constrained to be orthonormal and satisfy the ground state DFT equations. This leads to equation (10), which will then be used to determine Z and W.

$$\frac{\partial L}{\partial C_{\mu p}} = 0 \tag{10}$$

As all physical properties are invariant under unitary transformations the diagonal elements of the rotational Hessians are replaced by equations (11) and (12).[26]

$$(A+B)_{ia\,jb} = F_{ab}\delta_{ij} - F_{ij}\delta_{ab} + 4K^{S/T}_{ia\,jb} \tag{11}$$

$$(A-B)_{ia\,jb} = F_{ab}\delta_{ij} - F_{ij}\delta_{ab} \tag{12}$$

where

$$F_{pq} = h_{pq} + \sum_i [(pq|ii)] + V^{XC}_{pq}$$

such that h_{pq} and $V^{\mathrm{XC}}_{\mathrm{pq}}$ have the usual form, and $(pq|ii)$ can be seen in equation (13).[26,30]

$$\int\int dr^3 dr'^3 \phi_p(r)\phi_i(r')\frac{1}{|r-r'|}\phi_q(r)\phi_i(r') \tag{13}$$

Before the formal derivative of equation (7) is taken, the Lagrange multipliers must be solved with respect to the constraints. To do this, the constraint in equation (10) is expanded, summed over μ and right-multiplied by the coefficient matrix as seen in the following equation.

$$\begin{aligned} &Q_{pq} + \sum_{ia} Z_{ia} \sum_{\mu} \frac{\partial F_{ia}}{\partial C_{\mu p}} C_{\mu q} \\ &= \sum_{rs,r\leq s} W_{rs} \sum_{\mu} \frac{\partial S_{rs}}{\partial C_{\mu p}} C_{\mu q} \end{aligned} \tag{14}$$

The constraint Q_{pq} is defined as the partial derivative of the initial G functional with respect to the molecular orbital coefficients, which has been right-multiplied by the coefficient matrix. This term can be written in terms of the rotational Hessians as seen below.

$$\begin{aligned} &Q_{pq} = \sum_{\mu} \frac{\partial G[X,Y,Z]}{\partial C_{\mu p}} C_{\mu q} = \\ &\sum_{\mu} \frac{1}{2} \left\langle \begin{matrix} X+Y \\ X-Y \end{matrix} \middle| \begin{pmatrix} \frac{\partial (A+B)}{\partial C_{\mu p}} C_{\mu q} & 0 \\ 0 & \frac{\partial (A-B)}{\partial C_{\mu p}} C_{\mu q} \end{pmatrix} \middle| \begin{matrix} X+Y \\ X-Y \end{matrix} \right\rangle \\ &= \frac{1}{2} \sum_{ia}\sum_{jb} (X+Y)_{ia} \sum_{\mu} \frac{\partial (A+B)_{ia\,jb}}{\partial C_{\mu p}} C_{\mu q} (X+Y)_{jb} \\ &+ \frac{1}{2} \sum_{ia}\sum_{jb} (X-Y)_{ia} \sum_{\mu} \frac{\partial (A-B)_{ia\,jb}}{\partial C_{\mu p}} C_{\mu q} (X-Y)_{jb}. \end{aligned} \tag{15}$$

Equations (11) & (12) are then be substituted back into the expression to obtain the expanded form of equation (15) as seen in equation S1. The full derivatives of the Fock matrix (equation S2) and the coupling matrix (equation S3) are then plugged in to obtain equation S4.

To clarify the constraints, cases are attributed to the four different MO transitions: occupied to occupied, virtual to virtual, occupied to virtual, and virtual to occupied. The full derivation can be seen in equations S5 to S11. The definition of the relaxed difference density matrix T (equations (16) - (18)) as well as the linear transformation defined from TDDFT (equation (19)) are then plugged into the equation to simplify the constraints further and obtain equation S12.[26]

$$T_{ab} = \frac{1}{2} \sum_i ((X+Y)_{ia}(X+Y)_{ib} + (X-Y)_{ia}(X-Y)_{ib}) \tag{16}$$

$$T_{ij} = -\frac{1}{2} \sum_a ((X+Y)_{ia}(X+Y)_{ja} + (X-Y)_{ia}(X-Y)_{ja}) \tag{17}$$

$$T_{ia} = T_{ai} = 0 \tag{18}$$

$$H^{+}_{pq}[T] = \sum_{rs} [2(pq|rs) + 2f^{XC}_{pqrs}]T_{rs} \tag{19}$$

Applying symmetries of the coupling matrix then gives the simplified constraints for each case as shown by equations (20)-(23). It is important to note that the expanded versions of case 3 and case 4 can be seen in equations S13 and S14 respectively.

1) p and q are both occupied

$$\begin{aligned} Q_{ij} &= \Omega \sum_a ((X+Y)_{ia}(X-Y)_{ja} + (X-Y)_{ia}(X+Y)_{ja}) \\ &- \sum_a \varepsilon_a ((X+Y)_{ia}(X+Y)_{ja} + (X-Y)_{ia}(X-Y)_{ja}) + H^{+}_{ij}[T] \end{aligned} \tag{20}$$

2) p and q are both virtual

$$\begin{aligned} Q_{ab} =& \Omega \sum_i ((X+Y)_{ia}(X-Y)_{ib} + (X-Y)_{ia}(X+Y)_{ib}) \\ &+ \sum_i \varepsilon_i \left((X+Y)_{ia}(X+Y)_{ib} + (X-Y)_{ia}(X-Y)_{ib}\right) \end{aligned} \tag{21}$$

3) p is occupied and q is virtual

$$Q_{ia} = 2\sum_b (X+Y)_{ib} \sum_{jc} K^{S/T}_{abjc}(X+Y)_{jc} + H^+_{ia}[T] \tag{22}$$

4) p is virtual and q is occupied

$$Q_{ai} = 2\sum_j (X+Y)_{ja} \sum_{kb} K^{S/T}_{jikb}(X+Y)_{kb} \tag{23}$$

The definition of Q, as well as the expanded derivatives in equations S15 and S16 are then plugged into the energy functional to give equation (24). This equation solves the constrained optimization problem.

$$\begin{aligned} &Q_{pq} + \sum_{ia} Z_{ia}(\delta_{pi}\delta_{qa}\varepsilon_a + \delta_{pa}\delta_{iq}\varepsilon_q) + H^+_{pq}[Z] \\ &= \sum_{rs,r\leq s} W_{rs} \sum_\mu (\delta_{pr}\delta_{qs} + \delta_{ps}\delta_{qr}) \end{aligned} \tag{24}$$

C. Solve Lagrange Multipliers

Now that the constraints have been clarified, the next step is to use equation (24) to find Lagrange multipliers, Z and W. Analyzing the definition of W from the functional in equation (7), it is understood that $p \leq q$, and therefore the molecular orbitals increase monotonically in this method. To keep consistent with the implementation of TDDDFT analytical excited state gradients and take advantage of symmetric subroutines, however, a symmetry constraint is enforced such that $W_{ai} = W_{ia}$. This leads to equations (25) and (26) for the occupied to virtual elements in the W matrix.

$$Q_{ia} + Z_{ia}\varepsilon_a + H^+_{ia}[Z] = W_{ia} \tag{25}$$

$$Q_{ai} + Z_{ia}\varepsilon_i = W_{ia} \tag{26}$$

Equation (26) is then subtracted from equation (25) to get rid of W and find an equation for Z.

$$0 = Q_{ia} + Z_{ia}\varepsilon_a + H^+_{ia}[Z] - (Q_{ai} + Z_{ia}\varepsilon_i) \tag{27}$$

$$-(Q_{ia} - Q_{ai}) = (\varepsilon_a - \varepsilon_i)Z_{ia} + H^+_{ia}[Z] \tag{28}$$

$$-R_{ia} = (\varepsilon_a - \varepsilon_i)Z_{ia} + \sum_{jb} H^+_{jb}[Z] \tag{29}$$

Equation (29) results in a system of linear equations that can be solved to obtain vector Z as shown in equation (30),

$$-R_{ia} = \sum_{jb} (A+B)^{TDDFT}_{iajb} Z_{jb} \tag{30}$$

such that equations (31) and (32) are defined below.

$$R_{ia} = Q_{ia} - Q_{ai} \tag{31}$$

$$\sum_{jb} (A+B)^{TDDFT}_{iajb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + 2(ia|jb) + 2f^{XC}_{iajb} \tag{32}$$

With knowledge of Z, cases are applied to equation (24) to find W. The simplified definition for the four different cases are shown in equations (33)-(36), and the derivation can be seen in equations S17 - S20. Note that the unrelaxed difference density matrix is given by P=$T + Z + Z^*$.

1) p and q are both occupied

$$\begin{aligned} &W_{ij} = \\ &\frac{1}{1+\delta_{ij}} (\Omega \sum_a ((X+Y)_{ia}(X-Y)_{ja} + (X-Y)_{ia}(X+Y)_{ja}) \\ &- \sum_a \varepsilon_a ((X+Y)_{ia}(X+Y)_{ja} + (X-Y)_{ia}(X-Y)_{ja}) + H^+_{ij}[P])) \end{aligned} \tag{33}$$

2) p and q are both virtual

$$\begin{aligned} &W_{ab} = \\ &\frac{1}{1+\delta_{ab}} (\Omega \sum_i ((X+Y)_{ia}(X-Y)_{ib} + (X-Y)_{ia}(X+Y)_{ib}) \\ &+ \sum_i \varepsilon_i \left((X+Y)_{ia}(X+Y)_{ib} + (X-Y)_{ia}(X-Y)_{ib}\right)) \end{aligned} \tag{34}$$

3) p is occupied and q is virtual

$$W_{ia} = 2\sum_j (X+Y)_{ja} \sum_{kb} K^{S/T}_{jikb}(X+Y)_{kb} + \sum_i \varepsilon_i Z_{ia} \tag{35}$$

4) p is virtual and q is occupied

$$W_{ai} = W_{ia} \tag{36}$$

D. Full Derivative

After calculating the Lagrange multipliers, the derivative of the auxiliary functional, L, is taken with respect to the position of the nuclear coordinates.

$$\frac{dL^{S/T}}{dR_A} = \frac{dG^{S/T}}{dR_A} + \sum_{ia} Z_{ia}\frac{dF_{ia}}{dR_A} - \sum_{pq,p\leq q} W_{pq}\frac{dS_{pq}}{dR_A} \tag{37}$$

The functional G is then substituted into equation (37) as shown in equation S21. Rewriting the rotational Hessians in terms of the Fock matrix and using the definition of the relaxed difference density matrix, T, as well as its connection to the solution to the Lagrange multiplier, Z, the derivative of the functional G can be collapsed into derivatives of the Fock

matrix of particular orbital transitions as seen in equation (38).

$$\frac{dL^{S/T}}{dR_A} = \sum_{ab}\frac{dF_{ab}}{dR_A}T_{ab} + \sum_{ij}\frac{dF_{ij}}{dR_A}T_{ij} + \sum_{ia}\frac{dF_{ia}}{dR_A}Z_{ia} + 2\sum_{iajb}\frac{K^{S/T}_{iajb}}{dR_A}(X+Y)_{ia}(X+Y)_{jb} - \sum_{pq,p\leq q}W_{pq}\frac{dS_{pq}}{dR_A} \tag{38}$$

The relaxed difference density matrix, P, helps simplify the equation further.

$$= \sum_{pq}\frac{dF_{pq}}{dR_A}P_{pq} + 2\sum_{iajb}\frac{K^{S/T}_{iajb}}{dR_A}(X+Y)_{ia}(X+Y)_{jb} - \sum_{pq,p\leq q}W_{pq}\frac{dS_{pq}}{dR_A} \tag{39}$$

The first term in equation (39) is the derivative of the Fock matrix without any Hartree-Fock exchange. The next term represents the derivative of the coupling matrix, and the last term is based off of the Lagrange multiplier, W, which changes depending on the type of orbital transition as defined in the previous sections. All terms can be plugged into equation (39) to obtain equation S22 such that the square root of the overlap matrix is brought in by the use of Löwdin partial charge analysis. To simplify the long gradient form in equation S22, the following definitions are used:[31]

$$U_A = \sum_{ia}(X+Y)_{ia}q_{ia,A}$$

$$\Xi_A = \sum_B \gamma_{AB}U_B.$$

This results in the final gradient form shown in equation (40).

$$\begin{aligned} &2\sum_{\mu\in A,\nu\notin A}\frac{dh_{\mu\nu}}{dR_A}P_{\mu\nu} + 2\sum_{\mu,\lambda\in A,\nu,\kappa\notin A}\frac{d(\mu\nu|\lambda\kappa)}{dR_A}P_{\mu\nu} + \\ &2\sum_{\mu\in A,\nu\notin A}\frac{dV^{XC}_{\mu\nu}}{dR_A}P_{\mu\nu} + \\ &2\sum_{\mu\in A,\nu\notin A}S^{1/2}_{\mu\nu}\frac{dS^{1/2}_{\mu\nu}}{dR_A}(\Xi_A+\Xi_B)U_{\mu\nu} + \\ &4\sum_{\mu\in A,\nu\notin A}\frac{d\gamma_{AB}}{dR_A}U_AU_B - \sum_{\mu\in A,\nu\notin A}\frac{dS_{\mu\nu}}{dR_A}W_{\mu\nu} \end{aligned} \tag{40}$$

III. IMPLEMENTATION

The implementation of the TDDFT+TB analytical gradients mimics the implementation of the Slater-type atomic orbital spin-flip TDDFT based analytical gradient code implemented in the ADF engine of the Amsterdam Modelling Suite (AMS) and will be available for use in the AMS2023 release.

The overall flow of the code is as follows:
(1) Obtain the excitation energy and eigenvectors from linear response TDDFT+TB equations
(2) Obtain the R vector from the stationary requirement of molecular orbital coefficients
(3) Solve the Coupled Perturbed Kohn-Sham equations (CPKS) to obtain Lagrange multiplier Z
(4) Use R and Z to find Lagrange multiplier W
(5) Calculate gradient terms and evaluate overall gradient

Analyzing the first three terms in equation (40), it can be seen that these terms are exactly the same as the corresponding terms from TDDFT gradients.[32] These terms have already been implemented into the ADF engine by transforming the matrices back into density integrals as shown in equation (41).[32] The TDDFT+TB implementation reuses these subroutines for consistency. Note: A full straightforward derivative is shown by ζ, where a derivative with respect to a fixed stationary requirement is denoted by (ζ).[26]

$$\begin{aligned} &\sum_\sigma\int\rho^{P(\zeta)}_\sigma\left(T+V_{ext}+V_C+V^{XC}_\sigma\right) \\ &+\sum_\sigma\int\left(V^P_C\rho^{(\zeta)}_\sigma+V^\zeta_{ext}\rho^P_\sigma\right)+\sum_{\sigma\tau}\int\rho^P_\sigma f^{XC,FULL}_{\sigma,\tau}\rho^{(\zeta)}_\tau \end{aligned} \tag{41}$$

Even though the coupling matrix is the only approximation to TDDFT, TDDFT+TB introduces complexity in the gradient implementation. One example of this is through the use of Löwdin partial charge analysis. As the overlap matrix is a positive semi-definite matrix, there exists a square root that is a symmetric matrix by properties of semi-definite matrices. Hence, to implement the derivative of the square root of the coupling matrix into the ADF engine, the Sylvester equation must be used.[33] The Sylvester equation is defined by equation (42).

$$XC + CX = D \tag{42}$$

Such that in this case,

$$C = S^{\frac{1}{2}}$$

$$D = \nabla_\zeta S$$

$$X = \nabla_\zeta S^{\frac{1}{2}}.$$

As both C and D are known and calculated for other terms used in the gradient equation, these variables may be brought in and used in order to find the nuclear derivative of the square root of the overlap matrix.

IV. RESULTS

To assess the accuracy of the TDDFT+TB gradients, the analytical results were compared to numerical results using finite

difference methods. The code was further tested by completing excited state geometry optimizations to compare the optimized geometry and emission energy between TDDFT and TDDFT+TB. It is important to note that as an approximate method, it is not expected that TDDFT+TB will be as accurate as the results from TDDFT.

A. Computational Details

All of the test cases were completed in a development version of the Amsterdam Density Functional Engine in the Amsterdamn Modelling Suite (AMS).[34] Numerical vs. analytical calculations were completed as described in test set 1, and excited state geometry optimizations for TDDFT and TDDFT+TB were completed as described in test set 2. As the TDDFT+TB method was created as an approximation to TDDFT, the results are focused on the comparison between the two methods rather than the comparison to experiment.

Test Set 1: The chosen test set for numerical vs. analytical gradients includes 37 total molecules consisting of 9 diatomic molecules and 28 small organic molecules from the Thiel test set.[35] The molecules in the Thiel test set include a range of different organic molecules from aliphatic compounds and aromatic hydrocarbons to carbonyl compounds and more. A handful of compounds were tested with different basis sets and exchange correlation functionals for proof of concept. The reported results in the manuscript are all completed at the BP86/DZ level of theory, where BP86[36] is a GGA exchange correlation functional, and DZ refers to a double zeta basis set. The comparison between TDDFT and TDDFT+TB in tables S1 and S2 were calculated at the PBE/TZP level of theory such that PBE is a GGA exchange correlation functional, and TZP refers to a triple zeta polarized basis set. All calculations were calculated without symmetry, which is required for the TDDFT+TB method. Considering that the integrals in ADF are calculated on a numerical grid,[32] the numerical quality was set to VeryGood for diatomic molecules, and Good for the Thiel test set. All of the compounds were created in MacMolPlt[37] where diatomic molecules, in particular, were tested on and off the axis. Numerical gradients were tested by computing single point total energy calculations where each atom was displaced by 0.001 Å in the positive and negative x, y and z directions. Several different displacement and numerical quality values were additionally tested as seen in table S1 and S2. Overall, the gradients give a vector of size $3 \times N$, where N is the number of atoms in the system. For this test set, the mean absolute deviation (MAD) and root mean squared (RMS) values are reported between the analytical and numerical gradients for all atoms in all directions rather than reporting each individual difference. The equations for MAD and RMS can be seen in equation S23 and S24.

Test Set 2: The chosen test set for excited state optimizations includes 60 total chemical systems consisting of 9 diatomic molecules, 26 small organic molecules from the Thiel test set,[35] 1 gold nanocluster core, 10 ligand protected noble metal nanoclusters and 14 chromophores from Tussupbayev et al. 2015 paper.[38] The formal name of each chromophore is provided in the supporting information. The noble metal nanoclusters were chosen from a range of application projects that are either published or ongoing in the Aikens lab and optimized with different electronically excited states.[14,39–43] Most of the reported results are completed at the BP86/DZ level of theory, where BP86[36] is a GGA exchange correlation functional, and DZ refers to a double zeta basis set. A few others are calculated at the PBE/TZP level of theory where PBE is a GGA exchange correlation functional and TZP refers to a triple zeta polarized basis set. Further, for comparison with previous literature, the two emissive points in $Au_{14}Cd(S\text{-}Adm)_{12}$ were calculated at the Xalpha/DZ level of theory.[14] For faster convergence, excited state optimizations for all nanoclusters and chromophores were performed on 6 cores. There are no notable differences between the emission energy calculated in serial vs. parallel as seen in table S3; however, it is worth noting that the code does not quite scale linearly with the number of cores, but on average speeds up the calculation $0.80\times$ for each core (i.e. 6 cores would result in a calculation that finishes 4.8 times faster than the same calculation on one core). All of the compounds were created in MacMolPlt[37] for the initial input geometry and were optimized to obtain the ground state geometry. All ground state and most excited state geometry optimizations were performed with an energy and gradient convergence criteria of $1x10^{-5}$ Hartree and $1x10^{-3}$ Hartree/Angstrom respectively. Diatomic molecules were tightened to an energy and gradient convergence criteria of $1x10^{-5}$ Hartree and $1x10^{-4}$ Hartree/Angstrom respectively. The calculations were calculated without symmetry, which is required for the TDDFT+TB method. Scalar relativistic effects were added into the excited state optimizations with gold and silver using the zeroth-order regular approximation (ZORA).[44,45] As TDDFT+TB was created as an approximation to TDDFT, TDDFT is used to check the accuracy of the emission energy and geometry from the excited state geometry optimizations. For this purpose, the same AMS input file was created where the only change between the two methods was the keyword for TDDFT+TB in the EXCITATIONS block. The mean absolute deviation (MAD) and root mean squared (RMS) values are reported for the difference in emission energy between TDDFT and TDDFT+TB at the optimized excited state geometry.

B. Numerical vs. Analytical Gradients

To check the accuracy of the method, there are several different tests that can be completed. One of these is to check the numerical gradient value at different geometries and see if the analytical gradient is similar at that point. For this process, finite difference is used with a displacement of 0.001 Å for the numerical gradients. The results between the numerical and analytical gradients for TDDFT+TB are reported in table 1 for the S_1 states of diatomic molecules, and table 2 for the for the S_1 states of the Thiel test set. Recall that the MAD and RMS values are recorded for the numerical vs. analytical

gradient differences in the molecule between all atoms in all directions. Overall, the numerical vs. analytical gradients match very well where most molecules have a MAD value of less than 5.00×10^{-4}. The one molecule that seems to have the largest difference is LiH. At the examined geometry, the bond distance between Li and H is 2.43 Å. This distance is at a point on the dissociative wall of the potential energy surface for LiH where the gradient values are fairly large, and hence the numerical vs. analytical gradient difference is actually relatively low in comparison. It is important to keep in mind that the numerical gradients are based on finite difference, and therefore may change depending on the displacement value. In this case, since the gradient values are so large, if the displacement is lowered to 0.0005 Å, then the new MAD value becomes 1.79×10^{-4}, and the RMS value becomes 3.10×10^{-4}. Considering the numerical noise in the TDDFT and TDDFT+TB calculations and negligible differences between the different tested displacements, this is well within the acceptable range. All in all, the numerical vs. analytical gradients serve as one test in which the TDDFT+TB analytical gradients provide accurate results.

TABLE I. Numerical versus analytical gradient differences for diatomic molecules (Hartree/Angstrom)

Molecule	MAD	RMS
CO	7.12×10^{-5}	7.58×10^{-5}
Cl_2	1.95×10^{-5}	3.24×10^{-5}
Li_2	8.77×10^{-5}	1.52×10^{-4}
H_2	1.82×10^{-5}	3.15×10^{-5}
HCl	1.14×10^{-5}	1.98×10^{-5}
OH^-	6.97×10^{-5}	1.21×10^{-4}
LiH	1.53×10^{-3}	2.72×10^{-3}
NO^+	2.98×10^{-5}	3.59×10^{-5}
N_2	4.16×10^{-5}	7.21×10^{-5}

TABLE II. Numerical versus analytical gradient differences for organic molecules from the Thiel test set (Hartree/Angstrom)

Molecule	MAD	RMS
Acetamide	1.16×10^{-4}	1.62×10^{-4}
Acetone	5.67×10^{-4}	7.87×10^{-4}
Adenine	5.98×10^{-5}	7.17×10^{-5}
Benzene	4.74×10^{-5}	7.91×10^{-5}
Benzoquinone	9.51×10^{-5}	1.85×10^{-4}
Butadiene	3.22×10^{-4}	7.44×10^{-4}
Cyclopentadiene	5.61×10^{-5}	7.98×10^{-5}
Cyclopropene	2.54×10^{-4}	5.09×10^{-4}
Cytosine	9.36×10^{-5}	1.39×10^{-4}
Ethene	4.88×10^{-5}	7.93×10^{-5}
Formaldehyde	9.28×10^{-5}	1.45×10^{-4}
Formamide	9.91×10^{-5}	1.45×10^{-4}
Furan	8.12×10^{-5}	1.05×10^{-4}
Hexatriene	4.79×10^{-5}	7.00×10^{-5}
Imidazole	6.83×10^{-5}	9.05×10^{-5}
Naphthalene	6.76×10^{-5}	8.61×10^{-5}
Norbornadiene	1.50×10^{-4}	1.96×10^{-4}
Octatetraene	1.88×10^{-4}	2.49×10^{-4}
Propanamide	7.34×10^{-5}	1.21×10^{-4}
Pyrazine	3.02×10^{-5}	4.76×10^{-5}
Pyridazine	5.77×10^{-5}	8.15×10^{-5}
Pyridine	4.80×10^{-5}	7.02×10^{-5}
Pyrimidine	3.93×10^{-5}	6.65×10^{-5}
Pyrrole	5.31×10^{-5}	7.77×10^{-5}
Tetrazine	3.24×10^{-5}	4.65×10^{-5}
Thymine	9.89×10^{-5}	1.57×10^{-4}
Triazine	5.44×10^{-5}	7.50×10^{-5}
Uracil	8.77×10^{-5}	1.66×10^{-4}

C. Excited State Geometry Optimizations

Not only is the value of the derivative at a particular set of coordinates important to check, but the method should be able to complete a full excited state geometry optimization and find the minimum points on different excited state potential energy surfaces. In this section, the optimized excited state and emission energy difference at the minimum of that state between TDDFT and TDDFT+TB is reported in table 3 for diatomic molecules, table 4 for the Thiel test set, table 5 for chromophores and table 6 for the noble metal nanoclusters. It is important to note that some states become degenerate with the state below and therefore have issues fully converging to the optimization requirements outlined in the computational details. For this reason, the molecules were not all optimized at the S_1 state. The emission energy difference between TDDFT and TDDFT+TB has RMS and MAD values of 1.04 eV & 0.681 eV for diatomic molecules, 0.206 eV & 0.113 eV for the Thiel test set, 0.028 eV & 0.018 eV for noble metal nanoclusters, and 0.076 eV & 0.040 eV for the chromophore set respectively. The method does not work as well for diatomic molecules, which is likely a result of the approximation in the coupling matrix. In addition, for cases such as hydrogen, the optimized S_2 energy is so large with TDDFT (19.80 eV) that the TDDFT+TB equivalent (17.52 eV) has a relatively small error when the magnitude of the excitation energy is considered. This issue, however, is inherent to the method and not the gradients. Further, it can be concluded that optimizing degenerate states do not work well for this

TABLE III. Emission energy differences between TDDFT and TDDFT+TB for diatomic molecules (eV)

Molecule	State	Energy Difference (eV)
CO	S_1	0.89
H_2	S_2	2.28
Li_2	S_1	0.33
HeH^+	S_1	0.05
HCl	S_1	0.09
OH^-	S_4	0.09
LiH	S_1	0.07
NO^+	S_3	-1.80
N_2	S_1	-0.62

TABLE IV. Emission energy differences between TDDFT and TDDFT+TB for organic molecules from the Thiel test set (eV)

Molecule	State	Energy Difference (eV)
Acetamide	S_1	0.00
Acetone	S_2	0.03
Adenine	S_1	0.06
Benzene	S_1	0.04
Benzoquinone	S_3	0.09
Butadiene	S_2	0.04
Cyclopentadiene	S_2	0.04
Cyclopropene	S_1	0.35
Cytosine	S_1	0.02
Ethene	S_4	0.68
Formaldehyde	S_2	0.12
Furan	S_2	0.08
Hexatriene	S_1	0.01
Imidazole	S_2	-0.11
Naphthalene	S_1	0.13
Norbornadiene	S_1	0.13
Octatetraene	S_1	-0.02
Propanamide	S_1[a]	0.09
Pyrazine	S_6	0.37
Pyridazine	S_1	0.09
Pyridine	S_1	-0.03
Pyrimidine	S_1	0.02
Tetrazine	S_1	0.48
Thymine	S_1	0.14
Triazine	S_1	0.10
Uracil	S_1	0.14

[a] Reoptimized TDDFT from TDDFT+TB S_1 minimum

TABLE V. Emission energy differences between TDDFT and TDDFT+TB for chromophores in reference[38] (eV)

Molecule	State	Energy Difference (eV)
1	S_1	0.23
2	S_1	0.03
3	S_1	0.03
4	S_1	0.01
5	S_1	0.08
6	S_1	0.02
7	S_1	0.06
8	S_1	0.00
9	S_1	0.02
10	S_1	0.08
11	S_1	0.00
12	S_1	-0.01
13	S_1	0.00
14	S_1	0.00

method. This is a result of numerical inaccuracies in which the gradient may be using the wrong energy level upon displacing the starting geometry. Optimizing degenerate states is an issue with TDDFT as well and results in some states not being able to optimize at all, which is what happens with the S_1 state in pyrrole. In formamide, the S_1 state can be optimized with TDDFT but not with TDDFT+TB. This happens because the TDDFT+TB optimization misses the local minimum point and finds a lower energy geometry in which the molecule errors due to degeneracy with the state below. If the optimization with TDDFT+TB is started at the S_1 state of TDDFT, the method can obtain the minimum. In addition, TDDFT has issues optimizing excited states when the emission energy becomes lower than 0.50 eV. TDDFT+TB will still optimize these states as shown by the examples in chlorine and propanamide. If the optimization with TDDFT is started at the S_1 state of TDDFT+TB, the method can obtain the minimum in propanamide, but not chlorine.

TABLE VI. Emission energy differences between TDDFT and TDDFT+TB for noble metal nanoclusters (eV)

Molecule	State	Energy Difference (eV)
Au_7^{3+}	S_1	0.03
$Au_{22}(PA)_{18}$	S_1	0.02
$Au_{25}(SC_3H_7)_{18}{}^{1-}$	S_1[a]	0.02
$Au_{14}Cd(S\text{-}Adm)_{12}$	S_1	-0.01
$Au_{14}Cd(S\text{-}Adm)_{12}$	S_1'	0.00
$Au_{14}Cd(S\text{-}Adm)_{12}$	S_2	-0.01
$Ag_{29}(BDT)_{12}$	S_1	0.00
$Au_{18}(S\text{-}Adm)_8(SbPh_3)_8Br_2$	S_1	0.02
$Au_6(PPh_3)_6^{2+}$	S_1	0.07
$Au_2Ag_6(PPh_2Py)_2(SC_{10}H_{15})_6$	S_1	0.04

[a] TDDFT geometry converged to 1.32×10^{-3} constrained gradient max

Recall that the analytical gradients also work for singlet-triplet states. The chromophore set[38] was therefore tested to obtain the emission energy from the first triplet state as seen in table 7. Note that these are not unrestricted calculations and refer to triplet states calculated using the singlet orbitals and orbital energies; thus, the state is denoted by ST. Chromophore 14 was not able to optimize with TDDFT or TDDFT+TB and therefore was omitted from the set. The overall RMS and MAD values for this set are 0.092 eV and 0.059 eV respectively.

TABLE VII. Emission energy differences between TDDFT and TDDFT+TB for the first singlet-triplet state for chromophores in reference (eV)

Molecule	State	Energy Difference (eV)
1	ST_1	-0.21
2	ST_1	-0.06
3	ST_1	-0.13
4	ST_1	0.01
5	ST_1	-0.14
6	ST_1	-0.06
7	ST_1	-0.09
8	ST_1	-0.02
9	ST_1	0.10
10	ST_1	-0.06
11	ST_1	0.00
12	ST_1	-0.01
13	ST_1	-0.01

Overall, the TDDFT+TB emission energy obtained through

the analytical gradients match TDDFT very well in larger molecules and nanoclusters generally within 0.10 eV. The benefit of using TDDFT+TB is that the accuracy has shown to match TDDFT well, but drastically cuts on cost. Therefore, it is imperative to not only compare the emission energy, but also the total run time of the calculation. A few results are shown in table 8. Note: the run time is presented in 'days-hours:minutes:seconds'. In addition to run time and accuracy, it is important that this method can still obtain different emissive points. To double check that TDDFT+TB can achieve multiple minima, and not fall back into the same local minimum point, calculations were performed from an intermediate geometry on $Au_{14}Cd(S\text{-}Adm)_{12}$, which has been shown to have dual emission from states' S_1 and S_1'.[14] The results are displayed in table 9.

Overall, the TDDFT+TB method takes approximately a third of the overall run time compared to TDDFT. While this difference is not as important for diatomic and small organic molecules, it really adds up when computing larger systems and nanoclusters. $Au_{22}(PA)_{18}$, for example, has 256 total atoms and takes 17 days to optimize the S_1 state with TDDFT. With TDDFT+TB, the calculation achieves essentially the same result in less than a week. Further, on a different type of node, the same calculation optimizes a geometry that has an emission energy of 1.21 eV with TDDFT and 1.20 eV with TDDFT+TB. This means that the difference between TDDFT and TDDFT+TB is well within the error from the small fluctuations seen within the same calculation on different compute nodes.

D. Discussion

Overall, the TDDFT+TB gradient code has shown to reproduce emission energies on average within 0.70 eV of diatomic molecules, 0.15 eV for organic molecules, 0.02 eV for nanoclusters, and 0.04 eV for chromophores of various sizes. Of course, as an approximate method, TDDFT+TB gradients are not perfect and there exist test cases in which the TDDFT+TB results do not match as well with the results obtained from TDDFT. It is critical to keep in mind that the TDDFT+TB method has some problems modelling local transitions due to the atomic transition charges. This problem comes in with the definition of the TDDFT+TB method, specifically in the monopole approximation to the transition density. With this approximation, the basis functions that are on the same atom do not contribute to the atomic transition charges which underestimate vertical excitation energies for σ to π^* and n to π^* transitions.[25] This issue has been found to be less important as the system size increases and as the system becomes less symmetrical; thus, the method is ideal for larger systems.

The current state of the code is advantageous for larger chemical systems and plasmonic nanoparticles. As the chemical system gets bigger, the TDDFT+TB gradients seem to get more accurate compared to TDDFT, and the error is often significantly less than 0.30 eV. This is a good cost to accuracy relationship, especially for the continued study of photochemical systems.

V. CONCLUSION

Tight binding approximations are extremely useful and can drastically cut the cost of excited state calculations. This work demonstrated the derivation and implementation of the analytical excited state gradients for TDDFT+TB. To derive the analytical excited state gradients, four steps were introduced: defining an energy functional that is equivalent to the vertical excitation energy of that system, setting up an energy functional that is stationary with respect to the molecular orbital coefficients, solving the Lagrange multipliers after the constraints have been defined, and taking the full derivative of each term in the energy functional to obtain the full analytical gradient with respect to the position of the nuclear coordinates. This method is currently implemented into the ADF engine of the Amsterdam Modelling Suite and will be available for the 2023 release. The code works in serial and in parallel, with and without scalar relativistic effects, and produces emission energies for singlet-singlet and singlet-triplet excitations. Overall, the TDDFT+TB gradients have found to cut the overall cost of TDDFT gradients roughly by a factor of 3, while reproducing the TDDFT emission energy of different excited states within 0.15 eV for small organic molecules, and larger systems such as chromophores and noble metal nanoclusters. It is recommended that this method be used for chemical systems that are larger than 50 atoms in size.

SUPPLEMENTARY MATERIAL

See supplementary material for extended derivation, listing of the chromophore set, equations for MAD and RMS, numerical and analytical gradient differences at different displacements, and a comparison of emission energy and runtime with different chemical systems in serial and parallel.

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TABLE VIII. S_1 minimum calculated with TDDFT and TDDFT+TB in different chemical systems

Molecule	Method	Runtime	Emission Energy (eV)	Number of Geometry Steps
LiH	TDDFT	00:01:00	2.31	40
	TDDFT+TB	00:00:42	2.24	49
Octatetraene	TDDFT	00:19:03	3.63	6
	TDDFT+TB	00:05:08	3.65	6
Cytosine	TDDFT	00:15:55	1.23	9
	TDDFT+TB	00:04:59	1.21	9
Au_7^{3+}	TDDFT	01:10:13	1.76	13
	TDDFT+TB	00:17:00	1.73	10
$Au_{22}(PA)_{18}$	TDDFT	17-06:40:45	1.19	193
	TDDFT+TB	6-13:20:19	1.21	153

TABLE IX. Optimized minima of $Au_{14}Cd(S\text{-}Adm)_{12}$ on the first excited state singlet

State	Method	Runtime	Emission Energy (eV)	Number of Geometry Steps
S_1	TDDFT	5-20:02:55	1.11	50
S_1	TDDFT+TB	1-20:02:23	1.10	41
S_1'	TDDFT	5-07:50:17	0.88	51
S_1'	TDDFT+TB	3-17:14:54	0.88	108

Note– The authors declare no competing financial interest

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

The authors have no conflicts to disclose.

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