Natural Atomic Orbital Representation for Optical Spectra Calculations in the Exciton Scattering Approach

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ABSTRACT: The exciton scattering (ES) method allows efficient calculations of spectroscopic observables in large low-dimensional conjugated molecular systems. To compute the transition dipoles between the ground and excited electronic states, we should extract the ES dipole parameters from quantum chemistry calculations in simple molecular fragments. In this manuscript, we show how to retrieve these parameters from any reference quantum chemistry model that uses an arbitrary nonorthogonal and possibly overcomplete atomic orbital basis set. Our approach relies on the natural atomic orbital (NAO) representation, in which the basis functions are orthonormal and the atom-like character is preserved. We apply the ES approach, combined with the NAO analysis to optical spectra of branched phenylacetylene oligomers. Absorption spectra predicted by the ES method demonstrate close agreement with the results of direct quantum chemistry calculations, when the Time-Dependent Density Functional Theory (TD-DFT) being used as a reference. This testifies applicability of a variety of quantum-chemical techniques, where the NAO population analysis can be conducted, for the ES framework.

SECTION: Spectroscopy, Photochemistry, and Excited States
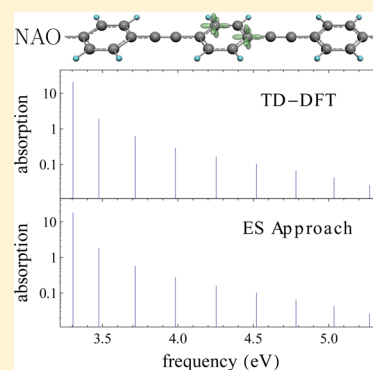
We recently developed the exciton scattering (ES) approach[1−6] for effective description of excited-state electronic structures in conjugated molecular networks featuring delocalized π-electronic system. The ES model is a multiscale method allowing us to compute accurately excited states of the entire structure from the results of quantum chemistry applied only to small molecular fragments. As a result, the absorption spectra can be accurately calculated with insignificant computational cost even for very large molecules.[6−8] The methodology is based on the quasiparticle nature of the electronic excitations in conjugated systems, which has been suggested by the fact that in the conjugated system the electron−hole binding energies are comparable to the optical gap,[9] which results in the exciton size to be on the nanometer length scale, by the electron−hole pair (exciton) interpretation of the optical response and scaling properties[10,11] as well as by the importance of exciton "center-of-mass" motion that has been recognized in interpreting the experimental data, obtained via the electron energy loss spectroscopy.[12,13]

In general, a branched conjugated molecule consists of linear segments connected by specific molecular branching centers (vertices).[14−23] Within the ES approach, electronic excitations in branched conjugated structures are viewed as states of quantum quasiparticles (excitons), which are represented by standing waves residing on the quasi-1D graph with edges and nodes corresponding to molecular linear segments and vertices, respectively. Even in large conjugated systems there is only a limited number of building block types: repeat units comprising linear segments and a few types of vertices. The concept of

building blocks in the ES picture allows for the characterization of exciton properties associated with any type of a building block, which makes the ES approach a multiscale modeling method; its key components are the scattering parameters.[2,3] For example, the exciton dispersion $\omega(k)$ determines the propagation of a particular exciton type along linear segments (and is a property of a repeat unit and the exciton mode quantum number), whereas the exciton behavior at the vertices is characterized by the corresponding scattering matrices $\Gamma(\omega)$. Consequently, finding the excitation energies ω and the exciton wave functions $\psi(x)$ (characterizing the "center of mass" motion of the bound electron−hole pair) is analogous to solving a "particle in a box" problem, with the only complication that the 1D "boxes", represented by the linear segments are connected at the vertices, and the actual boundary conditions are represented by the scattering matrices rather than some phenomenological arguments, and are frequency-dependent. This results in a set of ω-dependent homogeneous (without the right-hand-side) linear wave equations, referred to as the ES equations. All ES parameters can be obtained using traditional "reference" quantum-chemical excited states calculations in relatively simple molecular fragments associated with the building blocks of the original superstructure.[2,4,8] For example, the exciton spectrum $k(\omega)$ has been extracted as well as the reflection amplitude at the molecular termini, for

example, in molecular systems of phenylacetylene (PA), ladder-poly-*para*-phenylene (LPPP), and donor−acceptor molecules.[4,2] Furthermore, the scattering matrices of symmetric double, triple, and quadruple joints have been retrieved by utilizing their geometrical symmetries.[8] For the cases described above, the exciton dispersion and scattering matrices (which allow calculations of excited state transition energies in the supermolecular structures) can be readily obtained from precomputed excitation energies of small molecular fragments using reference semiempirical or ab initio technique. Here more detailed excited-state information available via quantum-chemical computation (such as the transition density matrices and/or the excited-state wave functions in the aforementioned molecular fragments) is not necessary.

Notably, computation of molecular optical spectra requires knowledge of the oscillator strengths associated with the optical transitions (equivalently the corresponding transition dipole moments). These quantities can also be calculated within the ES approach using the local excitation amplitudes, associated with repeat units and different molecular vertices, as an input. The energy-dependent ES transition dipole and charge parameters have been introduced to characterize the dependence of the transition dipoles and charges of individual building blocks on the local values of the exciton wave function $\psi(x)$ and the dual exciton wave function $\tilde{\psi}(x) = \text{div }\psi(x)/k$, respectively. Consequently, the total transition dipole of an excited state can be found by combining the contributions originating from all building blocks, that is, repeat units of the linear segments and molecular vertices.[3,6] As opposed to exciton spectra and scattering matrices, retrieving the dipole and charge parameters from quantum-chemical calculations does require the wave function information on the excited states in the molecular fragments, expressed in terms of the localized atomic orbital (AO) space, such as the transition density matrices, when the time-dependent Hartree−Fock (TDHF) or time-dependent density functional theory (TD-DFT) reference quantum-chemical techniques are employed for the excited-state computations. We previously extracted the ES dipole parameters in PA molecules[6,7] using the semiempirical collective electronic oscillator (CEO) method, which uses the TDHF approach combined with the INDO/S (intermediate neglect of differential overlap/spectroscopy) semiempirical Hamiltonian.[11] In the semiempirical theory, the AO basis is minimal and assumed to be orthogonal so that one can directly calculate the transition dipoles and transition charges of any part of the molecule from the corresponding transition density matrix and the dipole operator matrix.[24]

In contrast, accurate first-principle methods such as TD-DFT or wave-function-based approaches frequently use extensive finite basis sets of AOs represented by superpositions of Gaussians.[25−29] Such basis sets are generally nonorthogonal and frequently overcomplete. It is well-established that nonorthogonality of the AO basis leads to non-Hermitian terms in the Hamiltonian, which prevents accurate evaluation of physical quantities containing many-particle interactions.[30−32] In particular, it is expected that the original AO basis will be inadequate representation for extracting the ES dipole parameters. Consequently, a number of various transformations have been developed to correct the deficiencies described above, which became standard tools (e.g., used for various population analysis) in common quantum-chemical packages. In this study, we examine several representations to evaluate their quantitative performance for the ES approach.

The simplest Löwdin orthogonalization procedure, $|\phi_i^{(L)}\rangle = |\chi_i\rangle S^{-1/2}$, is commonly used to transform the AO basis $|\chi_i\rangle$ to the orthogonal basis $|\phi_i^{(L)}\rangle$, where $S_{ij} = \langle\chi_i|\chi_j\rangle$ is the corresponding overlap matrix.[30−34] However, the angular-symmetry of AOs in the original AO basis is not preserved under the Löwdin orthonormalization, which makes it problematic to evaluate transition dipoles for molecular components. More comprehensive natural bond orbital (NBO) method refers to a sequence of natural population analysis based on natural atomic orbital (NAO), natural hybrid orbital (NHO), NBO, and other representations. The NBO approach is well-known for accurately depicting the "natural Lewis structure" picture of the electronic wave function,[32,35] and NBOs have been viewed as a "chemist's basis set" for the compact expressions of atomic and bond properties.[32,36]

For example, the natural atomic population analysis is based on the formulation of a complete orthonormal basis set of NAOs from an arbitrary atom-centered orbital basis set.[37] Here the basis set of pre-NAOs $|\tilde{\phi}_i\rangle$ is first obtained as eigenvectors of the one-center symmetry-averaged blocks of the density matrix, thus preserving the exact free-atom angular momentum symmetries and rotational invariance in pre-NAOs.[37] The pre-NAOs are intra-atomic orthogonal $\langle\tilde{\phi}_i^A|\tilde{\phi}_j^A\rangle = \delta_{ij}$ (A denotes the atom); however, the orbital overlaps between different atomic centers are still nontrivial. Next, the orthonormal set of NAOs $|\varphi_i\rangle$ is derived by removing interatomic overlap from pre-NAOs by using the occupancy-weighted symmetry orthogonalization (OWSO) procedure[32] so that the natural atom-like feature of pre-NAOs is most preserved in the NAOs.[32,37] Consequently, the strict intra- and interatomic orthonormality of NAOs, $\langle\tilde{\phi}_i^A|\tilde{\phi}_j^B\rangle = \delta_{ij}\delta_{AB}$, satisfies the mathematical requirement of a Hermitian Hamiltonian (e.g., Fock or Kohn−Sham operator).[30−32,36]

Compared with the conventional Löwdin orthogonalization,[33] the NAOs inherit the atom-like character of angular momentum symmetries within the molecular environment.[36,37] Note that Löwdin orthogonalization is a special case of OWSO precedure where all orbitals are equally weighted and $T = S^{-1/2}$.[32] The NAO representation in the limit of periodic structures resembles the Wannier orbitals of solid-state physics localized on the lattice points. The NAO analysis can be used to evaluate physical properties related to electronic structures (e.g., population) on the level of AO.[36] Consequently, it is expected to be helpful for the ES method.

To extract the ES dipole parameters, we need to perform the NAO analysis of the quantum-chemical computation of the underlying molecular fragments to obtain the matrix T that transforms the AO basis set into the NAO basis set. The dipole matrix $\hat{\boldsymbol{\mu}}$ and transition density matrix ξ_ν for an excited state $|\nu\rangle$ in the AO space can be expressed in the NAO space as

$$\hat{\boldsymbol{\mu}}^{(NAO)} = T\hat{\boldsymbol{\mu}}^{(AO)}T^\dagger, \qquad \xi_\nu^{(NAO)} = T\xi_\nu^{(AO)}T^\dagger \qquad (1)$$

respectively. Because of the orthonormality and atomic angular symmetry in the NAO space, the transition density matrix ξ_ν^N of any molecular component N (e.g., the repeat unit) can be singled out as the corresponding diagonal block in the transition density matrix $\xi_\nu^{(NAO)}$ of the full fragment. Subsequently, the transition charge of a building block N is found as

$$q_\nu^N = \text{Tr}(\xi_\nu^N) \qquad (2)$$

instead of the ambiguous Mulliken population analysis $q_\nu^N = Tr(\xi_\nu S)$ in the AO space.

In the ES methodology, we define the transition dipole moment of a building block with respect to its internal coordinate system chosen identically for all building blocks of this type. Therefore, the dipole matrix of a building block can be extracted from a simple molecule sharing the same coordinate system with the addressed building block in the NAO representation. In practice, for example, the matrices of a PA repeat unit can be obtained from the NAO representation of diphenlyacetylene molecule, whereas those of molecular termini can be retrieved from the NAO of a phenyl ring. As a result, one can calculate the transition dipole moment of a molecular building block N from

$$\boldsymbol{\mu}_\nu^N = \mathrm{Tr}(\hat{\boldsymbol{\mu}}^N \xi_\nu^N) \tag{3}$$

Finally, the total transition dipole moment of the molecule is approximated as

$$\boldsymbol{\mu}_\nu = \sum_N \boldsymbol{\mu}_\nu^N + q_\nu^N r^N \tag{4}$$

where r^N is the position of the building block N in the molecule. Therefore, the procedure of extracting the ES dipole parameters and the use of these parameters to calculate optical spectra formulated previously for semiempirical methods[6,7] is fully transferable to the present case.

In the following we illustrate how the aforementioned dipole parameters can be retrieved from the quantum-chemical computations in conjugated molecules of moderate sizes using an example of branched phenylacetylenes. For all reference excited-state calculations we use TD-DFT approach with a hybrid exchange-correlation functional CAM-B3LYP[38,39] and 6-31G basis set. Molecular geometries used have been optimized at the same CAM-B3LYP/6-31G level. The range-corrected CAM-B3LYP model properly describes electronic excitations in π-conjugated polymers as tightly bound excitons.[40,41] All simulations have been conducted with the Gaussian 09 computational package[42] including the NBO module.[43] We quantitatively benchmark the performance of the original AO, Löwdin orthonormalized (LAO) (using $T = S^{-1/2}$), and NAO representations by extracting the dipole parameters using each representation for the underlying molecular building blocks. The accuracy of these tabulated parameter sets is then evaluated by calculating the state transition dipole moments/oscillator strengths for several molecules using the ES technique to be compared with the direct TD-DFT calculations.

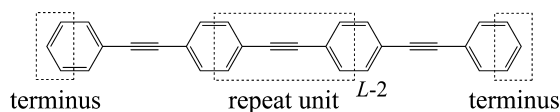We start with linear PA molecules shown in Figure 1 containing two types of building block: repeat unit and molecular terminus. The dipole matrices ($\hat{\boldsymbol{\mu}}_x$, $\hat{\boldsymbol{\mu}}_y$, and $\hat{\boldsymbol{\mu}}_z$) of the repeat unit and the terminus have been extracted from the corresponding dipole matrices of diphenylacetylene and phenyl ring, respectively. The energy-dependent ES parameters (the exciton spectrum $k(\omega)$ and the reflection amplitude at the

molecular termini) have been obtained for our reference quantum-chemistry CAM-B3LYP/6-31G using procedure outlined in refs 2 and 4. In addition, transition density matrices of several lowest excited states in the linear molecule P-15 have been reorganized and divided into blocks related to repeat units and termini. The transition charges and dipoles of individual building blocks were then calculated from eqs 2 and 3. The transition dipole $\mu(x)$ and charge $q(x)$ of a repeat unit for the lowest excited state in P-15 are shown in Figure 2 (x axis is
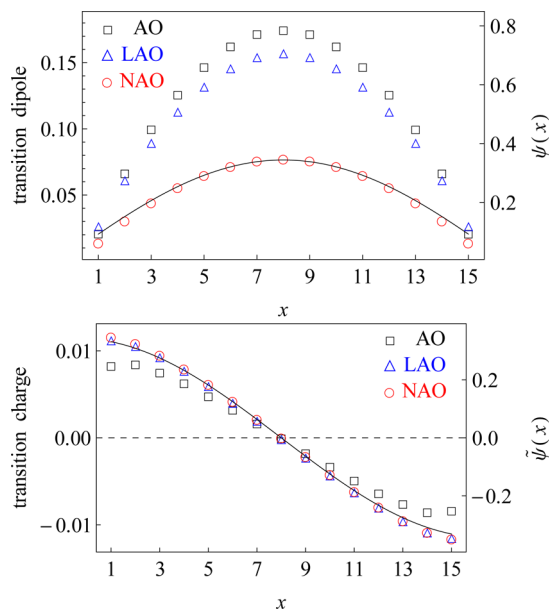

Figure 2. Transition dipoles (top) and charges (bottom) of the repeat units of the first excited state in the linear molecule P-15, calculated in AO, Löwdin orthonormalized (LAO), NAO representations. The related exciton wave function $\psi(x)$ and its dual counterpart $\tilde{\psi}(x)$ (black curves) are calculated and defined only at the integer positions x of the repeat units.

directed along the molecular backbone corresponding to the most significant transition dipole component for all lowest electronic states). In addition, Figure 2 displays the exciton wave function $\psi(x)$ and its dual counterpart $\tilde{\psi}(x)$ (which is defined as the first derivative of the wave function with respect to kx), whose profiles coincide with the transition dipole and charge distributions, respectively.

Figure 2 clearly illustrates a significant difference between extracted dipole parameters for various representations. The accuracy of the transition dipole calculations in terms of molecular building blocks can be verified by comparing the result of applying eq 4 to the output of the direct quantum chemistry, that is, transition charges and dipoles of individual building blocks computed in various representations. Table 1 shows the results for the lowest five excitations in the P-15 molecule. Only the transition charges and dipoles of building blocks retrieved using the NAO basis are able to quantitatively reproduce the molecular transition dipoles. Similar to what has been observed in semiempirical approaches,[6,7] the deviation of the transition dipole, calculated using the contributions from the building blocks, in NAOs, is attributed to neglecting the geometrical difference between the repeat units along the chain. Two other representations (the original AO basis and Löwdin orthogonal basis LAO) result in the incorrect transition dipole estimates for individual building blocks due to the non-

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Figure 1. Molecular structure of linear phenylacetylene (PA) oligomer with L repeat units denoted as P-L.

Table 1. Transition Dipole Moments of the First Five Excited States in the *P*-15 Oligomer[a]

mode	TD-DFT	AO	LAO	NAO	ES
1	13.3791	7.6111	8.2390	13.3988	12.9758
2	0.0001	0.0004	0.0001	0.0001	0.0000
3	3.8484	3.3452	2.5540	3.8778	3.8054
4	0.0001	0.0060	0.0000	0.0001	0.0000
5	2.0875	2.8871	1.5259	2.1202	2.0736

[a] These quantities obtained from the AO, LAO, and NAO basis sets (using their respective transition charges and dipoles of individual building blocks) are shown together with the results of direct TDDFT calculations compared with the ES model, whose parameters have been extracted using the NAO representation.

orthogonality of the AOs and the absence of free-atom features in LAOs, respectively.

To evaluate the performance of the NAO basis for the ES model, following refs 6 and 7 we further tabulated the frequency-dependent transition charge and dipole ES parameters of the PA repeat unit as the ratios $q(x)/\tilde{\psi}(x)$ and $\mu(x)/\psi(x)$, respectively, far from the molecular end. Taking into account transition charge and dipole deviations from the ES results in nearby repeat units, we also found the ES dipole parameters of terminus T as $q_T/\tilde{\psi}_T$ and μ_T/ψ_T.[6,7] Using these ES dipole parameters extracted from the NAO analysis, the molecular transition dipoles of any linear PA oligomer can be calculated accurately with negligible computational cost (e.g., the last column of Table 1 shows the ES results for the lowest five excited states in the *P*-15 oligomer). For selected molecules with the lengths ranging from 5 to 30 repeat units, the deviations in the transition dipole magnitudes for optically allowed states (e.g., states 1, 3, and 5 in Table 1) obtained with the ES model compared with that of the brightest state in direct quantum-chemical computation are found to be small (<5%) for all cases. Such accurate estimates are attributed to the orthonormality and well-preserved atom-like orbital features in the underlying NAO basis.

To perform calculations for more complicated molecular structures, we further consider meta- (*M*), ortho- (*O*), and symmetric triple (*Y*) molecular vertices shown in Figure 3.
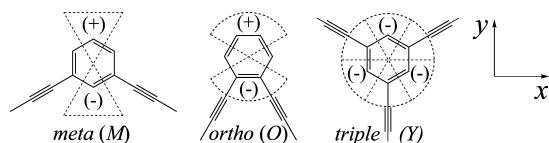

Figure 3. Molecular vertices of branched PA molecules. From left to right: meta-conjugated (*M*), ortho-conjugated (*O*), and symmetric triple (*Y*) joints. The overlap region attributed to the attached repeat units is marked with "(−)", whereas the nonoverlapping part of nearby repeat units is marked with "(+)".

Because of the spatial overlap of the repeat units attached to a branching center (region marked with "(−)" in Figure 3), the ES dipole parameters of these molecular joints have been extracted in a different way. Because in the NAO basis the transition charge can be calculated for individual atoms, one can find the effective transition charge of a joint by subtracting the contribution of the overlap region "(−)" from that of the vertex part "(+)". Transition dipole parameters of planar vertices are 2D vectors that can be projected on two principle axes *x* and *y* shown in Figure 3. Following the aforementioned method, the

transition charges and dipoles of the linear chains and termini can then be accurately retrieved using the NAO basis for any molecule with the characterized backbone. Therefore, in simple symmetric molecules with the addressed joint in the center, the transition dipole of the joint can be estimated as the difference between the total transition dipole of the molecule and the contribution of all repeat units and termini. Finally, the ES dipole parameters of a vertex can be readily retrieved by comparing the effective transition charge and the dipole to the excitation amplitudes (exciton wave function and its dual counterpart) at the vertex.[6,7]

Finally, to evaluate performance of the ES dipole parametrizations based on the NAO basis for complex molecules that include linear segments and symmetric vertices (*M*, *O*, and *Y*), we performed calculations for several branched PA molecules shown in the top panel in Figure 4. The comparison
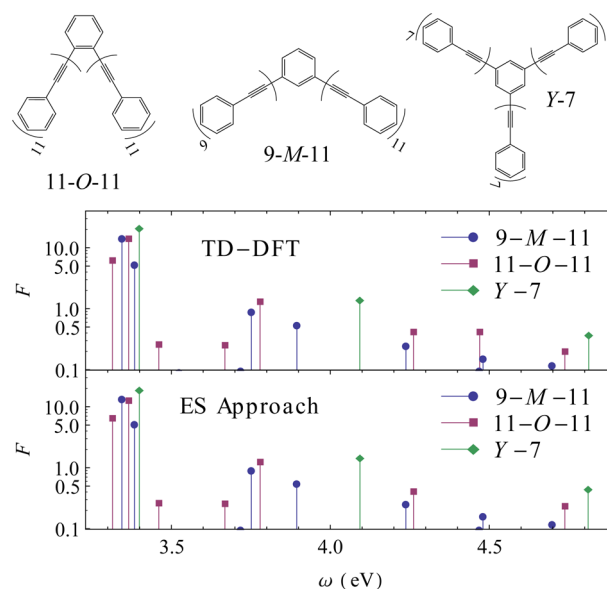

Figure 4. Comparison of the absorption spectra (oscillator strength vs transition frequencies) calculated using the ES approach and direct reference quantum-chemical technique for the selected molecules shown in the top panel.

of the absorption spectra obtained using the ES approach with the ones using direct reference quantum chemistry is illustrated in Figure 4. For such medium-sized molecular systems, the computational cost of the ES modeling is negligible, whereas the TD-DFT numerical cost is already significant. Overall, we observe a very good accuracy of the ES model with the deviations of the oscillator strengths between the ES and the reference quantum-chemical method for optically allowed states to be <10% in all cases for the molecules considered. One notable difference for the oscillator strength is observed for the resonant state of 11-*O*-11 molecule (4.469 eV), which was not accounted for in the ES approach.

In conclusion, accurate ES modeling of optical spectra in large conjugated molecular systems can be performed using dipole parametrization obtained from ab initio quantum-chemical computations with extended nonorthogonal AO basis sets via the NAO transformation. We have shown that neither the original AO nor standard Löwdin orthogonal representation is suitable for this purpose. In contrast, attributed to the orthonormalized, highly condensed, and atom-like basis orbitals, the NAO representation allows for

accurate estimates of the transition charges and dipoles for any molecular part, which guarantees correct extraction of the ES dipole parameters related to the building blocks. Using such extracted parameters, the ES calculations can accurately reproduce the results of the reference quantum chemistry technique. Good agreement for the calculated absorption spectra between the ES approach based on the NAO basis and the direct quantum-chemical computations is found to be similar to the results observed for semiempirical parametrizations,[6,7] where the orthogonality and atom-like orbital character is enforced in the Hamiltonian by construction. The NAO analysis is routinely available in many standard quantum-chemical packages via the NBO program.[43] Therefore, the ES approach designed for multiscale modeling of electronic excitations and spectroscopy of large conjugated molecules, can be readily applied as an extension to the currently available ab initio quantum-chemical methods.

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Notes

The authors declare no competing financial interest.

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