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Reliable Prediction of Charge Transfer Excitations in Molecular Complexes Using Time-Dependent Density Functional Theory

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Charge transfer (CT) molecular complexes (CTMC)[1] have recently received much interest in a broad variety of fields, for example, organic electronics,[2] (metal-)organic and molecular magnets,[3] nonlinear spectroscopy,[4] and molecular exciplexes.[5] In particular, photoinduced charge transfer, where little charge is transferred upon complexation, but significant charge is transferred upon photoexcitation, has generated much interest in the context of novel photovoltaic phenomena and devices.[6]

Despite its obvious importance, theoretical treatment of the electronic structure aspect of charge transfer excitations has largely been confined to either very small systems where ab initio wave function methods can be applied[7] or has relied on empirically calibrated hybrid methods.[8] Typically, excited states in general and optical spectra in particular can be predicted from first principles using time-dependent density functional theory (TDDFT), which has proven to be a reliable method for studying excited states in broad classes of relatively large systems with good precision,[9] However, it has been shown early on that the adiabatic spatially local functionals traditionally used within TDDFT do not allow for sufficient accuracy to describe CT excitations.[10−12] This deficiency, which is not cured by standard hybrid functionals, was attributed to spurious self-interaction[13] and missing derivative discontinuities,[14] two pervasive problems in density functional theory (DFT) that are intimately related.[15,16]

One way to mitigate the spurious self-interaction *and* to retain a good treatment of correlation is to deploy a range-separated hybrid functional.[15,17−19] In this approach, the exchange term in the Kohn−Sham energy functional is split into long-range and short-range terms, for example, via $r^{-1} = r^{-1}\mathrm{erf}(\gamma r) + r^{-1}\mathrm{erfc}(\gamma r)$. The short-range exchange is represented by a local potential derived from the local-density or the generalized gradient approximations. The long-range part is treated via an "explicit" or "exact" exchange term. If one assumes that an appropriate choice for γ is system independent, its value can be optimized using a molecular training set for optimizing its value. Such semiempirical approaches, typically with γ in the range of 0.3−0.5 a_0^{-1}, were shown to achieve impressive results for the ground-state properties of some classes of systems.[18,20,21] Furthermore, it was demonstrated on the benchmark model of Dreuw and Head-Gordon,[22] the $C_2H_4 \cdots C_2F_4$ dimer at large molecular distances, that the range-separated hybrid corrects the principal deficiencies of the charge transfer excitation prediction of TDDFT.[21,23]

While the correct behavior at asymptotically large distances is a major step forward, it is still no guarantee for predictive power at realistic donor−acceptor distances.[24] Asymptotically correct behavior is essentially a consequence of the long-range exact exchange, whereas quantitative prediction at intermediate distances requires a judicious choice of the semilocal functional, as well as of the range-split parameter, γ. This is nontrivial because assuming a system-independent γ, as done in most range-split hybrids, is only an approximation. A rigorous analysis, based on the adiabatic connection theorem, shows that in fact γ is itself a functional of the electron density, n.[19] For the homogeneous electron gas, Monte Carlo simulations show conclusively that $\gamma(n)$ strongly depends on the density.[21,25] Furthermore, ab initio system-specific determination of γ showed that good prediction of, for example, the ionization potential is possible, but that γ can vary substantially from 0.3 a_0^{-1} for Li_2 to 0.7 a_0^{-1} for, e.g., HF or O_2.[21] Proper description of symmetrical radical cations required even larger values, 0.9 a_0^{-1} and 1.4 a_0^{-1} for Ne_2^+ and He_2^+, respectively.[26]

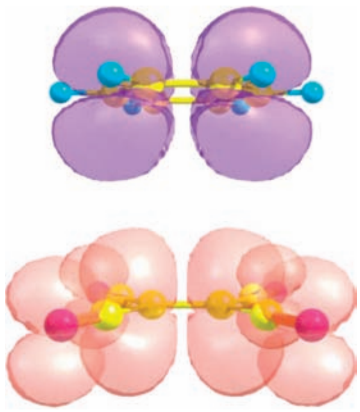

Figure 1. Density difference between the excited-state and ground-state in the benzene−TCNE complex, as computed from the excited and ground-state Kohn−Sham wave functions. Purple and pink indicate negative and positive electron densities, respectively, illustrating the charge transfer nature of the excitation.

In this Communication, we show that with the aid of a simple, physically motivated, first principles γ-determining step, range-separated hybrid functionals can be used successfully for quantitative calculation of CT excitation energies. This brings true predictive power to an important area usually considered "too difficult for DFT".

Our approach is tested on complexes formed by an aromatic donor (Ar = benzene, toluene, o-xylene, and naphthalene) and the tetracyanoethylene (TCNE) acceptor (see Figure 1), for which optical absorption is available both in gas phase and in solution,[27] as well as on a second set of Ar-TCNE (Ar = anthracene and various meso substituted derivatives) measurements in solution.[28]

All calculations were performed using QCHEM 3.1,[29] modified to include the range-separated BNL functional,[21] using the cc-pVDZ basis set.[30] The internal structure of the molecules in the complex is known to be little-perturbed by complex formation[11,12,31,32] and the equilibrium distance and relative orientation of the π-stacked

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10.1021/ja8087482 CCC: $40.75

donor and acceptor determined from the conventional B3LYP[33] hybrid functional is known to compare well with experiment (where available).[11,32] Therefore, B3LYP-optimized geometry was used throughout. Typical interplanar distances were 3.3−3.9 Å.

In exact Kohn−Sham theory, the energy of the highest occupied molecular orbital (HOMO) is equal and opposite to the ionization potential.[34] This can be used to select γ[21] by demanding that

$$-\varepsilon^{\gamma}_{\mathrm{HOMO}} = E_{gs}(N-1;\gamma) - E_{gs}(N;\gamma) \qquad (1)$$

where $\varepsilon^{\gamma}_{\mathrm{HOMO}}$ is the HOMO energy and the right-hand side of the equation is the difference of the self-consistent ground-state energies of the $N - 1$ and N electron system, all calculated for a given range-parameter, γ (this involves the typically successful approximation that the same γ is appropriate for both the N and $N - 1$ electron systems). Note that the precise value of γ will depend on the specific choice for the local exchange and the exchange-correlation functionals, but its determination procedure is universal.

In molecular complexes, the lowest photon energy required to induce a CT excitation, $h\nu_{\mathrm{CT}}$, is given for asymptotically large donor−acceptor distances by the Mulliken rule[1]

$$h\nu_{\mathrm{CT}} = \mathrm{IP(D)} - \mathrm{EA(A)} - 1/R \qquad (2)$$

where IP(D) and EA(A) are the donor ionization potential and acceptor electron affinity, respectively. The last term on the right-hand side is the Coulomb energy of attraction between the electron−hole pair formed by the charge transfer, where R is the intermolecular separation. For our TDDFT calculation to conform to the Mulliken rule, the ionization energies computed from eq 1 must correspond to the HOMO energy of the neutral donor, but also to the HOMO energy of acceptor *anion*. Thus, one needs to generalize eq 1 so as to yield, as closely as possible, two limits. We therefore look for γ that minimizes the following $J(\gamma)$ function

$$J(\gamma) = \sum_{i=D^0,A^-} |\varepsilon^{\gamma,i}_{\mathrm{HOMO}} + (E^{i}_{gs}(N_i-1;\gamma) - E^{i}_{gs}(N_i;\gamma))| \qquad (3)$$

For complexes where a range-parameter γ that renders a very small $J(\gamma)$ can be found (which is the case for all complexes we studied), we expect the range-separated hybrid to yield a quantitative description of CT excitations.

To examine the practicality of this approach, consider the example of benzene−TCNE, shown in Figure 2. In the top panel, we show the value of $J(\gamma)$ for γ in the range of 0.2−0.5 a_0^{-1}. $J(\gamma)$ changes considerably within this range, but a minimum close to zero is obtained for $\gamma^* = 0.331\ a_0^{-1}$. Importantly, often-used γ values, for example, 0.3, 0.4, or 0.5 a_0^{-1}, yield unacceptably large values for J, so that "γ-tuning" is essential. Once it is accomplished, TDDFT calculations using the optimal γ^* can be performed at various donor−acceptor distances. CT excitations are easily identified by searching for transitions dominated by excitation from a donor-localized orbital to an acceptor-localized orbital. The lowest such excitation energy (corresponding to a donor HOMO to acceptor LUMO transition) for the benzene−TCNE system is shown in the bottom panel of Figure 2. Clearly, because γ^* almost exactly nullifies J, convergence to Mulliken's rule at large R is excellent. For comparison, with $\gamma = 0.5$ the $1/R$ slope is still maintained, but the intercept is too high by ~1 eV. With B3LYP,[33] this Mulliken rule is completely violated: the slope is much too small and the intercept is more than 1 eV too low.

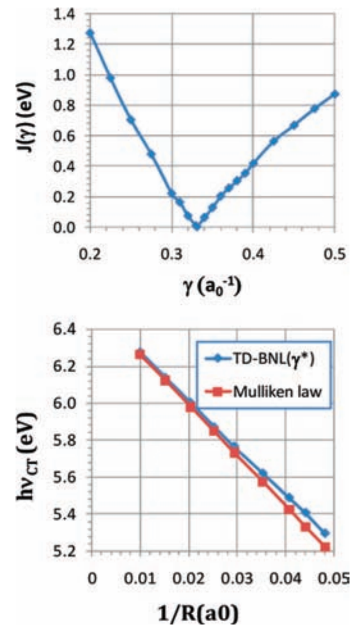

Figure 2. Tuning γ in the benzene−TCNE complex. Top: J of eq 3 as a function of γ. The optimal γ is 0.331 for which J is very small. Bottom: the Mulliken rule, compared to TDDFT results obtained from the optimal γ, as a function of inverse intermolecular separation.

Table 1. Excitation Energies (eV) and Oscillator Strengths of Several Gas Phase Ar−TCNE Systems: Theory and Experiment

	B3LYP			BNL γ^*			exp[27]	
Ar	E	f	BNL $\gamma = 0.5$	γ^*	E	f	E	f
benzene	2.1	0.03	4.4	0.33	3.8	0.03	3.59	0.02
toluene	1.8	0.04	4.0	0.32	3.4	0.03	3.36	0.03
o-xylene	1.5	~0	3.7	0.31	3.0	0.01	3.15	0.05
naphthalene	0.9	~0	3.3	0.32	2.7	~0	2.60	0.01

With the asymptotic behavior enforced, we expect proper balance between the local and nonlocal exchange components. In Table 1 we compare the calculated and experimental gas-phase results for various Ar−TCNE complexes. It is readily seen that the B3LYP results are unacceptably low and predictive power is absent. Results of generalized-gradient (GGA) calculations (not shown) are even lower than the B3LYP ones. With the range-split BNL functional,[21] excitation energies determined with an "off-the-shelf" γ value of 0.5 a_0^{-1} are much too high with respect to experiment. Similar conclusions for both B3LYP and computations with an otherwise-optimized range-separation parameter were drawn in ref 24. But with γ^*, quantitative agreement is obtained to within ±0.2 eV. For benzene and toluene, the theoretical oscillator strengths are also in good agreement with experiment but are too weak for xylene and naphthalene. This is likely a basis-set issue, as oscillator strengths are much more sensitive to the basis set than the excitation energies.

Most experimental data on CT excitations are collected in solution. This complicates direct comparison with theory due to the need for a solvation model. By comparing the calculated excitation energies of several Ar−TCNE systems in gas phase and in solution (using methylene chloride as the solvent) we found that the SS(V)PE solvation model,[35] as implemented in QCHEM, predicts very small changes in the excitation energy. For example, for toluene−TCNE the B3LYP CT excitation energy is reduced from 1.8 to 1.75 eV, that is, by merely 0.05 eV. Similar conclusions were reported for ground-state properties in a previous study[11] and a similar change was found by us with BNL calculations. Experimentally, the solvent effect is significantly larger, lowering the CT excitation energies by 0.32 eV on average. Thus, it is not possible to rely on the solvation model for this class of systems and the only reasonable way to proceed is to *assume* that subtraction of 0.32 eV from the gas phase calculations makes them comparable to experiments in solvent.

Using this assumption, we studied an additional series of anthracene substituted derivatives in methylene chloride. The results

Table 2. Excitation Energies (eV) in Solution of Several Substituted Anthracene−TCNE Systems: Calculation[a] and Experiment

			BNL			
substituent	PBE	B3LYP	E ($\gamma = 0.5$)	γ^*	E ($\gamma = 0.3$)	exp[28]
none	0.9	1.0	2.3	0.31	1.82	1.73
9-cyano	fail	0.5	2.6	0.30	2.03	2.01
9-chloro	0.9	1.0	2.3	0.31	1.82	1.74
9-carbo-methoxy	0.8	0.9	2.4	0.30	1.84	1.84
9-methyl	1.0	1.1	2.1	0.30	1.71	1.55
9-nitro	0.6	0.9	2.8	0.30	2.12	2.03
9.10-dimethyl	1.3	1.4	2.1	0.30	1.77	1.44
9-formyl	0.8	1.0	2.5	0.30	1.95	1.90
9-formyl 10-chloro	0.8	0.9	2.5	0.30	1.96	1.96

[a] Taking the gas phase result and subtracting 0.32 eV, as discussed in the text.

are given in Table 2. As before, GGA results are much too low, B3LYP results are somewhat larger but still unacceptable. BNL results with $\gamma = 0.5$ are too high, but BNL results with the optimal γ^* offer quantitatively meaningful agreement. The largest deviations are observed for the methyl and dimethyl substituents, 0.16 and 0.33 eV, respectively. This may be due to the simplistic treatment of solvation, which may be less than ideal for these two systems.

In summary, we have shown how charge transfer excitations can be calculated quantitatively for molecular complexes using TDDFT without an empirical range-constant. We demonstrated the predictive power of the approach using various aromatic donor−TCNE acceptor complexes. The approach relies on a first principles procedure for tuning the range-parameter in range-separated hybrid functionals (demonstrated here for the BNL functional, but applicable to other ones as well). This procedure is to be applied for each studied complex, in agreement with previous studies that have shown the necessity of molecule-specific range-parameter tuning for other properties.[21,26] It consists of a balanced minimization of the deviation of the HOMO eigenvalues from the total energy difference calculation of the ionization potential for both the neutral donor and the anionic acceptor. The minimal deviation obtained is an indication for the quality of the calculation and failure to obtain it can serve as a warning mechanism against spurious predictions. Once the range parameter is tuned, correct asymptotic behavior is guaranteed and remaining errors in the excitation energies are primarily due to the quality of the local correlation energy functional, the latter also being, in principle, dependent on the range-parameter.[19] This paves the way to systematic nonempirical quantitative studies of charge-transfer excitations in real systems, a task hitherto considered to be "too difficult for time-dependent density functional theory".

Acknowledgment. Work in Jerusalem was supported by a grant of the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities. Work in Rehovoth was supported by the Alternative Energy Research Initiative and the Lise Meitner Center for Computational Chemistry. We thank Professor Sanford Ruhman (Hebrew Univ.) for his indispensable advice.

Note Added after ASAP Publication. The reference in Table 2 was corrected from 27 to 28 in the version published on the web on February 25, 2009.

Supporting Information Available: Absolute energies and B3LYP-optimized geometries of the calculated structures and complete ref 29. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA8087482