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# Tight-binding approach to time-dependent density-functional response theory

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In this paper we propose an extension of the self-consistent charge-density-functional tight-binding (SCC-DFTB) method [M. Elstner *et al.*, Phys. Rev. B **58**, 7260 (1998)], which allows the calculation of the optical properties of finite systems within time-dependent density-functional response theory (TD-DFRT). For a test set of small organic molecules low-lying singlet excitation energies are computed in good agreement with first-principles and experimental results. The overall computational cost of this parameter-free method is very low and thus it allows us to examine large systems: we report successful applications to $C_{60}$ and the polyacene series.

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## I. INTRODUCTION

While ground-state properties of large systems can be calculated quite routinely, the prediction of optical spectra is still a complex task. In the past years, accurate methods emerged in this field, like the $GW$ method of Hedin[1] and the solution of the Bethe-Salpeter equation[2] in the context of solid-state physics or quantum chemistry approaches based on sophisticated configuration-interaction (CI) schemes.[3–5] Although these methods provide an accuracy that comes close to what can be achieved in experiment, they are limited to rather small systems.

Recently, the time-dependent (TD) extension of density-functional theory[6–11] (DFT) received a lot of attention since it shares the numerical efficiency and predictive power with a ground-state formulation. Within this theory, the linear response of the electron density can be treated exactly.[13,14] The TD density-functional response theory (DFRT) results in a simple scheme to calculate optical properties of finite systems[8,9,11] and bulk materials (see, e.g., Ref. 12 and references therein). In fact, the computational scheme resembles a random-phase approximation[15] (RPA), but all the exchange-correlation (XC) effects are in principle correctly included. Using the local density approximation (LDA) or the generalized gradient approximation (GGA) for the XC functional, promising results have been obtained for organic molecules,[16–19] a series of fullerenes,[20] and a variety of metal and semiconductor clusters.[21–25] There are also attempts to use more sophisticated XC functionals.[14,26,27]

However, although the TD-DFRT is much cheaper in terms of computational cost than the aforementioned methods, simulations of nanosystems with hundreds of atoms are still out of reach. For such complex systems, semi-empirical tight-binding (SE-TB) approaches have been shown to work satisfactorily.[28] In the SE-TB methodology, the many-body problem is recast into an effective Hamiltonian in order to reproduce the electronic energy levels obtained from experiment or first-principles results.[29,30] However, for the calculation of the excitation energies, a single-particle (SP) approximation (as energy differences between virtual and occupied levels) cannot in general be used in confined systems because of the strong electron-hole interaction.[31–33]

Several methods and approximations[34–39] have been proposed to treat this interaction, most of them in the context of optical properties of semiconductor clusters. In these methods the results may yet depend on the quality of the used parameters and the choice of the dielectric constant model.[40] Recently, a TB approach to the Bethe-Salpeter equation has been developed and successfully applied to silicon nanocrystals.[41]

Similar SE-TB models are also widely used in quantum chemistry for studying optical properties of organic molecules:[42,43] these methods are fully parametrized at the Hartree-Fock/CI-singles level. In all these TB approaches, the many-particle effects are calculated starting from quasiparticle energy levels. In this article we present a TB method to calculate optical properties of finite systems starting from the LDA (GGA) energy levels, i.e., within the TD-DFRT.

Extending the SCC-DFTB method,[44,45] we present a simplified calculation scheme for the TD-DFRT coupling matrix.[8,9] This scheme, which we will refer to as the $\gamma$ *approximation*, is numerically as efficient as the SE-TB methods, because no integral evaluations have to be done.

Before discussing the above-mentioned approximation in Sec. III we will first summarize the employed self-consistent charge-density functional tight-binding (SCC-DFTB) method in Sec. II. The accuracy of the $\gamma$ approximation is accessed in Sec. IV where we test the method on a set of organic molecules. Finally, in Sec. V we present applications to two more complex systems: $C_{60}$ and the polyacene series.

## II. SCC-DFTB

A detailed discussion of the SCC-DFTB scheme has been given elsewhere.[44,45] The model is derived from DFT by a second-order expansion of the DFT total energy functional with respect to the charge-density fluctuations $\delta\rho$ around a given reference density $\rho_0$:

$$E=\sum_i^{occ}\langle\psi^i|\hat{H}^0|\psi^i\rangle+\frac{1}{2}\int\int f_{uxc}[\mathbf{r},\mathbf{r}',\rho_0]\delta\rho\delta\rho'$$
$$-\frac{1}{2}\int\int\frac{\rho_0\rho_0'}{|\mathbf{r}-\mathbf{r}'|}+E_{xc}[\rho_0]-\int V_{xc}[\rho_0]\rho_0+E_{ii}, \tag{1}$$

where $\hat{H}^0=\hat{H}[\rho_0]$ is the effective Kohn-Sham Hamiltonian evaluated at the reference density, $\delta\rho$ and $\delta\rho'$ are shorthands for $\delta\rho(\mathbf{r})$ and $\delta\rho(\mathbf{r}')$, respectively, $\psi^i$ are Kohn-Sham orbitals, and

$$f_{uxc}[\mathbf{r},\mathbf{r}',\rho_0]=\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\left.\frac{\delta^2E_{xc}}{\delta\rho\delta\rho'}\right|_{\rho_0} \tag{2}$$

is the Coulomb-exchange-correlation kernel. Here $E_{xc}$ and $V_{xc}$ are, respectively, the exchange-correlation energy and potential, and $E_{ii}$ is the core-core repulsion energy.

To derive the total energy of the SCC-DFTB method, the energy contributions in Eq. (1) are further subjected to the following approximations: First, the Hamiltonian matrix elements $\langle\psi^i|\hat{H}^0|\psi^i\rangle$ are represented in a suitable set of localized atomic orbitals $\phi_\mu$,

$$\psi^i=\sum_\mu c_\mu^i\phi_\mu(\mathbf{r}). \tag{3}$$

To determine the basis functions $\phi_\mu$, we solve the atomic DFT problem by adding an additional harmonic potential $(r/r_0)^2$ to confine the atomic orbitals.[46,47] The Hamiltonian matrix elements in this linear combination of atomic orbitals (LCAO) basis, $H_{\mu\nu}^0$, are then calculated as follows: the diagonal elements $H_{\mu\mu}^0$ are taken to be the atomic eigenvalues and the nondiagonal elements $H_{\mu\nu}^0$ are calculated in a two-center approximation

$$H_{\mu\nu}^0=\langle\phi_\mu|\hat{T}+v_{eff}[\rho_\alpha^0+\rho_\beta^0]|\phi_\nu\rangle,\quad \mu\in\alpha,\quad \nu\in\beta$$

which are tabulated together with the overlap matrix elements $S_{\mu\nu}$ with respect to the interatomic distance $R_{\alpha\beta}$. Here, $v_{eff}$ is the effective Kohn-Sham potential and $\rho_\alpha^0$ are the reference densities of the neutral atoms $\alpha$.

Next, the charge-density fluctuations $\delta\rho$ are decomposed into atom-centered contributions $\delta\rho=\Sigma_\alpha\delta\rho_\alpha$ and $\delta\rho_\alpha$ is approximated by the monopolar term of a multipole expansion (see the Appendix):

$$\delta\rho_\alpha(\mathbf{r})\approx\Delta q_\alpha F_\alpha(\mathbf{r}), \tag{4}$$

where $F_\alpha(\mathbf{r})$ denotes a normalized spherical density fluctuation on atom $\alpha$ and $\Delta q_\alpha$ represents the Mulliken net charge on atom $\alpha$. The employed monopolar approximation accounts for the most important charge-transfer contributions.[44]

The second-order term in Eq. (1) then becomes

$$E_{2nd}=\frac{1}{2}\sum_{\alpha,\beta}^N\Delta q_\alpha\Delta q_\beta\gamma_{\alpha\beta},$$

where

$$\gamma_{\alpha\beta}=\int\int f_{uxc}[\mathbf{r},\mathbf{r}',\rho_0]F_\alpha(\mathbf{r})F_\beta(\mathbf{r}') \tag{5}$$

is introduced as shorthand notation and will be referred to as the $\gamma$ *functional*.

In the limit of large interatomic distances, the XC contribution vanishes within DFT and $E_{2nd}$ may be viewed as a pure Coulomb interaction between the point charges $\Delta q_\alpha$. In the opposite case, when the charges are located at one and the same atom, $\gamma_{\alpha\alpha}$ can be approximated by the chemical hardness $\eta_\alpha$,[48] or the Hubbard-like parameter $U_\alpha$: $\gamma_{\alpha\alpha}\approx2\eta_\alpha\approx U_\alpha$. Similar approximations are widely used in the previously reported SE-TB methods.[35–38,42,43] This on-site parameter can be calculated for any atom type within the DFT as the second derivative of the total energy of a single atom with respect to the occupation number of the highest occupied atomic orbital.[48] Using an interpolation formula,[44] the expression for $\gamma_{\alpha\beta}$ then only depends on the distance between the atoms $\alpha$ and $\beta$ and on the parameters $U_\alpha$ and $U_\beta$.

Within these approximations the XC effects in the $\gamma$-functional have been directly considered only for the on-site term. This is reasonable in both the LDA and GGA, for which the XC-functional contribution to the $\gamma$ functional is very short-ranged and decays as fast as the overlap of the $F$ functions.[49]

The remaining terms in Eq. (1), $E_{ii}$ and the energy contributions, which depend on $\rho_0$ only, are collected in a single energy contribution $E_{rep}$. This $E_{rep}$ is then approximated as a sum of short-range repulsive potentials, which depend on the diatomic distances.

With these definitions and approximations, the SCC-DFTB total energy finally reads

$$E_{tot}=\sum_i^{occ}\sum_{\mu\nu}c_\mu^ic_\nu^iH_{\mu\nu}^0+\frac{1}{2}\sum_{\alpha\beta}\gamma_{\alpha\beta}\Delta q_\alpha\Delta q_\beta+E_{rep}. \tag{6}$$

By applying the variational principle to the energy functional (6), one obtains the corresponding Kohn-Sham equations:

$$\sum_\nu c_\nu^i(H_{\mu\nu}-\epsilon_iS_{\mu\nu})=0\quad\forall\mu,i$$

$$H_{\mu\nu}=\langle\phi_\mu|H_0|\phi_\nu\rangle+\frac{1}{2}S_{\mu\nu}\sum_\zeta(\gamma_{\alpha\zeta}+\gamma_{\beta\zeta})\Delta q_\zeta,$$

which have to be solved iteratively for the wave function expansion coefficients $c_\mu^i$, since the Hamiltonian matrix elements depend on the $c_\mu^i$ due to the Mulliken net charges. In general, few cycles are required for convergence.

The repulsive pair potentials for $E_{rep}$ are constructed by subtracting the DFT total energy from the SCC-DFTB electronic energy [first two terms on the right-hand side of Eq.

(6)] with respect to the bond distance for a small set of suitable reference systems. It should be noted that the repulsive potential appears only in the total energy. It is required for geometry optimization but is not of interest for the calculation of optical properties which depend only on the Kohn-Sham orbitals and energies.

### III. THE $\gamma$ APPROXIMATION

The route to excitation energies within the TD-DFRT consists of two parts.[8,9] First, an ordinary self-consistent field (SCF) calculation has to be done in order to obtain the single-particle KS orbitals $\psi^i$ and the corresponding KS energies $\epsilon_i$. In a second step, the coupling matrix has to be built, which gives the response of the SCF potential with respect to a change in the electronic density. In the adiabatic approximation the coupling matrix takes the following form:[8,9]

$$K_{ij\sigma,kl\tau}=\int\int \psi^i(\mathbf{r})\psi^j(\mathbf{r})\times\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta^2E_{xc}}{\delta\rho_\sigma(\mathbf{r})\,\delta\rho_\tau(\mathbf{r}')}\right)\times\psi^k(\mathbf{r}')\psi^l(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}', \tag{7}$$

where $\sigma$ and $\tau$ are spin indices. We consider only closed-shell systems. The true excitation energies ($\omega_I$) are then found by solving the eigenvalue problem

$$\sum_{ij\sigma}[\omega_{ij}^2\delta_{ik}\delta_{jl}\delta_{\sigma\tau}+2\sqrt{\omega_{ij}}K_{ij\sigma,kl\tau}\sqrt{\omega_{kl}}]F^I_{ij\sigma}=\omega_I^2F^I_{kl\tau}, \tag{8}$$

where $\omega_{ij}=\epsilon_j-\epsilon_i$ ($i,k$ are occupied KS orbitals, whereas $j,l$ are unoccupied ones).

In the $\gamma$-approximation the coupling matrix (7) is treated as follows: We decompose the transition density between different orbitals $p^{ij}(\mathbf{r})=\psi^i(\mathbf{r})\psi^j(\mathbf{r})$ into atom-centered contributions $p^{ij}(\mathbf{r})=\Sigma_\alpha p^{ij}_\alpha(\mathbf{r})$. Similar to the derivation of the second-order term in the SCC-DFTB scheme [see Eq. (4)], $p^{ij}_\alpha$ is subjected to a multipole expansion and a monopole approximation (see the Appendix):

$$p^{ij}_\alpha(\mathbf{r})\approx q^{ij}_\alpha F_\alpha(\mathbf{r}), \tag{9}$$

where $q^{ij}_\alpha$ are the Mulliken atomic transition charges:

$$q^{ij}_\alpha=\frac{1}{2}\sum_{\mu\in\alpha}\sum_{\nu}(c^i_\mu c^j_\nu S_{\mu\nu}+c^i_\nu c^j_\mu S_{\nu\mu}). \tag{10}$$

The monopolar approximation in Eq. (9) is well justified for large interatomic distances since higher-order multipolar interactions decay more rapidly then the monopolar term. For short distances, on the other hand, additional terms may be needed, as discussed in the next section.

Next, we rewrite the functional derivative of the XC energy using the set of variables $\rho=\rho_\uparrow+\rho_\downarrow$ (the total density) and $m=\rho_\uparrow-\rho_\downarrow$ (the magnetization):

$$\frac{\delta^2E_{xc}}{\delta\rho_\sigma\,\delta\rho'_\tau}=\frac{\delta^2E_{xc}}{\delta\rho\,\delta\rho'}+(2\delta_{\sigma\tau}-1)\frac{\delta^2E_{xc}}{\delta m\,\delta m'}. \tag{11}$$

Equation (11) is valid if the ground-state density is spin unpolarized and spin-orbit interactions are neglected, since in this case mixed derivatives with respect to the density $\rho$ and the magnetization $m$ vanish.

TABLE I. Values for the parameters $U$ and $M$ used in this work, in eV. These values have been obtained by numerical atomic calculations, as explained in the text.

| Element | $U$ | $M$ |
|---|---|---|
| H | 11.425 | −1.970 |
| C | 9.921 | −0.618 |
| N | 11.725 | −0.694 |
| O | 13.481 | −0.759 |

The coupling matrix (7) now reads

$$K_{ij\sigma,kl\tau}=\sum_{\alpha\beta}q^{ij}_\alpha q^{kl}_\beta[\tilde{\gamma}_{\alpha\beta}+(2\delta_{\sigma\tau}-1)m_{\alpha\beta}], \tag{12}$$

where

$$\tilde{\gamma}_{\alpha\beta}=\int\int' f_{uxc}[\mathbf{r},\mathbf{r}',\rho]F_\alpha(\mathbf{r})F_\beta(\mathbf{r}'), \tag{13}$$

$$m_{\alpha\beta}=\int\int' \left.\frac{\delta^2E_{xc}}{\delta m(\mathbf{r})\,\delta m(\mathbf{r}')}\right|_{\rho}F_\alpha(\mathbf{r})F_\beta(\mathbf{r}'). \tag{14}$$

The last two expressions are then further approximated. The expression in Eq. (13) is formally equivalent to the $\gamma$ functional in Eq. (5) and it only differs by the actual density $\rho$ entering the kernel $f_{uxc}$. As in the SCC-DFTB formulation, the on-site term ($\tilde{\gamma}_{\alpha\alpha}$) can be approximated by an Hubbard-like term $\tilde{U}_\alpha$. This can be calculated as the second derivative of the total energy with respect to the occupation number of the highest occupied atomic orbital, but of an atom of charge $\Delta q_\alpha$ [see Eq. (4)]. However, we found that the dependence of the Hubbard term from the atomic charge is small: thus, at least for systems with small charge transfer, this difference can be ignored, leading to $\tilde{U}_\alpha\approx U_\alpha$. Then, using the same interpolation expression[44] as in the ground state for the two-center term, we obtain $\tilde{\gamma}_{\alpha\beta}=\gamma_{\alpha\beta}$.

Turning to the term involving the magnetization in Eq. (14), we take it to be strictly on-site because of its very short-ranged nature. This is consistent with the approximation made for the $\gamma$ functional. The integral itself is approximated by the quantity $M$, which like the Hubbard parameter, can be obtained from atomic DFT calculations [$M=\frac{1}{2}(\partial\epsilon^{HOMO}_\uparrow/\partial n_\uparrow-\partial\epsilon^{HOMO}_\uparrow/\partial n_\downarrow$] of a neutral atom: for reasons similar to the previous case, we neglect charge-transfer effects. The employed values for $U$ and $M$ for different elements are reported in Table I. These values have been obtained by GGA numerical atomic calculations.[50]

With these approximations, the coupling matrix in Eq. (12) can be easily constructed. The excitation energies obtained from Eq. (8) and the required singlet oscillator strengths can be calculated using[8]

$$f^I = \frac{2}{3}\omega_I \sum_{k=x,y,z} \left| \sum_{ij} \langle \psi^i | \mathbf{r}_k | \psi^j \rangle \sqrt{\frac{\omega_{ij}}{\omega_I}} (F^I_{ij\uparrow} + F^I_{ij\downarrow}) \right|^2, \tag{15}$$

where the transition-dipole matrix elements are

$$\langle \psi^i | \mathbf{r} | \psi^j \rangle = \sum_\alpha \mathbf{R}_\alpha q^{ij}_\alpha . \tag{16}$$

Considering the minimal basis set employed, systems with hundreds of atoms can be easily investigated. For very large systems, the bottleneck is the solution of the eigenvalue problem in Eq. (8), although the direct full-matrix diagonalization can be avoided using the Davidson's iterative subspace algorithm.[52] For the calculations of the lowest excited states, the size of the coupling matrix can also be drastically reduced: in fact, if the collective effects are not too strong, i.e., if the off-diagonal matrix elements in Eq. (12) are small, then only the inclusion of a small set of occupied and unoccupied Kohn-Sham (KS) orbitals is required. In this way, the optical spectrum of a system with 100 atoms can be obtained in few minutes on a common workstation.

Finally, we note that expression (12) can easily be implemented into any TB scheme. However, to obtain reliable results the response kernel must be used in conjunction with the proper LDA (GGA) KS orbital energy differences. We note further that the coupling correction are smaller than in quasiparticle approaches:[37,41] considering the TD-DFRT formulation in Eq. (7) we see that only exchangelike integrals appear and that the (screened) Coulomb integrals are replaced by the small ones from the XC-functional derivative (see, for example, Ref. 51).

## IV. RESULTS

### Organic molecules

In order to check the accuracy of our approximations, we calculated the vertical excitation energies for a set of small organic molecules. For these systems the absorption spectra are well known, and in addition, first-principles calculations are feasible. Since the optical properties of such molecules are very sensitive to the various approximations they can serve as a sound benchmark test. The test set contains only low-lying transitions with clear valence character since excitations to Rydberg states are of course out of the scope of our method.

Table II lists the results of our approach together with the experimental values and those obtained from first-principles TD-DFRT, as implemented in the GAUSSIAN 98 program.[53] For the latter we used the gradient corrected XC-functional B-PW91,[54,55] both in the SCF and response part of the calculation. The Gaussian basis set employed was 6-311 $+$G**,[56] which includes diffuse and polarization functions and can be considered sufficient for the transitions studied. All the calculations were done at optimized geometries at the respective level of theory. To classify the symmetry of the excited state wave function we followed the prescription given in Ref. 8. In addition to the true excitation energies ($\omega_I$), Table II also lists the SP energy differences ($\omega_{KS}$) of the most dominant transition in a CI-like expansion.[8,9]

Turning first to the first-principles results, we find a mean absolute error of 0.37 eV for the triplet and 0.36 eV for the singlet excitations. These values are of the same magnitude as those reported by Bauernschmitt and Ahlrichs[16] for other XC functionals on a smaller test set.

Considering now the results of the $\gamma$ approximation, we find a remarkably good performance, at least for the singlet excitations. The error of 0.38 eV is very close to the first-principles results. Having in mind the various approximations done in the ground-state as well as the response part of the calculation, the success of the method is encouraging.

We note that in our method the lower singlet/triplet transition energies are in general overestimated compared to the TD-DFRT results. This is mainly due to the fact that the $\omega_{KS}$ energies, from the SCC-DFTB ground-state calculation, are in general larger than the first-principles results. As a matter of fact, this shortcoming improves the final singlet energy in comparison with the experimental results: in fact the first-principles results are in general too low.[20] On the other hand, the accuracy of triplet excitation energies is less convincing: compared to experimental results we find an error of 0.64 eV. We also found a smaller coupling contribution for the triplet excitations than the first-principles results. For the triplet excitations only the magnetization part of the coupling matrix (12) is responsible for the shift away from the $\omega_{KS}$ values. This means that the employed on-site approximation for the magnetization kernel is too rigid and the inclusion of two-center terms is required. This can be done by the numerical evaluation of the exchange-correlation integrals in Eq. (14).

Another limitation of the $\gamma$ approximation is related to the monopolar approximation in Eq. (9). Inspection of Table II clearly shows that the $\gamma$ approximation is fine for $\pi\rightarrow\pi^*$ transitions but fails for $n\rightarrow\pi^*$ (or $\sigma\rightarrow\pi^*$) promotion. This is due to the fact that the Mulliken atomic transition charges in Eq. (10) are zero for this type of transition, thus leading to no coupling (i.e., the singlet and triplet transition energy are equal to each other and equal to $\omega_{KS}$). For an improvement the employed Mulliken approximation (see the Appendix) must be removed for the on-site terms: then the calculation of all the one-center Coulomb and XC integrals (which are beyond the monopolar term) is needed. Similar integrals are, for example, included in the intermediate neglect of differential overlap method.[43,57]

However, both of these improvements are beyond a simple tight-binding scheme, because they require numerical integration from wave functions. They also do not change the final optical spectra significantly, because the oscillator strength is zero for the triplet excitations (without spin-orbit coupling) and very small for $n\rightarrow\pi^*$ transitions.[58]

## V. APPLICATIONS

In order to further test the performance of our method, we now present applications to more complex systems, for

TABLE II. Calculated excitation energies $\omega_I$ within the $\gamma$ approximation in comparison with first-principles results and experiment. $\omega_{KS}$ is the SP energy difference of the most dominant transition. In parentheses the character of this transition is indicated. All energies are in eV.

| | | $\gamma$ approximation | | TD-DFRT | |
|---|---|---|---|---|---|
| Molecule/State | Expt. | $\omega_I$ | $\omega_{KS}$ | $\omega_I$ | $\omega_{KS}$ |
| Ethylene | | | | | |
| $^3B_{1u}(\pi\rightarrow\pi^*)$ | 4.40 [a] | 5.47 | 6.30 | 4.16 | 5.66 |
| $^1B_{1u}(\pi\rightarrow\pi^*)$ | 7.65 [b] | 7.81 | 6.30 | 7.44 | 5.66 |
| Propene | | | | | |
| $^3A'(\pi\rightarrow\pi^*)$ | | 5.24 | 5.94 | 3.95 | 5.26 |
| $^1A''(\sigma\rightarrow\pi^*)$ | | 7.05 | 7.05 | 6.36 | 6.37 |
| $^1A'(\pi\rightarrow\pi^*)$ | 7.19 [c] | 7.30 | 5.94 | 6.69 | 5.26 |
| Butadiene | | | | | |
| $^3B_u(\pi\rightarrow\pi^*)$ | 3.20 [d] | 3.72 | 4.21 | 2.83 | 3.88 |
| $^3A_g(\pi\rightarrow\pi^*)$ | 4.95 [d] | 5.62 | 6.07 | 4.91 | 6.09 |
| $^1B_u(\pi\rightarrow\pi^*)$ | 5.92 [d] | 5.55 | 4.21 | 5.43 | 3.88 |
| $^1B_g(\sigma\rightarrow\pi^*)$ | | 6.43 | 6.43 | 6.08 | 6.11 |
| $^1A_g(\pi\rightarrow\pi^*)$ | 5.80 [d] | 6.44 | 6.07 | 6.16 | 6.14 |
| $^1A_u(\sigma\rightarrow\pi^*)$ | | 5.59 | 5.59 | 6.36 | 6.36 |
| Cyclopropene | | | | | |
| $^3B_2(\pi\rightarrow\pi^*)$ | 4.16 [e] | 4.83 | 5.43 | 3.77 | 5.01 |
| $^1B_2(\pi\rightarrow\pi^*)$ | 6.45 [f] | 6.21 | 5.43 | 6.00 | 5.01 |
| Benzene | | | | | |
| $^3B_{1u}(\pi\rightarrow\pi^*)$ | 3.89 [g] | 4.69 | 5.28 | 3.90 | 5.07 |
| $^3E_{1u}(\pi\rightarrow\pi^*)$ | 4.85 [g] | 5.04 | 5.28 | 4.55 | 5.07 |
| $^3B_{2u}(\pi\rightarrow\pi^*)$ | 5.69 [g] | 5.28 | 5.28 | 4.87 | 5.07 |
| $^1B_{2u}(\pi\rightarrow\pi^*)$ | 4.89 [g] | 5.28 | 5.28 | 5.17 | 5.07 |
| $^1B_{1u}(\pi\rightarrow\pi^*)$ | 6.20 [g] | 5.65 | 5.28 | 5.91 | 5.07 |
| Pyridine | | | | | |
| $^3B_1(n\rightarrow\pi^*)$ | 4.10 [h] | 4.47 | 4.47 | 3.71 | 4.09 |
| $^3B_2(\pi\rightarrow\pi^*)$ | 4.84 [i] | 4.92 | 5.06 | 4.36 | 4.44 |
| $^1B_1(n\rightarrow\pi^*)$ | 4.51 [b] | 4.47 | 4.47 | 4.37 | 4.09 |
| $^1B_2(\pi\rightarrow\pi^*)$ | 5.00 [j] | 5.39 | 5.06 | 5.28 | 4.44 |
| $^1A_1(\pi\rightarrow\pi^*)$ | 6.45 [j] | 5.81 | 5.26 | 5.94 | 5.93 |
| $^1B_2(\pi\rightarrow\pi^*)$ | 7.23 [j] | 7.01 | 5.85 | 6.48 | 6.48 |
| $^1A_1(\pi\rightarrow\pi^*)$ | 7.23 [j] | 7.03 | 5.65 | 6.69 | 6.70 |
| Formaldehyde | | | | | |
| $^3A_2(n\rightarrow\pi^*)$ | 3.50 [k] | 4.54 | 4.54 | 3.09 | 3.58 |
| $^1A_2(n\rightarrow\pi^*)$ | 3.79 [k] | 4.54 | 4.54 | 3.83 | 3.58 |
| $^3A_1(\pi\rightarrow\pi^*)$ | 5.82 [k] | 7.26 | 8.05 | 5.61 | 7.33 |
| Ketene | | | | | |
| $^3A_2(\pi\rightarrow n)$ | | 4.40 | 4.40 | 3.30 | 3.61 |
| $^1A_2(\pi\rightarrow n)$ | 3.84 [l] | 4.40 | 4.40 | 3.71 | 3.61 |
| $^3A_1(\pi\rightarrow\pi^*)$ | | 6.18 | 6.62 | 5.14 | 6.12 |
| Propynal | | | | | |
| $^3A''(n\rightarrow\pi^*)$ | 2.99 [m] | 4.04 | 4.04 | 2.74 | 3.15 |
| $^1A''(n\rightarrow\pi^*)$ | 3.56 [n] | 4.04 | 4.04 | 3.37 | 3.15 |
| Glyoxal | | | | | |
| $^3A_u(n\rightarrow\pi^*)$ | 2.38 [b] | 2.42 | 2.42 | 1.53 | 1.93 |
| $^1A_u(n\rightarrow\pi^*)$ | 2.73 [b] | 2.42 | 2.42 | 2.14 | 1.93 |
| Abs. err. singlets (16 comp.) | | 0.38 | 0.83 | 0.36 | 0.84 |
| Sign err. singlets | | 0.05 | −0.51 | −0.24 | −0.78 |
| Abs. err. triplets (13 comp.) | | 0.64 | 0.96 | 0.37 | 0.66 |
| Sign err. triplets | | 0.57 | 0.89 | −0.36 | 0.43 |

[a] Reference 74.
[b] Reference 75.
[c] Reference 77.
[d] Reference 78.
[e] Reference 79.
[f] Reference 80.
[g] Reference 81.
[h] Reference 82.
[i] Reference 83.
[j] Reference 76.
[k] Reference 84.
[l] Reference 85.
[m] Reference 86.
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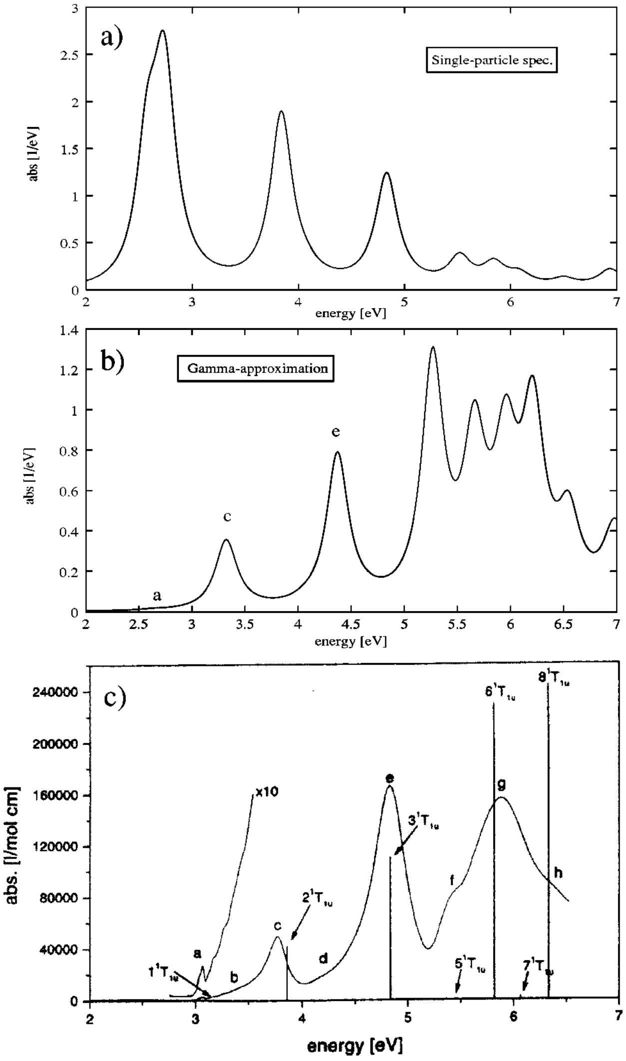

FIG. 1. (a) Calculated absorption spectrum of $C_{60}$ in the SP approximation: a Lorentzian broadening of 0.35 eV has been used. (b) Calculated absorption spectrum in the $\gamma$ approximation. (c) Experimental absorption spectrum in solution from Ref. 20. The superimposed lines are the TD-DFRT results, blueshifted by 0.35 eV. Figure 1(c) is reproduced with permission from Ref. 20, Copyright (1998) American Chemical Society.

which first-principles results are also available. We report calculations on the fullerene $C_{60}$ and the polyacene series.

### A. $C_{60}$

The fullerene $C_{60}$ has been the subject of many experimental[59–66] as well as theoretical[67–69] studies in the past. It may therefore serve as a good benchmark for our method, especially for the oscillator strengths that have not been examined up to now. Recently Bauernschmitt *et al.*[20] reported a combined theoretical/experimental study on a series of fullerenes from $C_{60}$ to $C_{80}$. They recorded the absorption spectrum in solution at room temperature as reported in Fig. 1(c). Shown as a line spectrum, the diagram also contains their TD-DFRT results. The authors uniformly blueshifted the obtained theoretical spectrum by 0.35 eV to facilitate the comparison with experiment.

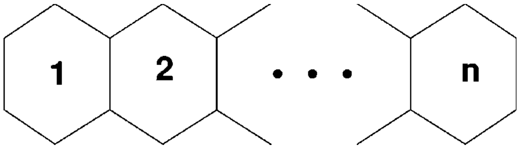

FIG. 2. Schematic viewgraph of the polyacenes: $n$ is the number of monomers.

In our study, we first optimized $C_{60}$ with the SCC-DFTB method. The obtained structure is in good agreement with experiment as shown in Ref. 47. To illustrate the important role of the coupling correction, we then calculated the absorption spectrum in the SP approximation. As can be seen in Fig. 1(a) this approach fails to reproduce the experimental spectrum. As is well known, the SP approximation cannot be used when the coupling between different electronic transitions becomes important, giving rise to collective effects. These effects are correctly described within the $\gamma$ approximation, as shown in Fig. 1(b). The lower excitations are drastically screened, shifting much oscillator strength to the 5–7 eV plasmonlike regime. The main features in the experimental spectrum are reproduced correctly, whereas the peak positions are systematically redshifted similar to the already mentioned TD-DFRT results.

### B. The polyacene series

The polyacenes ($C_{4n+2}H_{2n+4}$) are linear chains of anelated polycyclic aromatic hydrocarbons, as shown in Fig. 2. The monomer ($n=1$) is benzene. Naphtalene has $n=2$, anthracene $n=3$, tetracene $n=4$, and so on.

These systems are one of the most studied $\pi$-$\pi^*$ systems.[70,71] The optical spectrum of these molecules has been widely investigated in the past with semiempirical approaches.[72,73] The LDA is expected to work well for this highly homogeneous system, as confirmed by recent first-principles TD-LDA calculations.[19] Thus, these systems provide an excellent basis to check the performance of the $\gamma$ approximation also from a quantitative point of view.

In Fig. 3 we report the results of our method in comparison with first-principles[19] and experimental results (see references in Ref. 19), for polyacenes with $n=2$ up to $n=7$ (the results for benzene are already reported in Table II). We compare the lowest ($B_{2u}$) singlet and triplet excitation energies and the most intense singlet one ($B_{3u}$). The agreement is very good: for the reported singlet energies, the $\gamma$ approximation mean deviation from the first-principles results is only 0.08 eV. The mean deviation for triplet excitations is higher (0.22 eV), as previously noted. These results confirm the good performance of our method in describing $\pi$-$\pi^*$ systems.

## VI. CONCLUSIONS

In conclusion, we have implemented a tight-binding version of the TD-DFRT, which yields reasonable agreement for optical spectra with experiments and first-principles calculations at a highly reduced cost. The method presented (SCC-DFTB plus the $\gamma$ approximation) works without any

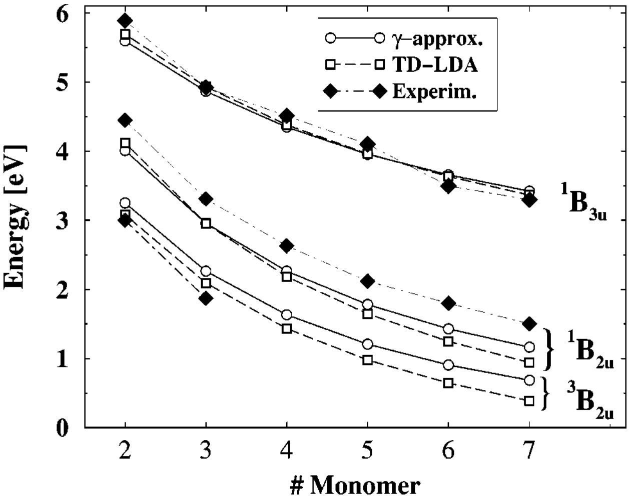

FIG. 3. Comparison between the $\gamma$ approximation, TD-LDA results, and experimental values for the polyacene series.

empirical parameter and can be used to study very large systems with hundreds of atoms and without symmetry, for which first-principles calculations are out of reach, or when a large number of different conformations has to be investigated.

Very good results have been obtained for $\pi$-$\pi^*$ systems. In this context, the method is useful to study biological and organic molecules which are of interest for optoelectronic applications. Further improvements of our method, concerning a better description of $\omega_{KS}$, triplet, and $n$-$\pi^*$ excitations, are in progress. Extensions of the method for calculations of optical properties of complex bulk materials are also envisaged.

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## APPENDIX

In this short appendix we briefly report conditions under which the Mulliken charges represent a monopolar approximation for atomic density fluctuations (4) and for atomic transition densities (9).

Consider a generical molecular orbital product expressed in a LCAO basis (3):

$$p^{ij}(\mathbf{r})=\psi^i(\mathbf{r})\psi^j(\mathbf{r})=\sum_{\mu}\sum_{\nu} c^i_\mu c^j_\nu \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}). \tag{A1}$$

When $i$ is an occupied orbital and $j$ unoccupied one then $p^{ij}(\mathbf{r})$ is a transition density, whereas the total charged density can be obtained from

$$n(\mathbf{r})=\sum_{i}^{occ} p^{ii}(\mathbf{r}). \tag{A2}$$

Applying the *Mulliken approximation*, which means $\phi_\mu(\mathbf{r})\rightarrow S_{\mu\nu}\phi_\nu(\mathbf{r})$, and symmetrizing, the expression (A1) can be directly decomposed in atomic centered contributions:

$$p^{ij}=\sum_{\alpha} p^{ij}_\alpha(\mathbf{r}),$$

where

$$p^{ij}_\alpha(\mathbf{r})=\sum_{\mu}|\phi_\mu(\mathbf{r})|^2 Q^{ij}_\mu, \quad \mu\in\alpha \tag{A3}$$

with

$$Q^{ij}_\mu=\sum_{\nu}\frac{1}{2}(c^i_\mu c^j_\nu S_{\mu\nu}+c^i_\nu c^j_\mu S_{\nu\mu}).$$

The square of a generic atomic orbital $\mu$ on atom $\alpha$ is

$$\begin{aligned}|\phi_\mu(\mathbf{r})|^2&=|R_{\alpha,l_\mu}(r)|^2\left|Y_{l_\mu,m_\mu}\left(\frac{\mathbf{r}}{r}\right)\right|^2\\&=|R_{\alpha,l_\mu}(r)|^2\sum_{lm}G^\mu_{lm}Y_{l,m}\left(\frac{\mathbf{r}}{r}\right),\end{aligned} \tag{A4}$$

where $R_{\alpha,l_\mu}(r)$ is the normalized radial part of the atomic orbital, $Y_{l,m}$ are normalized real spherical harmonics, and $G^\mu_{lm}$ is a Gaunt coefficient ($G^\mu_{lm}=\int Y_{l_\mu,m_\mu}Y_{l_\mu,m_\mu}Y_{l,m}d\Omega$).

Then we ignore the $l$ dependence of the radial part in $|R_{\alpha,l_\mu}(r)|^2$: this is a reasonable approximation for the valence orbitals. In this way the expression (A3) becomes

$$p^{ij}_\alpha(\mathbf{r})=\sum_{lm}Y_{l,m}\left(\frac{\mathbf{r}}{r}\right)|R_\alpha(r)|^2\sum_{\mu\in\alpha}G^\mu_{lm}Q^{ij}_\mu. \tag{A5}$$

The monopolar term is easily obtained because $G^\mu_{00}=1/\sqrt{4\pi}$:

$$p^{ij}_\alpha(\mathbf{r})|_{00}=\frac{1}{4\pi}|R_\alpha(r)|^2\sum_{\mu\in\alpha}Q^{ij}_\mu. \tag{A6}$$

Thus $(1/4\pi)|R_\alpha(r)|^2=F_\alpha(\mathbf{r})$ is a normalized spherical density distribution and $\Sigma_{\mu\in\alpha}Q^{ij}_\mu$ is exactly the expression in Eq. (10). From Eqs. (A2) and (A6), the monopolar approximation for the total density leads to the Mulliken charges.[44]

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