

Extended Huckel Tight-Binding Approach to Electronic Excitations

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Abstract

In this work we propose the application of a self-consistent Extended Huckel Tight Binding method in the computation of the absorption optical spectrum of molecules within the linear response time dependent Density Functional formalism. The Extended Huckel Tight Binding approach (EHTB) is presented as an approximation to the Kohn-Sham energy functional. The method is applied to the computation of excitation energies and oscillator strengths of benzene, pyridine, naphthalene, diazines, and the fullerenes: $C_{60}(I_h)$, $C_{70}(D_{5h})$ and $C_{80}(D_2)$. The very good agreement with experimental data is very encouraging and suggests the possibility of using the EHTB as an efficient and reliable computational tool to study optical properties of a wide variety of molecular systems.

I. INTRODUCTION

In the last decade, the Tight-Binding (TB) approach has become the most promising electronic structure tool for the simulation of ground state properties in large systems, particularly nanostructured materials, molecular devices, and biomolecules. Some representative examples of the intense activity in the development of efficient and transferable TB methodologies are the NRL-TB total energy method [1], the Density Functional TB method (DFTB) [2], the *ab-initio* TB method (AITB) [3], the non-conventional TB method [4], the environment dependent TB method [5] and the orthogonal and non-orthogonal TB method of Voityuk [6,7]. These methodologies become even more attractive due to recent developments in computationally efficient order-N algorithms and the use of parallel architectures [8,9].

Alternatively, the Extended Huckel TB (EHTB) approach [10-12] and related methodologies [13-16] are very useful in the understanding of the electronic structure of molecules, solids and crystals [17] due to their simplicity and the chemical insight they provide. The flexibility of the EHTB approximations renders an accuracy in the calculation of ground state molecular properties comparable with that of modern TB theories [1-7], providing at the same time an interpretation framework similar to that in the original EH formulation. Also, in this approximation, the original scaling with distance of the EH Hamiltonian matrix elements (the Wolfsberg-Helmholz approximation) has been revised to solve problems due to *counterintuitive orbital mixing* [12] and distance dependence [13-14]. In addition, it has been found that the original EHTB method fails to yield good potential energy surfaces. This problem has been addressed in the ASED method of Anderson [13-14] which adds a two-body electrostatic energy correction. Self-consistent charge corrections have also been introduced in the valence ionization orbital energies to include the effects of charge transfer [15]. Moreover, reliable EHTB parameterization based on Density Functional Theory (DFT) first principles methods has recently been developed for transition metals [18] and H, C and O elements [19].

While impressive advances have been reached in the description of ground state structures and energetics by using TB and EHTB approximations, developments involving the description of excited states have not met with similar success. Likewise, applications of TB and EHTB to problems where the knowledge of the properties of excited states is important,

like the computation of optical properties of materials, are not common. In particular, the application of these methodologies to the description of electronic optical spectra is still an evolving problem where accurate information regarding excited state properties is required in the parameterization of the Hamiltonian. When predicting optical spectra, some approximations have been proposed for the computation of excitation energies and oscillator strengths in the realm of TB methods. The most crude one involves the use of the vertical excitation between holes (occupied) and particles (holes) states. This approximation fails in systems with strong interactions between quasi-particles leading to collective excitations such as plasmon resonances observed in clusters. Other methodologies have emerged in the context of many-body theories. Thus, recently, using Hedin’s GW approximation, in which the self-energy is given as the product of the Green function (G) and the screening interaction (W) [20], the DFTB method has been employed to study polyacenes ($C_{4n+2}H_{2n+4}$) up to $n = 30$ [21]. Many-body effects have also been incorporated by using time dependent density functional theory (TDDFT) [22-24]. In particular, an approach within the linear response version of TDDFT (LR-TDDFT) [25] has recently been developed in the context of the self-consistent charge DFTB (SC-DFTB) method [26]. This scheme, called the “ γ -approximation” [26] has been reported to yield reasonable agreement with experiments and first-principle DFT calculations for excitations where the final state is singlet in organic molecules, fullerenes and polyacenes. In addition, this approximation has been benchmarked with respect to TDDFT in the case of a set of small molecules [27]. Despite this success, the approximations used in the frame of TDDFT for the evaluation of the Coulomb-exchange-correlation kernel lead to less satisfactory results in the prediction of singlet-triplet transitions between states of different symmetry (as is the case of $n \rightarrow \pi^*$ transitions), where the ground and excited states are incorrectly predicted to be degenerate [26]. Nevertheless, these limitations do not significantly affect the final predicted optical spectra, given that for singlet-triplet excitations, the oscillator strength is zero (in absence of spin-orbit coupling) and very small for transitions between states of different symmetries.

The TB approach to LR-TDDFT is based on two main assumptions: (i) using an ordinary ground-state TB calculation (DFTB as in Ref. [26]), one can obtain a description similar to that rendered from the local density approximation DFT (LDA-DFT) for the orbital difference between hole and particle states, and (ii) the TDDFT Coulomb-exchange-correlation kernel can be modeled with the same kind of approximations as in ground state

TB (at least at the DFT-LDA approximation). In this work, we make use of these two assumptions to apply the self-consistent EHTB method to the calculation of electronic excitations. With this in mind, in Sec. II we introduce the model EHTB Hamiltonian within the framework of DFT theory based on the premise that the qualitatively correct order of the energy and symmetry of the ground state Kohn-Sham orbitals can be recovered using a zero order Extended Huckel Hamiltonian which incorporates, in a self-consistent manner, the Coulombic effects through the off-diagonal two-center Hamiltonian elements, and the exchange-correlation effects in the on-site diagonal and off-diagonal part. Due to the success of the EHTB method in the qualitative understanding of many aspects of molecular structure problems [17,28], we think that this is a quite reasonable assumption. In Sec. III we present our approach to the LR-TDDFT based on the γ -approximation [26], providing an analysis of the approximations introduced in the calculations of excitation energies and oscillator strengths. The main contribution of the present work is the incorporation, through the use of spectroscopic Slater-Condon factors, of the on-site off-diagonal elements of the Coulomb-Exchange-Correlation coupling matrix, in a fashion similar to that employed in the semiempirical ZINDO method [29-30]. As in the case of the EHTB Hamiltonian, no exhaustive parameterization is performed. Therefore, at this point, we can only expect our results to be qualitatively correct and provide the foundation for a proof of concept of the proposed formalism. In Sec. IV, the present methodology is tested for benzene, pyridine, naphthalene, pyridazine, pyrimidine and pyridazine. For this set of molecules, the experimental spectra are well known, and many LR-TDDFT and semiempirical methodologies have been benchmarked. Since excitations to Rydberg states are out of the scope of the present TB method, only valence excitations are considered. In Sec. V we apply this methodology to fullerenes. This problem has been the subject of many experimental and theoretical studies. One interesting aspect of this problem is the observation of collective effects associated with the π -plasmonic resonances. Finally, Sec. VI presents the concluding remarks of this work.

II. THE SELF-CONSISTENT EXTENDED HUCKEL TIGHT-BINDING METHOD

The Self-Consistent EHTB (SC-EHTB) method is an approximation to the second-order expansion of the DFT total energy functional [2,31-32] (in atomic units),

$$E = \sum_i^{occ} 2 \int \psi_i \hat{H}^0 \psi_i d\mathbf{r} + \frac{1}{2} \int \int' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho_0 \delta \rho_0'} \right) \delta \rho \delta \rho' d\mathbf{r} d\mathbf{r}' + E_{REP}(\rho_0). \quad (1)$$

In this expression, ρ_0 is a known reference density, in which the one-electron Kohn-Sham type Hamiltonian, \hat{H}^0 , is evaluated, and $\{\psi_i\}$ are the Kohn-Sham orbitals, which are the same for spin α and β . The second term in Eq. (1) is the second-order correction to \hat{H}^0 , due to charge-density fluctuations with respect to ρ_0 , $\delta \rho = \rho(\mathbf{r}) - \rho_0(\mathbf{r})$. This term depends on the Coulomb-exchange-correlation kernel evaluated over $\delta \rho$ and $\delta \rho'$ (which denotes $\delta \rho(\mathbf{r})$ and $\delta \rho(\mathbf{r}')$). The last term, $E_{REP}(\rho_0)$, contains the Coulomb-exchange-correlation double-counting terms of the sum over eigenvalues as well as the ion-ion repulsion, and only depends on the reference density ρ_0 . This last term is approximated as a sum over atom-pairs of a short-range repulsive potential. For sake of simplicity, we consider only closed shell systems, however, extension to open shell systems is straightforward [33].

To derive the SC-EHTB equations, the KS orbitals, are expanded into a basis of Slater-type orbitals (STO), $\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$. The \hat{H}^0 matrix elements of Eq. (1), are calculated using the Extended Huckel approximation [10-17]: the diagonal elements, $H_{\mu\mu}^0 = \int \phi_{\mu} \hat{H}^0 \phi_{\mu} d\mathbf{r}$, are taken as the valence state ionization energies ($VSI E_{\mu}$) of orbital μ , and the off-diagonal elements, $H_{\mu\nu}^0$, are calculated using the Wolfsberg-Helmholtz formula,

$$H_{\mu\nu}^0 = \int \phi_{\mu} \hat{H}^0 \phi_{\nu} d\mathbf{r} = \frac{1}{2} K_{EH} (H_{\mu\mu}^0 + H_{\nu\nu}^0) S_{\mu\nu}. \quad (2)$$

where, $S_{\mu\nu}$ is the overlap integral over the atomic basis set, and the K_{EH} constant is evaluated using the weighted distance-dependent expression of Calzaferri and coworkers [14,34]:

$$K_{EH} = 1 + [\kappa + \Delta^2 - \Delta^4 \kappa] e^{-\delta(r_{\alpha\beta} - d_0)}, \quad (3)$$

with

$$\Delta = \frac{H_{\mu\mu}^0 - H_{\nu\nu}^0}{H_{\mu\mu}^0 + H_{\nu\nu}^0}. \quad (4)$$

In Eq. (3), $r_{\alpha\beta}$ denotes the distance between atoms α and β where the μ and ν orbitals are centered, d_0 is the sum of the μ and ν orbital radii evaluated as in Ref. [14], and κ and δ are

empirical parameters. Even though in the present work we adopt the values of $\kappa = 1.0$ and $\delta = 0.20 \text{ \AA}^{-1}$ as employed in references [14,34], it is important to mention that a suitable parameterization can be chosen in order to obtain a better fit to the experimental data. The computations of the $H_{\mu\nu}^0$ matrix elements were carried out using the EHTB parameters listed on Table I.

In order to evaluate the second term of Eq.(1), an approximate expression for the charge density fluctuation is employed. Within the frame of the basis set expansion employed here, the density fluctuation is given by,

$$\begin{aligned}\delta\rho(\mathbf{r}) &= \rho(\mathbf{r}) - \rho_0(\mathbf{r}) \\ &= \sum_{\mu} \sum_{\nu} \delta P_{\mu\nu} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}),\end{aligned}\quad (5)$$

where the fluctuation in the density matrix is defined as,

$$\delta P_{\mu\nu} = \sum_i 2(C_{\mu i} C_{\nu i} - C_{\mu i}^0 C_{\nu i}^0). \quad (6)$$

In order to decompose $\delta\rho(\mathbf{r})$ into atom-centered contributions, the orbital product $\phi_{\mu}^*(\mathbf{r})\phi_{\nu}(\mathbf{r})$ is expressed in the following form,

$$\phi_{\mu}^*(\mathbf{r})\phi_{\nu}(\mathbf{r}) = \begin{cases} F^{\alpha}(|\mathbf{r} - \mathbf{R}_{\alpha}|) & \text{if } \mu = \nu, \mu \in \alpha \\ \phi_{\mu}^*(\mathbf{r})\phi_{\nu}(\mathbf{r}) & \text{if } \mu \neq \nu, \mu \in \alpha, \nu \in \alpha \\ \frac{1}{2}[F^{\alpha}(|\mathbf{r} - \mathbf{R}_{\alpha}|) + F^{\beta}(|\mathbf{r} - \mathbf{R}_{\beta}|)]S_{\mu\nu} & \text{if } \mu \neq \nu, \mu \in \alpha, \nu \in \beta \end{cases} \quad (7)$$

where $F^{\alpha}(|\mathbf{r} - \mathbf{R}_{\alpha}|)$ is a function that describes a spherical radial approximation for the density on atom α . Notice that, for two orbitals centered in different atoms, the orbital product given by Eq. (7) is related to the well known Mulliken approximation, while for two different orbitals centered on the same atom ($\mu \neq \nu, \mu \in \alpha, \nu \in \alpha$, in Eq. (7)), the corresponding expression for the orbital product closely resembles the approximations used in the semiempirical Intermediate Neglect of Differential Overlap (INDO) method [29-30]. Using Eq.(7), $\delta\rho$ can be written as the sum of atom-centered contributions,

$$\delta\rho(\mathbf{r}) = \sum_{\alpha} \delta\rho_{\alpha}, \quad (8)$$

where,

$$\delta\rho_\alpha = \delta q_\alpha F^\alpha(|\mathbf{r} - \mathbf{R}_\alpha|) + \frac{1}{2} \sum_{(\mu>\nu)\in\alpha} (\delta P_{\mu\nu} \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) + \delta P_{\nu\mu} \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r})), \quad (9)$$

$$\delta q_\alpha = \frac{1}{2} \sum_{\mu\in\alpha} \sum_{\nu} (\delta P_{\mu\nu} S_{\mu\nu} + \delta P_{\nu\mu} S_{\nu\mu}). \quad (10)$$

The first term in Eq. (9) contains the Mulliken charge density fluctuation $\delta q_\alpha = q_\alpha - q_\alpha^0$, which arises from the monopolar approximation to the charge transfer contribution as incorporated in the DFTB method [2]. The second term involves a correction to the monopolar approximation for the fluctuations in the off-diagonal on-site charge density.

Incorporating all these results and neglecting all the two-center terms as well as the three and four on-site orbital integrals, the second term of Eq.(1) finally becomes,

$$\frac{1}{2} \left(\sum_{\alpha\beta} \delta q_\alpha \delta q_\beta \gamma_{\alpha\beta} + \sum_{\alpha} \sum_{(\mu>\nu)\in\alpha} \delta P_{\mu\nu}^2 \Gamma_{\mu\nu} \right), \quad (11)$$

with,

$$\gamma_{\alpha\beta} = \int \int' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho_0 \delta\rho_0'} \right) F^\alpha(\mathbf{r}) F^\beta(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (12)$$

$$\Gamma_{\mu\nu} = \int \int' \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho_0 \delta\rho_0'} \right) \phi_\mu^*(\mathbf{r}') \phi_\nu(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (13)$$

In Eqs. (11)-(13) the KS orbitals are assumed to be real ($P_{\mu\nu} = P_{\nu\mu}$). The functional $\gamma_{\alpha\beta}$ is approximated as in semiempirical methods by the expression [31,35],

$$\gamma_{\alpha\beta}(r_{\alpha\beta}) = \frac{f_g}{\left[\left(\frac{f_g}{\gamma_{\alpha\beta}(0)} \right)^m + r_{\alpha\beta}^m \right]^{1/m}} \quad (14)$$

where $r_{\alpha\beta}$ is the distance between the α and β centers and f_g is known as the Weiss factor [32]. The value $\gamma_{\alpha\beta}(0)$ is the limit for $r_{\alpha\beta} = 0$, that is, where the two centers α and β are located at the same point in space, and it is approximated as the average of the one-center integrals, $\gamma_{\alpha\beta}(0) = \frac{1}{2}(\gamma_{\alpha\alpha}(0) + \gamma_{\beta\beta}(0))$. In addition, the one center integrals, $\gamma_{\alpha\alpha}(0)$, can be approximated by the chemical hardness of the neutral atoms, given by

$$\gamma_{\alpha\alpha}(0) = \frac{\partial^2 E_\alpha}{\partial q_\alpha^2} \quad (15)$$

ignoring for the moment, the small dependence on the charge fluctuations. Values of $\gamma_{\alpha\alpha}(0)$ for the atoms considered in this work are listed in Table I. In the present calculations we used a value of $m = 1$, as in the formula of Mataga and Nishimoto [35], and the Weiss factor was set equal to 1.2 for $r_{\alpha\beta} \leq 4.0$ au, and 1.0 for large distances.

For the evaluation of $\Gamma_{\alpha\beta}$, additional parameters are required. These are taken, as in the ZINDO semiempirical method, from the spectroscopic values of the Slater-Condon integrals [30,36],

$$\begin{aligned}
\langle ss|pp\rangle &= F^0(ss) \\
\langle sp|sp\rangle &= \frac{1}{3}G^1(sp) \\
\langle pp|p'p'\rangle &= F^0(pp) - \frac{2}{25}F^2(pp) \\
\langle pp'|pp'\rangle &= \frac{3}{25}F^2(pp)
\end{aligned} \tag{16}$$

In this equation $\langle\mu\mu|\nu\nu\rangle$ represents the one-center two-electron integral, $\int\int\phi_\mu(\mathbf{r})\phi_\mu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\nu(\mathbf{r})\phi_\nu(\mathbf{r})d\mathbf{r}d\mathbf{r}'$. Using these approximate integrals we can evaluate, under the Hartree-Fock approximation for the exchange part, the integrals of Eq. (13). For the atoms considered in this paper, the relevant F^0 , F^2 and G^1 integrals are shown in Table I. It is worth noticing that the procedure described above takes into account the exchange contribution into Eq. (13), and as in any Hartree-Fock like formalism, it leaves out the on-site correlation.

The last term of Eq.(1) is the repulsion potential, which is crucial for the correct description of the potential energy surface. However, at fixed geometries, it does not affect the excitation energies (spectrum) and the KS orbitals. Given that in the present work we employ geometries optimized by first principle methodologies, we do not discuss in detail the approximations involved in the calculations of this term. Suffice it to say that recent tight-binding models based on the Extended Huckel scaling law show excellent results both for optimized geometries and energetics [18-19].

Applying the variational principle to Eq.(1), together with the previous approximations, we obtain a set of Kohn-Sham like equations of the form, $HC = SCE$. Since the elements of the KS Hamiltonian matrices depend on the density matrix through the atomic charges and the off-diagonal one-center density matrix elements, these equations must be solved

iteratively for the KS orbital coefficients, $C_{\mu i}$. In general, only few cycles are required for convergence.

The KS hamiltonian in the present methodology finally reads as,

$$H_{\mu\nu} = \begin{cases} -V S I E_{\mu} + \sum_{\beta} \gamma_{\alpha\beta} \delta q_{\beta} & \text{if } \mu = \nu, \mu \in \alpha \\ P_{\mu\nu} \Gamma_{\mu\nu} & \text{if } \mu \neq \nu, \mu \in \alpha, \\ H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_{\xi} (\gamma_{\alpha\xi} + \gamma_{\beta\xi}) \delta q_{\xi} & \text{if } \mu \neq \nu, \mu \in \alpha, \nu \in \beta \end{cases} \quad (17)$$

The main difference between this approach and standard SC-EHTB methodologies is the incorporation of self-consistency not only in the diagonal part, but more importantly, in the off-diagonal on-site and two-center integrals. This apparent subtle modification is crucial for a proper description of two-center Coulombic interactions and the on-site exchange part. The off-diagonal on-site exchange integrals are evaluated within the semiempirical framework, and their values are obtained from atomic spectra through Slater-Condon parameters. It is important to emphasize that the main assumption of the present methodology consists in considering *the SC-EH as an approximation to the KS density functional of Eq. (1)*.

III. EXTENDED HUCKEL APPROACH TO LINEAR RESPONSE TIME DEPENDENT DENSITY FUNCTIONAL

In Linear Response Time Dependent DFT (LR-TDDFT) the computation of electronic spectra consists of two parts. The first involves the calculation of the KS orbital spectra and the corresponding density matrix. Following this step, the LR-TDDFT formalism can be employed to compute the "true" excitation energies and oscillator strengths. If the solution of the SC-EHTB model of the previous section is interpreted as an approximation to the energy functional of Eq. (1), then the use of this TB approximation in conjunction with TDDFT is justifiable for the calculation of excitation energies. In TDDFT, the frequency w_I , associated with the excitation energies of the molecular interacting system corresponding to the poles of the frequency-dependent linear response, are obtained by solving the following eigenvalue problem [25] (for closed shells):

$$\sum_{ijkl\sigma} \left[w_{ij}^2 \delta_{ik} \delta_{jl} \delta_{\sigma\tau} + 2\sqrt{w_{jk}} K_{ij\sigma,kl\tau} \sqrt{w_{kl}} \right] F_{ij\sigma}^I = w_I^2 F_{kl\tau}^I \quad (18)$$

In this equation, σ and τ are spin indexes, i and k denote occupied orbitals (holes), j and l are virtual ones (particles), $w_{ij} = \epsilon_i - \epsilon_j$, is the energy difference between the one-particle KS orbitals, and $K_{ij\sigma,kl\tau}$ are the coupling-matrix elements. Within the so-called adiabatic local density approximation (ALDA) [22-25], the term $K_{ij\sigma,kl\tau}$ is given by

$$K_{ij\sigma,kl\tau} = \int \int' \psi_{i,\sigma}^*(\mathbf{r}) \psi_{j,\sigma}(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho_0 \delta \rho_0'} \right) \psi_{k,\tau}^*(\mathbf{r}') \psi_{l,\tau}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (19)$$

Making use of Eq. (7) for the basis set orbital products, and assuming closed shell systems ($\psi_{i,\alpha} = \psi_{i,\beta} = \psi_i$), together with the approximation that the transition density product $p_{ij\sigma} = \psi_{i,\sigma}^*(\mathbf{r}) \psi_{j,\sigma}(\mathbf{r})$ can be decomposed into atom-centered contributions, the following relations are obtained,

$$\begin{aligned} p_{ij\sigma} &= \psi_{i,\sigma}^*(\mathbf{r}) \psi_{j,\sigma}(\mathbf{r}) \\ &= \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{ij} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \\ &\approx \sum_{\alpha} q_{\alpha}^{ij} F_{\alpha}(\mathbf{r}) + \sum_{\alpha} \sum_{(\mu>\nu) \in \alpha} (P_{\mu\nu}^{ij} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r}) + P_{\nu\mu}^{ji} \phi_{\nu}^*(\mathbf{r}) \phi_{\mu}(\mathbf{r})) \end{aligned} \quad (20)$$

where

$$q_{\alpha}^{ij} = \frac{1}{2} \sum_{\mu \in \alpha} \sum_{\nu} (P_{\mu\nu}^{ij} S_{\mu\nu} + P_{\nu\mu}^{ji} S_{\nu\mu}), \quad (21)$$

and,

$$P_{\mu\nu}^{ij} = C_{\mu i} C_{\nu j}. \quad (22)$$

Under these approximations, and defining the magnetization as the difference of the spin densities, $m = \rho^{\alpha} - \rho^{\beta}$, the coupling matrix, Eq. (19), can finally be cast as

$$\begin{aligned} K_{ij\sigma,kl\tau} &= \sum_{\alpha\beta} q_{\alpha}^{ij} q_{\beta}^{kl} [\tilde{\gamma}_{\alpha\beta} + (2\delta_{\sigma\tau} - 1)m_{\sigma\beta}] \\ &+ \sum_{\alpha} \sum_{(\mu>\nu) \in \alpha} (P_{\mu\nu}^{ij} P_{\mu\nu}^{kl} + P_{\mu\nu}^{ij} P_{\nu\mu}^{kl} + P_{\nu\mu}^{ji} P_{\mu\nu}^{kl} + P_{\nu\mu}^{ji} P_{\nu\mu}^{kl}) \tilde{\Gamma}_{\mu\nu}. \end{aligned} \quad (23)$$

In Eq. (23),

$$\tilde{\gamma}_{\alpha\beta} = \int \int' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \right) F^{\alpha}(\mathbf{r}) F^{\beta}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (24)$$

$$m_{\alpha\beta} = \int \int' \frac{\delta^2 E_{xc}}{\delta m(\mathbf{r})\delta m(\mathbf{r}')} F^\alpha(\mathbf{r}) F^\beta(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (25)$$

$$\tilde{\Gamma}_{\mu\nu} = \int \int' \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \right) \phi_\mu^*(\mathbf{r}') \phi_\nu(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (26)$$

Let us recall that, following from Eq. (20), these expressions are valid as long the ground state density is spin-unpolarized and spin-orbit interactions are neglected, although, after the excitation, the system may become spin-polarized. The first two and third expressions resemble the γ approximation of DFTB [26]. Thus, the first one, $\tilde{\gamma}_{\alpha\beta}$, is equivalent to the functional of Eq. (12) with the final density ρ replacing the reference density ρ_0 . If the second derivative of the atomic energy with respect to the number of electrons (or the density) is known, then the on-site term, $\tilde{\gamma}_{\alpha\beta}$, can be evaluated on an atom with charge δq_α . If this charge fluctuation is sufficiently small so that it could be ignored, it is possible to use the values of the ground state γ integrals, and as a zero-order approximation, the following equality for diagonal and non-diagonal terms can be used: $\tilde{\gamma}_{\mu\nu} = \gamma_{\mu\nu}$. Furthermore, following Ref. (24), the magnetization integrals, $m_{\alpha\beta}$ given by Eq. (25) can be approximated, after neglecting charge-transfer effects, by their atomic GGA-DFT values taken from [26],

$$m_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial \epsilon_{\uparrow}^{HOMO}}{\partial n_{\uparrow}} - \frac{\partial \epsilon_{\downarrow}^{HOMO}}{\partial n_{\downarrow}} \right) \quad (27)$$

Similarly, the integrals in Eq. (26) involve atomic quantities that can in principle be obtained from DFT calculations. However, in keeping with the spirit of the semiempirical methods employed to evaluate Eq. (13), we compute this integral using the Slater-Condon spectroscopic parameters. In addition to this approximation, the approach adopted in this work rests on the assumption that the exchange integrals can be computed as in the case of conventional Hartree-Fock theory. The values of the parameters employed in the calculation of integrals (24)-(26) are also listed in Table I.

The excitation energies, w_I , are obtained from the eigenvalues of Eq. (18). Despite the considerable simplifications introduced in the evaluation of the TD-DFT response kernel, the direct diagonalization for systems with a large number of particle and hole states remains the main computational bottleneck. In order to circumvent these problems, some iterative approaches, based on the Lanczos [37-38] and the Davidson [39-40] algorithms have been proposed. In the present work, we make use of the SSYEVR routine in the LAPACK library

[41]. In this routine, the problem is reduced to a tri-diagonal form, and the eigenspectrum is computed using a relatively robust representation where Gram-Schmidt orthogonalization is avoided as far as possible. The spectrum is calculated in all cases within an energy window of 20 eV (let us point out that this value is larger than that required for the kind of valence space excitations considered in this work) [42].

Additional simplifications can be introduced if the coupling between different one-electron transitions is weak, which allows one to discard the matrix elements with $i \neq k$ and $j \neq l$ in Eq. (17). In this case, the problem is reduced to a series of 2×2 eigenvalue equations. The solutions are given by,

$$w_{ij}^{(S,T)} \approx \sqrt{w_{ij} [w_{ij} + 2 (K_{ij\uparrow,ij\uparrow} \pm K_{ij\uparrow,ij\downarrow})]} \quad (28)$$

In Eq. (28) the plus sign describes the singlet-singlet transitions, w_{ij}^S , while the minus corresponds to the singlet-triplet transitions, w_{ij}^T . This approximation is an attempt to correct the individual excitation energies from possible collective effects.

Once the excitation energies are known, the corresponding oscillator strength for the I th transition (in atomic units) can be obtained by the following expression [25],

$$f^I = \frac{2}{3} w_I \left(|\mathbf{x}^\dagger \mathbf{S}^{-1/2} \mathbf{F}_I|^2 + |\mathbf{y}^\dagger \mathbf{S}^{-1/2} \mathbf{F}_I|^2 + |\mathbf{z}^\dagger \mathbf{S}^{-1/2} \mathbf{F}_I|^2 \right) \quad (29)$$

In this equation, $(\mathbf{x}, \mathbf{y}, \mathbf{z})$ represent the transition dipole vectors, whose matrix elements are given by,

$$\begin{aligned} x_{ij} &= \langle \psi_i | x | \psi_j \rangle = \sum_{\alpha} x_{\alpha} q_{\alpha}^{ij}, \\ y_{ij} &= \langle \psi_i | y | \psi_j \rangle = \sum_{\alpha} y_{\alpha} q_{\alpha}^{ij}, \\ z_{ij} &= \langle \psi_i | z | \psi_j \rangle = \sum_{\alpha} z_{\alpha} q_{\alpha}^{ij}. \end{aligned} \quad (30)$$

where $\mathbf{R}_{\alpha} = (x_{\alpha}, y_{\alpha}, z_{\alpha})$, corresponds to the cartesian coordinates (in bohrs) of atom α in a fixed coordinate system, and q_{α}^{ij} are the Mulliken transition matrix population elements. The diagonal \mathbf{S} matrix is defined as

$$S_{ij\sigma,kl\tau} = \frac{\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l}}{(\epsilon_l - \epsilon_k)} > 0, \quad (31)$$

and \mathbf{F}_I is the eigenvector obtained by solving Eq. (18).

IV. ABSORPTION SPECTRA OF ORGANIC MOLECULES

In order to test the accuracy of the approximations described above, we have calculated the excitation energies for benzene, naphthalene and several nitrogen heterocycles such as pyridine, pyrazine, pyridimine and pyridazine. For these systems, the experimental absorption spectra for low-lying transitions are well known [43-47]. For the azines, we make use of the results reported in Ref. [43]. The molecular geometries computed at the PBE/PBE/6-311G** level of theory were taken from the NIST Computational Chemistry Comparison and Benchmark database [48]. Table II shows the experimental and calculated results for the low energy singlet-singlet electronic transitions, ω , and the oscillator strengths f_I . Table II also lists the values, in the weak interaction limit, of Eq. (28), ω^S , as well as the calculated orbital energy difference of the dominant transition, ω^0 . The results in Table II show that the approximated form of the excitation energy (ω^S) given by Eq. (28) accounts for most of the observed excitation energies. Relatively large deviations between ω^S and ω are observed only for the naphthalene molecule, indicating larger many-body collective effects in this molecule. Due to the fact that KS virtual orbitals, are evaluated over an N-electron system, while the Hartree-Fock virtual orbitals, are evaluated over a N+1 electron one, the differences between Kohn-Sham orbital energies, which enter in the diagonal of Eq. (18), are usually excellent approximations for the excitation energies [49-52], which is the reason behind the accuracy of the excitation energies in TDDFT related methodologies.

Calculation of the absorption spectra of benzene indicates that $\pi \rightarrow \sigma^*$ transitions over 7.0 eV do not exhibit appreciable intensities. A broad feature above 12.0 eV corresponding to $\sigma \rightarrow \sigma^*$ transitions is also observed. The computed results for the three dominant $\pi \rightarrow \pi^*$ transitions in benzene [43] are presented in Table II. The first two are dipole forbidden, while the third is allowed with an oscillator strength of 0.69. The results for the transitions to the $^1B_{1u}$ and $^1E_{1u}$ states are in good agreement with the experimental ones, and it is observed how the ω^S recovers most of the corrections. For the lower energy band, $^1B_{2u}$, the w_I is predicted to be 0.45 eV above the corresponding experimental value. Notice that the approximations used in our model lead to transition energies equal to vertical excitation energies. A similar trend is observed in the case of excitation to triplet states. The computed transition energies for the $^3B_{1u}$, $^3E_{1u}$ and $^3B_{2u}$ bands are 4.58 eV, 4.93 eV and 5.17 eV respectively (not shown in Table II), in good agreement with the corresponding

experimental values of 3.89 eV, 4.85 eV and 5.69 eV [44]. The reasonable agreement between the predicted transition energies for benzene and the corresponding experimental values is very encouraging and provides some confidence in the reliability of the formalism presented in this work.

Given that pyridine can be considered as a benzene molecule where a carbon atom has been replaced by nitrogen, it is reasonable to expect similarities between both electronic spectra[44]. The lone pair on nitrogen is responsible for the allowed $n \rightarrow \pi^*$ transition, predicted to have an excitation energy of 4.35 eV, in good agreement with the experimental value of 4.31 eV (See Table II). As expected, the next four bands are related to the three benzene $\pi \rightarrow \pi^*$ excitation bands. Thus, as shown in Table II, the bands corresponding to the 1B_2 and 1A_1 excitations in pyridine correlate with the corresponding $^1B_{2u}$ and $^1B_{1u}$ bands in benzene, while the degenerate pair 1A_1 and 1B_2 near 6.82 eV correlates with benzene’s $^1E_{1u}$ band at 6.93 eV. Similarly, the results in Table II show an excellent qualitative agreement between the computed and experimental oscillator strengths, indicating a relatively intense (and probably broad) band corresponding to 1A_1 and 1B_2 transitions in pyridine. In addition, the computed excitation energy for the 3B_1 ($n \rightarrow \pi^*$) transition was found to be in excellent agreement with the corresponding experimental value (4.25 vs 4.10 eV [44]). Finally, the calculation of pyridine’s absorption spectrum also reveals a series of transitions above 7.5 eV which despite being allowed, exhibit relatively small oscillator strengths (less than 0.01). As with the case of benzene and pyridine, a reasonably good agreement between the calculated and experimental excitation energies corresponding to $\pi \rightarrow \pi^*$ transitions in naphthalene and the diazines considered in this work is observed.

Overall, with the exception of the low energy $^1B_{3u}$ ($n \rightarrow \pi$) transition in pyrazine where our calculations underestimate the excitation energy by 1.25 eV, the results listed in Table II show a very good agreement between theory and experiment for the singlet-singlet excitations of the molecules considered in this study (mean absolute error = 0.23 eV). Similar deviations from experimental excitation energies have been obtained with most TDDFT functionals for sulfur-free organic compounds [28]. The relatively large deviation in the case of the $^1B_{3u}$ ($n \rightarrow \pi$) transition of Pyrazine, could be the result of the underestimation of the HOMO-LUMO gap by the SC-EHTB method using the parameters listed in Table I. In the case of the singlet-triplet excitation energies for benzene, pyridine and naphthalene, we find an absolute error of 0.55 eV with respect to the experimental values reported in the

literature. These errors are mainly due to an overestimation of the vertical energies and a bad representation of the magnetization kernel of Eq. (24). It is interesting to notice that even with a very limited parameterization, our results are similar to the ones obtained with the γ approximation of Ref. [26] using the DFTB. Given the nature of the approximations used and the little effort in the parameterization of the Hamiltonian, these results are very encouraging and suggest that the EHTB could become a highly reliable computational tool for predicting the absorption spectra of a wide variety of molecular systems.

V. ABSORPTION SPECTRA OF FULLERENES

Since their discovery, the electronic absorption spectra of fullerenes have attracted great interest. Experimental absorption data for energies below 7.0 eV are widely available in the literature for the most abundant fullerenes, C_{60} (I_h) and C_{70} (D_{5h}), not only in room temperature solutions, but also in the gas phase and solid state [53]. Bauerbschmitt has reported experimental and theoretical TD-DFT results of fullerenes of sizes between C_{60} and C_{80} [53]. These results show that important collective effects appear below 7.0 eV. The purpose of this section is to explore the utility of the present approach for the qualitative description of fullerene’s optical absorption spectra in the π -plasmonic regime (5.0-7.0 eV). Specifically, the method is used to calculate the UV-vis region allowed transitions of $C_{60}(I_h)$, $C_{70}(D_{5h})$ and $C_{80}(D_2)$.

In these calculations, the fullerene structures were taken from M. Yoshida’s Fullerene Structure Library [53]. The experimental energies in hexane solution reported in Ref. [53], as well as the calculated transition energies and oscillator strengths obtained in this work are shown in Table III. As observed in this table, the theoretical assignment of the bands, including their number and relative intensities is qualitatively consistent with the results reported in the experimental literature. However, in general it is found that the predicted peak energies are systematically blue shifted by 0.30-0.40 eV. A similar trend has also been reported by a theoretical study based on TDDFT calculations [53].

VI. CONCLUSIONS

We have implemented an Extended Huckel version of the LR-TDDFT, which allows a qualitative prediction of dipole allowed transitions of benzene, naphthalene, and nitrogen heterocycles with an error of near 0.26 eV. Very good agreement with experiment is also obtained in the case of C_{60} , C_{70} and C_{80} fullerenes.

The results obtained in this work suggest that the combination of EHTB with LR-TDDFT can provide a reliable tool for the prediction of electronic transition energies and oscillator strengths of local excitations like in $\pi \rightarrow \pi^*$ transitions in organic molecules. The extension of the model to the prediction of the optical properties of solids as well as nanoparticles is in progress.

The results in this work indicate that the present methodology can yield better estimated for some problems in which the standard TDDFT methodologies render substantial errors. Thus, for instance, charge-transfer excitations are usually underestimated using standard XC functionals, because they exhibit incorrect long range dependence with the distance; however, the empirical nature of the approximated kernel of Eq. (14) allows to recast in a better way these deficiencies inherent to the DFT functionals. In addition, the performance of the methods presented in this work suggests the possibility of applying it to the description of problems resembling those previously treated with similar methodologies [26,34].

Finally we briefly discuss the numerical efficiency of our approximations. The method scales as $N_{occ}^2 N_{vir}^2$, where N_{occ} is the number of holes and N_{vir} the number of particles that are used in the representation of the linear response coupling matrix, $K_{ij\sigma,kl\tau}$. Reduction of the computational time can be obtained by using a minimal valence basis set, with their corresponding integrals approximated by simple empirical functions. The limiting factor is therefore the construction of the response matrix which took 1500 min for the C_{80} cluster in a Pentium 3 1.80 GHz processor, which is at least an order of magnitude shorter than a typical first principle DFT calculation with a split-valence basis set, and comparable with a ZINDO-CIS semiempirical calculation.

Certain commercial software is identified in this paper in order to specify the computational procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to

imply that the software identified is necessarily the best available for the purpose.

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Table I. Values of the Extended Huckel Tight-Binding parameters used in this work.

Element	H	C	N
H_{ss}/eV	-11.60	-21.40	-26.60
H_{pp}/eV		-10.00	-11.60
$\xi_s=\xi_p$	1.300	1.625	1.750
$F^0(\text{ss})=F^0(\text{pp})$	12.85	11.11	12.01
$G^1(\text{sp})$		6.90	8.96
$F^2(\text{pp})$		4.51	6.46
$\gamma_{\alpha\alpha}(0)$	11.42	9.21	11.73
$m_{\alpha\alpha}^0$	-1.97	-0.62	-0.76

Table II. Singlet electronic excitation energies (in eV) and oscillator strength (in au) for model compounds. w^0 correspond to the calculated orbital energy difference of the dominant transition. w^S correspond to the value by Eq. (21). Experimental values were taken from refs. [44] and [46].

Molecule	Excitation	Exp.		Calc.			
		ω	f_I	ω	ω^S	ω^0	f_I
Benzene	$^1B_{2u} (\pi \rightarrow \pi^*)$	4.72	0.00	5.17	5.17	5.17	0.00
Benzene	$^1B_{1u} (\pi \rightarrow \pi^*)$	6.07	0.10	5.78	5.54	5.17	0.00
Benzene	$^1E_{1u} (\pi \rightarrow \pi^*)$	6.93	0.69	6.80	6.72	5.17	0.55
Pyridine	$^1B_1 (n \rightarrow \pi^*)$	4.31	0.00	4.35	4.34	4.31	0.00
Pyridine	$^1B_2 (\pi \rightarrow \pi^*)$	4.76	0.04	5.40	5.37	4.81	0.03
Pyridine	$^1A_1 (\pi \rightarrow \pi^*)$	6.17	0.10	6.11	6.10	5.22	0.01
Pyridine	$^1A_1 (\pi \rightarrow \pi^*)$	6.82	1.30	7.17	7.22	5.51	0.43
Pyridine	$^1B_2 (\pi \rightarrow \pi^*)$	6.82	1.30	7.20	7.20	5.89	0.39
Naphtalene	$^1B_{2u} (\pi \rightarrow \pi^*)$	3.97	0.01	4.06	3.75	3.41	0.02
Naphtalene	$^1B_{1u} (\pi \rightarrow \pi^*)$	4.65	0.10	4.31	4.00	3.91	0.05
Naphtalene	$^1B_{2u} (\pi \rightarrow \pi^*)$	5.89	1.00	5.74	5.48	4.37	1.12
Naphtalene	$^1B_{1u} (\pi \rightarrow \pi^*)$	6.13	0.30	5.81	5.44	4.88	0.03
Pyridazine	$^1B_1 (n \rightarrow \pi^*)$	3.30	0.01	3.49	3.49	3.48	0.00
Pyridazine	$^1A_1 (\pi \rightarrow \pi^*)$	4.90	0.02	5.41	4.99	4.57	0.01
Pyridazine	$^1B_2 (\pi \rightarrow \pi^*)$	6.30	0.10	6.43	6.28	5.95	0.09
Pyrimidine	$^1B_1 (n \rightarrow \pi^*)$	3.85	0.01	4.32	4.31	4.29	0.00
Pyrimidine	$^1B_2 (\pi \rightarrow \pi^*)$	4.99	0.05	5.20	4.90	4.81	0.04
Pyrimidine	$^1B_1 (n \rightarrow \pi^*)$	6.34	0.01	6.10	5.99	5.51	0.00
Pyrimidine	$^1A_1 (\pi \rightarrow \pi^*)$	6.48	0.16	6.26	6.20	6.01	0.02
Pyrimidine	$^1A_1 (\pi \rightarrow \pi^*)$	7.23	1.00	7.18	6.90	6.57	0.43
Pyrimidine	$^1B_1 (\pi \rightarrow \pi^*)$	7.23	1.00	7.21	7.01	6.60	0.37
Pyrazine	$^1B_{3u} (n \rightarrow \pi^*)$	3.82	0.01	2.57	2.57	2.56	0.00
Pyrazine	$^1B_{2u} (\pi \rightarrow \pi^*)$	4.68-4.81	0.10	4.20	4.10	2.99	0.11
Pyrazine	$^1B_{1u} (\pi \rightarrow \pi^*)$	6.31	0.15	6.04	5.90	5.03	0.07
Pyrazine	$^1B_{1u} (\pi \rightarrow \pi^*)$	7.52	1.00	7.10	5.99	6.50	0.10
Pyrazine	$^1B_{1u} (\pi \rightarrow \pi^*)$	7.52	1.00	6.28	5.85	6.55	0.12

Table III. Assignment of fullerenes absorption spectrum for optically allowed transitions. Experimental values were taken from reference [53].

Molecule	Exp.	Calc.	ω	f_I
	ω	Assignment		
$C_{60}(I_h)$	3.04	${}^1T_{1u}$	2.80	0.00
	3.78	${}^1T_{1u}$	3.50	0.14
	4.84	${}^1T_{1u}$	4.40	0.37
	5.46	${}^1T_{1u}$	5.01	0.01
	5.88	${}^1T_{1u}$	5.30	0.77
$C_{70}(D_{5h})$	1.95	${}^1E'_1$	1.60	0.00
	2.27	${}^1E'_1$	2.06	0.01
	2.62	${}^1E'_1$	2.12	0.05
	3.24	${}^1A''_2$	2.75	0.21
	3.70	${}^1E'_1$	3.21	0.09
	3.70	${}^1A''_2$	3.25	0.06
$C_{80}(D_2)$	1.43-1.57	1B_3	1.21	0.03
	2.06	1B_2	1.69	0.01
	2.06	1B_1	1.75	0.01
	2.47	1B_2	2.09	0.02
	2.61	1B_1	2.25	0.01