Excitation energies through Becke’s exciton model within a Cartesian-grid KS DFT

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Abstract

Photon-induced electronic excitations are ubiquitously observed in organic chromophore. In this context, we present a simple, alternative time-independent DFT procedure, for computation of single-particle excitation energies, in particular, the lower bound excited singlet states, which are of primary interest in photochemistry. This takes inspiration from recently developed Becke’s exciton model, where a key step constitutes the accurate evaluation of correlated singlet-triplet splitting energy. It introduces a non-empirical model, both from “adiabatic connection theorem” and “virial theorem” to analyze the role of $2e^-$ integral in such calculations. The latter quantity is efficiently mapped onto a real grid and computed accurately using a purely numerical strategy. Illustrative calculations are performed on 10 π-electron organic chromophores within a Cartesian-grid implementation of pseudopotential Kohn-Sham (KS) DFT, developed in our laboratory, taking SBKJC-type basis functions within B3LYP approximation. The triplet and singlet excitation energies corresponding to first singly excited configuration, are found to be in excellent agreement with TD-B3LYP calculations. Further, we perform the same for a set of larger molecular systems using the asymptotically corrected LC-BLYP, in addition to B3LYP. A systematic comparison with theoretical best estimates demonstrates the viability and suitability of current approach in determining optical gaps, combining predictive accuracy with moderate computational cost.

Keywords: Density functional theory, adiabatic connection theorem, virial theorem, Becke’s exciton model, range-separated hybrid functional, singlet-triplet splitting.

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I. INTRODUCTION

Over the past decades, Kohn-Sham density functional theory (KS-DFT) has emerged as a very powerful and successful tool for ground-state calculations of many-electron systems, such as atoms, molecules and solids. Moreover, its time-dependent (TD) variant, generally entitled linear-response (LR)-TDDFT has been developed for computing excitation energies, mostly for discrete spectrum. In comparison to the conventional wave function-based formalisms, such as configuration interaction (CI), multireference CI, complete active space self-consistent field, equation-of-motion coupled cluster etc., LR-TDDFT has gained popularity due to its reasonable trade-off between accuracy and efficiency. This is evident from its applicability to medium and large systems. However, despite its huge success, it has well-known difficulties regarding double excitation, charge transfer and Rydberg excitation. This is mainly due to the adverse effects of exchange-correlation (XC) potential within adiabatic approximation. A detailed analysis could be found in [6].

Besides TDDFT, attempts were also made to obtain excited states within a time-independent DFT rubric–several elegant approaches are available in the literature. In particular, the ∆SCF method was developed within the standard self-consistent field iteration, by adopting non-Aufbau occupations at each iterations, and it targets the non-Aufbau solutions using the ground-state functional. It has favorable scaling like ground-state DFT, and hence smaller computational resource compared to LR-TDDFT methods. Although it already provides a good estimation of excitation energies for molecular systems, its tendency to variationally collapse to the ground state is a serious concern. Such features during the ∆SCF procedure has been characterized in recent times; this is particularly severe in systems with a dense energy spectrum near the Fermi energy levels. Several sophisticated schemes were put forth to alleviate this issue, which include a few constrained-DFT formalisms as well as gentlest ascent dynamics and meta dynamics related methods, etc. These are often somehow involved, but are quite successful where TDDFT fails to perform well. Furthermore, a lot of recent developments have been placed in the field of unconstrained excited-state orbital relaxation that have the same complexity as normal ground-state or TDDFT, while using a simple ∆SCF-style ansatz. On the other hand, orbital energies themselves have physical meaning as excitation energies, but are quite sensitive to the choice of density functionals and its implementations. In a
recent article \[26\], KS-DFT has been used successfully to extract the photo-electron and electronic excitation spectrum for molecules from orbital energies through range-separated (RS) XC functionals. Moreover, efforts are also known the development of multi-reference (MR)-DFT by means of configurations mixing such as, multiconfiguration pair DFT \[27\] and MR-DFT with generalized auxiliary systems \[28\].

In a series of articles, Becke \[29–32\], introduced a simple novel model for estimation of lowest single-particle excitation energies via correlated singlet-triplet splitting (STS) energy. It offers an accurate, economical way to compute optical gaps in large molecules. The main focus here lies in the lowest singlet excited state, which are of fundamental interest in photochemistry. While triplet states can be easily obtained, \textit{in principle}, standard DFT cannot be used in a singlet excited state due to its multi-determinantal nature. The present scheme advocates two separate single-determinant DFT calculations—one for the closed-shell ground state and another for open-shell lowest triplet excited state, followed by a simple two-electron integral (Coulomb self energy) evaluation corresponding to the HOMO-LUMO transition. We note that there is no concern about standard density functionals applied on a given triplet excited state as it is represented by a single Slater determinant and is characterized by Fermi hole. Thus the main ingredient is the correlated STS energy which can be approached by means of (i) adiabatic connection theorem \[29\] and (ii) virial theorem \[30\]. In a sense, this avoids the configuration mixing and is altogether non-empirical.

In the present work, we have adopted the above approach for lowest single-particle excitation energy corresponding to singlet excited state in molecules. The required computations are performed following a pseudopotential KS-DFT implemented in Cartesian coordinate grid (CCG), as developed in our laboratory \[33–41\]. The pertinent two-electron integral (from appropriate orbitals obtained after solving the lowest triplet excited state) is carried out numerically using a recently designed algorithm \[41\]. This employs the Fourier convolution theorem in conjunction with a RS Coulomb interaction kernel. The latter is efficiently mapped onto the real grid through a simple grid optimization prescription, giving rise to some constraints in RS parameter. The “adiabatic” model \[29\] corresponding to correlated STS energy is also provided accurately, leading to an easy route to compute the singlet excitation energy. Following the arguments of Becke \[30\], an elegant “virial” theorem is then engaged to analyze the role of two-electron integral in determining the correlated STS energy. Both procedures are applied to calculate optical gaps arising from both $\pi \rightarrow \pi^*$ and
$n \rightarrow \pi^*$ transitions in a decent number of molecules adopting B3LYP \[42\] functional. For a proper comparison, we carry out parallel calculations corresponding to lowest triplet excited states, from GAMESS quantum chemistry package \[43\] using TD-B3LYP method, which reveals a better accuracy. Further, to extend the scope and applicability of this approximation, we execute the same using “virial” theorem for a set of large molecular systems, and employing an additional XC functional from RS hybrid \[44\] family. The effectiveness of this scheme is illustrated by the respective statistical analysis. The article is organized as follows. The underlying theorem of single-particle excitation energy along with a brief summary of our KS-DFT framework in CCG, is provided in Sec. II. Section III offers the necessary computational and technical details. Finally, the feasibility, performance and accuracy of our results are critically assessed in Sec. IV. Some concluding remarks as well as the future prospects are given in Sec. V.

II. METHODOLOGY

Let us consider an excitation of a given system, corresponding to an electronic configuration $\varphi_i \varphi_f$ from a closed-shell ground state. Assuming completely filled closed-shell core, this is spanned by four Slater determinants: $|\varphi_i^\alpha \varphi_f^\alpha\rangle$, $|\varphi_i^\alpha \varphi_f^\beta\rangle$, $|\varphi_i^\beta \varphi_f^\alpha\rangle$ and $|\varphi_i^\beta \varphi_f^\beta\rangle$, where $\alpha$ and $\beta$ denote up and down spin. Therefore, the coupled excited states are found by diagonalizing the Hamiltonian matrix in the space of above four determinants. As such, the singlet state is given by $|\psi_S\rangle = \frac{1}{\sqrt{2}} \{|\varphi_i^\alpha \varphi_f^\beta\rangle - |\varphi_i^\beta \varphi_f^\alpha\rangle\}$, whereas the three degenerate triplet states are written as follows: $\psi_T = |\varphi_i^\alpha \varphi_f^\alpha\rangle$ or $\frac{1}{\sqrt{2}} \{|\varphi_i^\alpha \varphi_f^\beta\rangle + |\varphi_i^\beta \varphi_f^\alpha\rangle\}$ or $|\varphi_i^\beta \varphi_f^\beta\rangle$. The corresponding singlet and triplet energies (identified by “S” and “T” subscripts) are,

\[ E_S = E^{\alpha\beta} + K_{if} \]  
\[ E_T = E^{\alpha\alpha} \text{ or } E^{\alpha\beta} - K_{if} \text{ or } E^{\beta\beta}, \]  

where $E^{\sigma_1 \sigma_2}$ is the energy of a given determinant of form $|\varphi_i^{\sigma_1} \varphi_f^{\sigma_2}\rangle$, $(\sigma_1, \sigma_2) \in \{\alpha, \beta\}$, and $K_{if}$ is the 2e$^-$ integral (or Coulomb self-energy of product of transition orbitals) defined as,

\[ K_{if} = \int \int \frac{\varphi_i(r_1)\varphi_f(r_1)\varphi_i(r_2)\varphi_f(r_2)}{|r_1 - r_2|} \, dr_1 dr_2. \]  

Now combining Eqs. (1), (2), one can connect singlet and triplet excitation energy as follows,

\[ E_{0S} = E_{0T} + 2K_{if}, \]
where $E_{0S} = E_S - E_0$, $E_{0T} = E_T - E_0$, while $E_0$ signifies the ground-state energy of a certain closed-shell system. But Eq. (4) is highly inaccurate for singlet excitation energy, $E_{0S}$. The problem lies in the determination of $2K_{if}$ term, also called the zeroth-order (or uncorrelated) STS energy. In order to tackle this issue, recently some novel proposals (semi-empirical [29] as well as non-empirical [29, 30]) have appeared in the literature to derive a simplified formula for correlated STS energy.

A. The adiabatic connection theorem

One can make use of the well-known “adiabatic connection” theorem [45] to approach the correlated STS energy in single-particle excitations, which we are discussed here. For a specific excited configuration, all the orbitals involved in Eqs. (1), (2) are same. In that case, singlet and triplet states have same density and non-interacting kinetic energy. Then their energy difference can be written as ($\Delta E^0_{STS} = 2K_{if}$),

$$\Delta E_{STS} = \Delta E^0_{STS} + \Delta E^\text{corr}_{ST},$$

where $\Delta E^\text{corr}_{ST}$ represents the singlet-triplet correlation energy difference. Recently, a non-empirical formula [29] has been proposed for it, based on the inter-electronic cusp condition, and its effect on electron correlation. Accordingly, it can be expressed as,

$$\Delta E^\text{corr}_{ST} = -0.4 \int 4 \varphi_i^2(r_1) \varphi_j^2(r_1) z_C^2 \left[ 1 - \frac{\ln(1 + z_C)}{z_C} \right] dr_1. \quad (6)$$

The only unknown quantity, the correlation length $z_C$, measures the spatial extent of electron correlation in configuration, $\varphi_i \varphi_j$. Now if one allows a “strictly correlated electrons” limit, $z_C$ can be written in terms of two-electron integral, $K_{if}$, as in the following,

$$0.4 z_C^2 \int 4 \varphi_i^2(r_1) \varphi_j^2(r_1) \, dr_1 = 2K_{if}. \quad (7)$$

A detailed derivation could be found in [29].

B. The virial exciton model

From the above discussion, it is clear that, one may add a correlation correction term, $\Delta E^\text{corr}_{STS}$, to $2K_{if}$ to recover the desired correlated STS energy. As suggested in [30], one
may also further proceed to approximate this by noting that it comprises the kinetic and potential energy contributions,

$$\Delta E_{\text{STS}}^{\text{corr}} = \Delta T_{\text{STS}}^{\text{corr}} + \Delta V_{\text{STS}}^{\text{corr}}.$$  

(8)

Now invoking the standard virial theorem, the above equation can be simplified as,

$$\Delta E_{\text{STS}}^{\text{corr}} = \frac{1}{2} \Delta V_{\text{STS}}^{\text{corr}}.$$  

(9)

One may further presume that the non-local part of $\Delta V_{\text{STS}}^{\text{corr}}$ is dominated by pair-density effects. In that scenario, correlation would then lower the potential energy of singlet state relative to triplet state, by $\Delta V_{\text{STS}}^{\text{corr}} = -2K_{if}$. Hence, one can write,

$$\Delta E_{\text{STS}}^{\text{corr}} = -K_{if}.$$  

(10)

which surprisingly leads to a very simple relation as below,

$$\Delta E_{\text{STS}} = 2K_{if} - K_{if} = K_{if}.$$  

(11)

It may be noted that, this model (as well as that in II(A)) is also a purely non-empirical one. But obviously, this expression for correlated STS energy is much simpler involving only the two-electron integral.

C. The semi-empirical approach

As implied, both the routes in Eqs. (5), (11) are purely non-empirical, suggesting $\Delta E_{\text{STS}}$ to be less than $2K_{if}$. This prompts one to formally define a molecule-independent re-scaling parameter $f$ such that,

$$\Delta E_{\text{STS}} = 2fK_{if}, \quad 0 < f < 1.$$  

(12)

and if determined semi-empirically, it might offer good excitation energies overall, as long as de-localization error [46] is not a serious issue. This led to a semi-empirical technique [29] to obtain an optimum value of $f$. This was accomplished in [29] by fitting the results with best estimated theoretical excitation energy data set of [47], resulting in a value for $f$ as 0.486. It is surprisingly close to 0.5, as also appears from a consideration of II(B). The same author has also reported that the obtained mean average error (using this $f$) remains similar to that in non-empirical calculations, in II(A).
III. COMPUTATIONAL DETAILS

Our desired quantity, the singlet excitation energy $E_{0S}$ can be obtained from two single-determinant calculations (both are spin polarized), namely, one for closed-shell ground state and another for fully relaxed triplet state. These are computed using our in-house pseudopotential KS-DFT program in CCG [48]. An initial version was first developed by the corresponding author in 2008, on the basis of works [33–37], which has been later extended by his group [38–41]. Since the details have been published in the above references, here we give only some essential aspects. Accordingly, the single-particle KS equation in presence of pseudopotential is written as (atomic unit employed unless stated otherwise),

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ion}}^p(r) + v_{\text{ext}}(r) + v_h[\rho(r)] + v_{\text{xc}}[\rho(r)]\right]\varphi_i^\sigma(r) = \epsilon_i \varphi_i^\sigma(r),$$  \hspace{1cm} (13)

where $v_{\text{ion}}^p$ denotes the ionic pseudopotential, written as below,

$$v_{\text{ion}}^p(r) = \sum_{\text{atom } A} v_{\text{ion},a}^p(r - R_a).$$  \hspace{1cm} (14)

In the above equation, $v_{\text{ion},a}^p$ signifies ion-core pseudopotential associated with atom A, situated at $R_a$. The classical Coulomb (Hartree) term, $v_h[\rho(r)]$ describes usual electrostatic interaction amongst valence electrons, whereas $v_{\text{xc}}[\rho(r)]$ represents the non-classical XC part of latter, and $\{\varphi_i^\sigma, \sigma = \alpha \text{ or } \beta\}$ corresponds to a set of $N$ occupied orthonormal spin molecular orbitals (spin-MOs).

Now various quantities like localized basis function, two-electron potential, MOs and electron density are directly set up on a 3D cubic box,

$$r_i = r_0 + (i-1)h_r, \quad i = 1, 2, 3, ...., N_r, \quad r_0 = -\frac{N_r h_r}{2}, \quad r \in \{x, y, z\},$$  \hspace{1cm} (15)

where $h_r, N_r$ denote grid spacing and total number of points along three directions respectively. While one-electron contributions of KS-Fock matrix are evaluated through well-established recursion relations, the two-electron matrix elements are computed via direct numerical integration in the grid,

$$F_{\mu\nu}^{\text{hxc}} = \langle \chi_\mu(r_g)|v_{\text{hxc}}(r)|\chi_\nu(r_g)\rangle = h_x h_y h_z \sum_g \chi_\mu(r_g)v_{\text{hxc}}(r_g)\chi_\nu(r_g).$$  \hspace{1cm} (16)

where $v_{\text{hxc}}$ refers to the classical (Hartree) and non-classical (XC) potential combined. The construction of HF exchange in KS-Fock matrix has been documented in our earlier work [41]; hence not repeated here.
The actual implementation of the central quantity, $K_{if}$, is quite different from the original prescription in [29]. Here, we use the Fourier convolution theorem (FCT) using a range-separated technique in Coulomb interaction kernel, instead of the multi-center numerical integral procedure put forth in [49]. According to [41], this two-electron integral $K_{if}$ can be rewritten as,

$$K_{if} = \int \int \frac{\varphi_i(r_1)\varphi_f(r_1)\varphi_i(r_2)\varphi_f(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$

$$= \int \varphi_i(r_1)\varphi_f(r_1)v_{if}(r_1) \, dr_1. \quad (17)$$

Now, the main concern lies in the evaluation of $v_{if}$ integral which is related to electro static potential integral evaluation in [41]. Again, this can be recast as,

$$v_{if}(r_1) = \int \frac{\varphi_i(r_2)\varphi_f(r_2)}{|r_1 - r_2|} \, dr_2$$

$$= \int \frac{\varphi_{if}(r_2)}{|r_1 - r_2|} \, dr_2 = \varphi_{if}(r_1) \ast v^c(r_1) \quad (18)$$

The last expression is in terms of convolution integral, where $\varphi_{if}$ denotes simple multiplication of $i$th and $f$th MO from lowest triplet excited state and $v^c(r)$ represents the Coulomb interaction kernel. Now one can invoke the FCT to further simplify this integral,

$$v_{if}(r) = \mathcal{F}^{-1}\{v^c(k)\varphi_{if}(k)\} \quad \text{where} \quad \varphi_{if}(k) = \mathcal{F}\{\varphi_{if}(r)\} \quad (19)$$

Here $v^c(k)$ and $\varphi_{if}(k)$ stand for Fourier integrals of Coulomb kernel and MOs respectively. The main concern lies in an accurate mapping of the former, which has singularity at $r \to 0$. In order to alleviate this problem, we apply a simple RS technique from [41], expanding the kernel into long- and short-range components with a suitably chosen RS parameter ($\zeta$). This gives rise to the following expression,

$$v^c(r) = \frac{\text{erf}(\zeta r)}{r} + \frac{\text{erfc}(\zeta r)}{r} \quad (20)$$

$$v^c(r_g) = v^c_{\text{long}}(r_g) + v^c_{\text{short}}(r_g).$$

In the above equation, erf($x$) and erfc($x$) denote error function and its complement respectively, while the second expression is written in real-space CCG. The Fourier integral of Coulomb kernel can be separated out as follows: (i) FT of short-range part is treated analytically and (ii) long-range portion is computed directly from FFT of corresponding real-space CCG values. Then the remaining problem lies in finding an optimum value of
parameter $\zeta_{\text{opt}}$ for successful mapping of Coulomb kernel in CCG from \textit{first principles}. In this regard, we proposed a simple procedure which is found to be sufficiently accurate for lowest triplet excited states (as exemplified in results that follows) as well. This prompts us to write,

$$\zeta_{\text{opt}} \equiv \text{opt} \ E_{\text{tot}} = \text{opt} \ E_{\text{tot}, N_x, N_y, N_z} \text{ at fixed } h_r,$$

(21)

using a suitably defined constraint \cite{41} ($\zeta \times L = 7$), where $L (= N_r h_r; \ r \in \{x, y, z\})$ is the smallest side of simulating box. In the same spirit, other necessary quantities such as correlation length, $z_C$ and singlet-triplet correlation energy difference, $\Delta E_C$ are directly computed in real-space grid using pseudo KS orbitals $\varphi_i$ and $\varphi_f$.

The strategy as outlined for HF exchange component, is implemented in case of B3LYP, containing a fixed amount of former with conventional DFT XC functional. As such, the XC energy corresponding to this functional is defined as follows,

$$E_{\text{xc}}^{\text{B3LYP}} = (1 - a_0)E_{\text{LSDA}}^\text{x} + a_0E_{\text{HF}}^\text{x} + a_x E_{\text{B88}}^\text{x} + a_c E_{\text{LYP}}^\text{c} + (1 - a_c)E_{\text{VWN}}^\text{c}.$$  

(22)

Throughout our current presentation, we use the recommended values of $a_0, a_x, a_c$, as advocated in \cite{50}, i.e., 0.2, 0.72, 0.81 for B3LYP. This is computed using KS orbitals obtained from the solution of Eq. (13) in real-space CCG. The relevant LDA- and GGA-type functionals in connection with B3LYP are: (i) Vosko-Wilk-Nusair (VWN)–with the homogeneous electron gas correlation proposed in parametrization formula V \cite{51} (ii) B88–incorporating Becke \cite{52} semi-local exchange (iii) Lee-Yang-Parr (LYP) \cite{53} semi-local correlation. All these are adopted from density functional repository program \cite{54} except LDA.

The present work employs SBKJC \cite{55} effective core potential basis sets for species containing Group II elements. These are imported from EMSL Basis Set Library \cite{56}. The norm-conserving pseudopotential matrix elements in contracted basis are collected from GAMESS \cite{43}. The triplet calculations refer to \textit{restricted} open-shell, so that orbitals $\varphi_i$ and $\varphi_f$ are well defined. The convergence criteria imposed in this communication are slightly tighter than our earlier works \cite{33, 34, 37}; this is to generate accurate orbital energies, especially for triplet excited states. Changes in following quantities were followed during self-consistent field process, \textit{viz.}, (i) orbital energy difference between two successive iterations and (ii) absolute deviation in density matrix elements. They both were required to remain below a prescribed threshold set to $10^{-8}$ a.u.; this ensured that total energy maintained a convergence of at least this much, in general. In order to perform discrete Fourier
transform, standard FFTW3 package \cite{57} was invoked. The resulting generalized matrix-eigenvalue problem is solved through standard LAPACK routine \cite{58} easily. All molecular calculations are performed with calculated geometry (B3LYP XC functional and cc-PVTZ basis set), taken from NIST database \cite{59} (otherwise stated below). Other details including scaling properties may be found in references \cite{33--41}.

IV. RESULT AND DISCUSSION

A set of 10 selective organic chromophores (π containing molecules) from our previous work \cite{41} has been chosen, excluding those which have degenerate frontier orbitals, as the method in its present form is not applicable for these. These results pertain to the pseudopotential approximation neglecting the effects of core electrons. This may, by and large, be justifiable on the ground that only valence excitations are taken into account. By doing so, one can make a balance between accuracy and cost. To establish the effectiveness of this approach, we have chosen “SBKJC” type of pseudopotential basis set which does not contain any diffuse function, and this suffices in our present scenario. It may be emphasized that, in this exploratory study, only lowest singlet and triplet excited state corresponding to first single excitation, is pursued for each molecule.

Each calculation begins by optimizing the non-uniform grid for a given molecule, both in its closed-shell ground and lowest excited triplet state separately, employing a simple procedure as reported earlier \cite{38, 39}. Individual singlet excitation energies (in eV) through B3LYP XC functional, are displayed in Table I, along with mean absolute error (MAE) and mean error (ME) statistics. It contains both non-empirical and empirical excitation values as following: (i) PR₁ represents Eq. (12) using semi-empirical re-scaling parameter \( f = 0.486 \) (ii) PR₂ presents Eq. (5) using non-empirical model from “adiabatic connection” (iii) PR₃ refers to results from Eq. (11) using non-empirical model from virial theorem. To put things in perspective, column 6 reports the respective TD-B3LYP energies employing same functional and basis set, computed from GAMESS \cite{43}. The correlation lengths \( z_C \) manifestly fall into two distinct groups with \( \pi \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) transition—a feature that has been observed in \cite{29}. Furthermore, in consonance with their finding, we also witness a similar kind of pattern in the calculated \( z_C \) values, having smaller \( \varphi_i \varphi_f \) overlap for the \( n \rightarrow \pi^* \) transition for current set of molecules. Overall, the obtained singlet excitation
energies are within fraction of eV compared to the TD-B3LYP results. As expected from [30], the correlated virial theorem (PR3) confers remarkable improvement over the adiabatic connection formula (PR2). Here, the MAE value is about two times smaller compared to the latter one. On the other hand, the semi-empirical approach (PR2) performs very close to PR3 results, as evidenced from the proximity in their corresponding MAE values. The worst case candidate is propene, with an excitation energy 0.55 eV too low, in comparison to TD-B3LYP result. We note that the MAE and ME remain same in magnitude and sign, indicating a systematic error in calculated values. Out of three methods, the virial PR3 route provides the best estimate in exciting energies; quite competitive with that of TD-B3LYP, with an MAE of 0.34 eV.

Next we analyze the effects of triplet excitations and correlated STS term separately for B3LYP functional in Table II, giving a side-by-side comparison with TD-B3LYP in both cases. As singlet excitation energies are obtained from these two above quantities, a detailed assessment of them is worthwhile considering. Due to the superior performance, henceforth in future proceedings, we engage only the PR3. The $E_{0T}$ error metrics are: MAE = 0.40 eV and ME = −0.39 eV, having very similar magnitude, but different sign. The triplet MAE remains only marginally larger than singlet MAE values of PR3 results of previous table. On the other hand, STS measures read: MAE = 0.70 eV and ME = 0.69 eV, showing very close agreement in magnitude and also importantly without changing sign. However, magnitude of these errors (MAE and ME) in STS are relatively larger than the $E_{0T}$ errors.
A careful look on respective ME in these two quantities reveals that, ME in STS is about 75% larger compared to that in $E_{0T}$, but with an opposite sign. And that makes the singlet excitation energies more close to TD-B3LYP results, occurring through a systematic error cancellation. This leads us to conclude that, *STS term and not $E_{0T}$*, is the major source of error. It is worthwhile mentioning that, the success of this approach relies on an accurate estimation of the two-electron integral, which in turn depends on the accuracy of triplet excited state. Thus it is evident that our current prescription can be reliably used for determining optical gaps using the non-empirical time-independent methods of Sec. II, at least for small molecular systems.

At this stage, in order to assess the validity and usefulness, an additional set of larger molecular systems are taken up in Tables III and IV. We consider a representative set of 16 organic chromophores and 5 linear acene molecules with 2–6 rings for which accurate theoretical reference data is available \[^{60}\]. All the molecular geometry of Table III are taken from \[^{60}\] whereas for Table IV, these are optimized with B3LYP and cc-pVDZ basis set using GAMESS. Since the present scheme has earlier been verified to deliver practically identical results as that of GAMESS, for brevity, we have employed the same for calculation of $E_0$ and $E_T$ in the same basis. In addition to B3LYP, another XC functional from RS hybrid family, has been invoked. Accordingly, the inter-electronic space is separated through the

### Table II: Triplet excitation energies and correlated STS energies (in eV) using B3LYP functional.

| Molecule          | State      | $E_{0T}$ | $E_T$ | $\Delta E_{STS}$ |
|-------------------|------------|----------|-------|------------------|
| Ethylene          | $B_{1u}(\pi \rightarrow \pi^*)$ | 4.47     | 4.03  | 3.40             |
| Propene           | $A'(\pi \rightarrow \pi^*)$ | 4.44     | 4.03  | 2.82             |
| 1,3-Butadiene (E) | $B(\pi \rightarrow \pi^*)$ | 3.26     | 2.71  | 2.44             |
| 1,3-Pentadiene (E)| $A'(\pi \rightarrow \pi^*)$ | 3.24     | 2.71  | 2.30             |
| 1,3,5-Hexatriene (E)| $B_u(\pi \rightarrow \pi^*)$ | 2.42     | 1.85  | 2.02             |
| 2,4-Hexadiene (E,E) | $B_u(\pi \rightarrow \pi^*)$ | 3.22     | 2.70  | 2.23             |
| 1,3-Cyclo-pentadiene | $A'(\pi \rightarrow \pi^*)$ | 3.21     | 2.70  | 1.96             |
| Thiophene         | $B_2(\pi \rightarrow \pi^*)$ | 3.88     | 3.47  | 1.78             |
| Formaldehyde      | $A_2(n \rightarrow \pi^*)$ | 3.19     | 3.20  | 0.34             |
| Acetaldehyde      | $A''(n \rightarrow \pi^*)$ | 4.39     | 4.44  | 0.29             |

ME – 0.39 – 0.69 – 0.69 –
### TABLE III: Excitation energies (in eV) of organic chromophores from “virial theorem”.

| Molecule          | State  | $E_{0T}$ | $E_{0S}$ (PR3) | Lit.† |
|-------------------|--------|----------|----------------|-------|
|                   |        | B3LYP    | LC-BLYP        | B3LYP | LC-BLYP |
| Cyclopropene      | $B_2(\pi \rightarrow \pi^*)$ | 4.03     | 4.05           | 7.04  | 7.07    | 7.01 |
| Norbornadiene     | $A_2(\pi \rightarrow \pi^*)$ | 4.62     | 4.23           | 5.77  | 5.45    | 4.91 |
| Naphthalene       | $B_{2u}(\pi \rightarrow \pi^*)$ | 3.22     | 3.53           | 4.74  | 5.20    | 4.64 |
| Furan             | $B_2(\pi \rightarrow \pi^*)$ | 4.15     | 4.25           | 6.65  | 6.85    | 6.57 |
| Pyrrole           | $B_2(\pi \rightarrow \pi^*)$ | 4.45     | 4.52           | 6.88  | 7.07    | 6.85 |
| Pyridine          | $B_1(n \rightarrow \pi^*)$   | NC       | 4.22           | NC    | 4.65    | 4.74 |
| Pyridazine        | $B_{3u}(n \rightarrow \pi^*)$ | 2.76     | 2.78           | 3.35  | 3.34    | 3.57 |
| s-tetrazine       | $B_2(\pi \rightarrow \pi^*)$ | 1.39     | 1.63           | 1.83  | 2.07    | 2.15 |
| Acetone           | $A_2(n \rightarrow \pi^*)$   | 3.71     | 3.80           | 3.98  | 4.08    | 4.11 |
| Formamide         | $A''(n \rightarrow \pi^*)$   | NC       | 5.03           | NC    | 5.25    | 5.42 |
| Acetamide         | $A''(n \rightarrow \pi^*)$   | 5.20     | 5.15           | 5.45  | 5.37    | 5.46 |
| Propanamide       | $A''(n \rightarrow \pi^*)$   | 5.64     | 5.19           | 6.07  | 5.40    | 5.49 |
| Thymine           | $A'(\pi \rightarrow \pi^*)$  | 3.51     | 3.59           | 5.50  | 5.73    | 5.48 |
| Uricil            | $A''(n \rightarrow \pi^*)$   | 4.28     | 3.76           | 5.66  | 5.86    | 4.66 |
| Imidazole         | $A'(\Pi \rightarrow \pi^*)$  | NC       | 4.75           | NC    | 7.15    | 6.89 |
| E-Octatetraene    | $B_{2u}(\pi \rightarrow \pi^*)$ | 1.93     | 1.92           | 4.32  | 3.69    | 4.22 |

MAE from Lit. results [30]: 0.27, 0.23
ME from Lit. results [30]: −0.16, −0.07
MAE from TBE-2 results [47]: 0.38, 0.45
ME from TBE-2 results [47]: −0.05, −0.09

*a MAE and ME values from RO-PBE0 calculations using 6-31G* are 0.37 and −0.22 respectively [21].

*b MAE and ME values from RO-LCω-PBE0 calculations using 6-31G* are 0.31 and −0.05 respectively [21].

†NC denotes “not converged”.

This corresponds to $E_{0S}$, from [30].

The use of a RS-operator $g(\gamma, r)$ such that,

$$
\frac{1}{r} = \frac{\tilde{g}(\gamma, r)}{r} + \frac{\tilde{g}(\gamma, r)}{r},
$$

where $\tilde{g}(\gamma, r)$ represents the complementary RS-operator. Here, $\gamma$ is an important RS parameter which has a pivotal role to adjust the contribution of HF exchange between short-range (SR) and long-range (LR) region, for a specific $g(\gamma, r)$. In particular, we consider the long-range correction (LC) scheme presented in [61], given by,

$$
E_{xc}^{\text{LC}} = E_{\text{dfa, sr}}^{\text{xc}}(\gamma) + E_{x, lr}^{\text{xc}}(\gamma) + E_{c, dfa}^{\text{xc}}
$$

$$
g(\gamma, r) = \text{erf}(\gamma r) \quad \text{and} \quad \tilde{g}(\gamma, r) = \text{erfc}(\gamma, r).
$$

It uses full HF exchange at LR region ($E_{x, lr}^{\text{xc}}$) in contrast to the conventional hybrid functionals, and successfully mitigates the lack of having correct asymptotic behaviour of exact
**TABLE IV: Excitation energies (in eV) of linear acenes from “virial theorem”**.

| Number of rings | $E_{0T}$  | $E_{0S}$ (PR$_3$) | Lit.† |
|-----------------|-----------|-------------------|-------|
|                 | B3LYP     | LC-BLYP           |       |
| 2               | 3.24      | 3.56              | 4.75  | 5.22 | 4.65 |
| 3               | 2.22      | 2.46              | 3.71  | 4.43 | 3.58 |
| 4               | 1.55      | 1.81              | 2.85  | 3.41 | 2.75 |
| 5               | 1.08      | 1.32              | 2.30  | 2.96 | 2.22 |
| 6               | 0.75      | 0.98              | 1.89  | 2.50 | 1.82 |

MAE from Lit. results [30] | 0.09 | 0.70 |
ME from Lit. results [30] | −0.10 | −0.70 |
MAE from experimental results [62] | 0.09 | 0.60 |
ME from experimental results [62] | −0.16 | −0.60 |

† This corresponds to $E_{0S}$, from [30].

Exchange at LR region present in hybrid family. But at the same time, it fails to achieve the standard energy calculations at the level of hybrid ladder. To be consistent with B3LYP, we utilize the particular LC-BLYP (with $\gamma = 0.33$), where interelectronic distance dependent B88 exchange [61] (in place of original B88 exchange [52]) and LYP [53] semi-local correlational functionals were used as $E^{\text{dia, sr}}(\gamma)$ and $E^{c, \text{dia}}$ respectively.

The calculated $E_{0S}$, as computed above, are compared with the all-electron results from Becke’s “virial theorem” method [30] along with respective MAE and ME values for two concerned functionals at the bottom. As in Table II, here also, due to the proximity of PR$_3$ results to that of TD-B3LYP, it suffices to report only PR$_3$ excitation energies. For sake of completeness, this also accompanies the lowest triplet excitation energies. Note that, for three molecules (pyridine, formamide, imidazole), the spin-restricted triplet calculations did not lead to convergence in the default options, for B3LYP. Hence they are not included in MAE and ME evaluations. It is evident that the performance of B3LYP (excitation energies are overestimated) is usually much more consistent than that of LC-BLYP. A systematic error cancellation may be involved in these calculation. On the other hand, the MAE value of LC-BLYP (0.23) is slightly lower than that of B3LYP (0.27), but did not outperform extensively as was expected from the foregoing discussion. Initially, one may draw the conclusion that the effect of full HF exchange at long-range does not have significant impact on excitation energies, despite the fact that it enriches the behavior of frontier orbitals involved in $K_{ij}$ calculations. Such discrepancy has occurred due to the fact that we assume $\gamma$
is independent of system size. However, it has been shown that it is possible to attain a higher level of performance provided one treats $\gamma$ as a system-dependent parameter (functional of $\rho$) tuned from first principles [44]. It is our belief that, an optimally tuned $\gamma$ (perhaps in the spirit of size dependency principle) will provide better results than the conventional hybrid and RS hybrid functionals. Note that, the less dramatic performance of LC-BLYP in both ground and triplet excited state has negligible effect on singlet excitation energy, relative to the STS term, which is in harmony with the observation made in [31]. Additionally, we have also estimated MAE and ME values from TBE-2 results [47]. It is found that these in Table III (with respect to TBE-2), do not alter significantly from their counterparts in Becke [30], which was of course, expected. So the basic conclusions will remain same. Furthermore, we have also quoted restricted open-shell KS (ROKS) error statistics (MAE and ME) for different XC functionals in footnote of Table III from [21]. They are all-electron ROKS lowest vertical excitation results computed using 6-31G* basis set. Our performance (MAE and ME from TBE-2) are in harmony with ROKS MAE and ME values. A similar qualitative trend is also found for linear acenes, given in Table IV, where again both $E_{0S}$ as well as $E_{0T}$, are given. In this occasion, the better compatibility of MAE and ME values signify that the error is systematic in nature in case of LC-BLYP. But these are always overestimated and the extent is larger than B3LYP. This may arise due to a greater involvement of $\gamma$ on system size; hence possibly requires an optimally tuned $\gamma$ in these cases. This demands further elaborate investigation, and may be considered in future works.

V. FUTURE AND OUTLOOK

We have examined the feasibility and practicability of a simple yet accurate time-independent DFT approach for realistic calculation of single excitation energies through DFT in CCG. This was applied to a host of organic chromophores and linear acenes having $\pi$ network. The excitation energies were estimated using two representative set of functionals—each from respective hybrid and RS hybrid within a pseudopotential approximation. The obtained results for all these species, from virial theorem are in quite good agreement with the reference results. It can be easily extended to the excitation energies in charge transfer complexes [32, 63] as well. Its application with RS hybrid, hyper, as well as local hybrid XC functionals would further enhance the scope in a wide range of systems. It may also be
desirable to examine its performance in various excited configurations other than the lowest excited state. But this may pose some computational challenge regarding the state-specific SCF convergence. In such occasions, some solution, as suggested in [17, 22–24, 64], may offer some valuable guidelines. To conclude, the present work has demonstrated the usefulness of a simple scheme in predicting optical gap in organic chromophores within a CCG-DFT.

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