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On the Accuracy of Computed Excited-State Dipole Moments

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The dipole moments of furan and pyrrole in many electronically excited singlet states have been determined using coupled cluster theory including large one-electron basis sets. The inclusion of connected triple excitations is shown to uniformly *decrease* the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) excitation energies by 0.04−0.24 eV, with an average reduction of 0.08 eV. Using a basis set larger than DZP^{++}D (double-ζ plus polarization augmented with atom- and molecule-centered diffuse functions) uniformly *increases* the computed EOM-CCSD excitation energies by 0.03−0.29 eV, with an average increase of 0.20 eV. The corresponding shifts in excited-state dipole moments are more erratic. Including connected triple excitations changes the computed dipole moments by an rms amount of 0.17 au. More importantly, using a larger basis set shifts the dipole moments by an rms amount of 0.52 au, with an increase or a decrease being equally likely. The CC dipole moments are compared to those from time-dependent density functional theory (TD-DFT) computed by Burcl, Amos, and Handy [*Chem. Phys. Lett.* **2002**, *355*, 8]. For 29 excited states of furan and pyrrole, the predicted TD-DFT dipole moments differ from the CC results by rms amounts of 1.6 au (HCTH functional) and 1.5 au (B97-1 functional). Including the asymptotic correction to TD-DFT developed by Tozer and Handy [*J. Chem. Phys.* **1998**, *109*, 10180; *J. Comput. Chem.* **1999**, *20*, 106] reduces the rms differences for both functionals to 1.2 au. If those Rydberg excited states with very large polarizabilities are excluded, the rms differences from the CC results for the remaining 17 excited states become 1.31 au (HCTH) and 0.88 au (B97-1). For asymptotically corrected functionals and this subset of states, the rms differences from the CC results are only 0.54 au (HCTHc) and 0.34 au (B97-1c). Thus, the Tozer−Handy asymptotic correction for TD-DFT significantly improves the predictions of excited-state dipole moments. For excited states without very large polarizabilities, good agreement is achieved between excited-state dipole moments computed by coupled cluster theory and by the asymptotically corrected B97-1c density functional.

Introduction

Time-dependent density functional theory (TD-DFT)[1–8] has become a common method for studying molecules in electronically excited states due to its favorable scaling with respect to system size. However, functionals commonly used in ground-state investigations are known to predict excitation energies that are far too low (typically by 0.5−0.8 eV) and too close together for Rydberg excited states. In addition, Dreuw et al.[9] have emphasized the inability of TD-DFT with local exchange−correlation functionals to describe charge-transfer excited states. These problems notwithstanding, TD-DFT excitation energies are often accurate for excitation of electrons into valence orbitals, usually to within 0.4 eV—or even less for hybrid functionals. Implementation of energy derivatives for TD-DFT was reported by Van Caillie and Amos,[10,11] allowing study of excited-state potential energy surfaces, including molecular rearrangement following electronic excitation.

Tozer and Handy[12,13] appeared to overcome the problem with excitation energies for Rydberg states via a numerical method which uses a previously determined ionization energy to graft in the correct long-range behavior of the exchange-correlation potential. In 2002, Burcl, Amos and Handy[14] (BAH) tested TD-DFT with a variety of exchange-correlation functionals on a large number of singlet excited states of furan and pyrrole “de facto standard medium-sized molecules for the comparison of theoretical and many experimental results for their excited states”.[14] BAH were able to compare their computed TD-DFT excitation energies to extensive previous experimental and theoretical work.[15,16] Serrano-Andrés et al.[17] had reported CASPT2 excitation energies for furan and pyrrole. Christiansen, Jørgensen and co-workers[18–20] had performed extensive coupled cluster (CC) computations, including corrections for triple excitations, on the excitation energies of both furan and pyrrole. Palmer et al.[21,22] had studied the electronic states of furan and pyrrole by VUV absorption, near threshold electron energy-loss spectroscopy and multireference configuration interaction calculations. BAH concluded that the Tozer−Handy asymptotic correction dramatically improved the calculated TD-DFT energies for furan and pyrrole. The majority of excitation energies obtained with the asymptotically corrected “B97-1c” functional agreed with the CC results to within 0.12 eV - even those of the Rydberg states.

TABLE 1: Dipole Moments for Selected Singlet States of the Furan Molecule in au Reported in Ref 14

state	B97-1	B97-1c[a]	CCSD/(D+7)[b]	CASSCF[c]
1 $^1A_2$	−0.365	0.321	−0.356	−0.423
1 $^1B_2$	1.348	0.767	1.264	0.123
1 $^1B_1$	−0.014	0.208	−0.145	−0.185
3 $^1B_1$	−0.930	−0.015	−0.714	−0.953

[a] Includes Tozer−Handy asymptotic correction. [b] Originally from ref 18. [c] Originally from ref 17.

BAH also reported TD-DFT dipole moments for the singlet excited states of furan and pyrrole, but more limited data

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TABLE 2: CC Vertical Excitation Energies of Furan and Pyrrole in eV

	DZP^{++}D CCSD	DZP^{++}D CC3	aug-cc-pVTZ+D CCSD	previous CC	present extrapolated CC
			Furan		
2 $^1A_1$ (V)	6.80	6.57	6.93	6.57[a]	6.69
3 $^1A_1$ ($1a_2 \rightarrow 3d_{xy}$)	7.47	7.40	7.69	7.53[a]	7.62
1 $^1A_2$ ($1a_2 \rightarrow 3s$)	5.99	5.91	6.17	6.04[a]	6.08
2 $^1A_2$ ($1a_2 \rightarrow 3p_z$)	6.68	6.59	6.87	6.73[a]	6.78
3 $^1A_2$ ($1a_2 \rightarrow 3d_{a1}$)	7.04	6.95	7.21	7.05[a]	7.12
4 $^1A_2$ ($1a_2 \rightarrow 3d_{a1}$)	7.30	7.22	7.48	7.33[a]	7.40
5 $^1A_2$ ($1a_2 \rightarrow 4s$)	7.62	7.55	7.79	7.70[b]	7.72
1 $^1B_1$ ($1a_2 \rightarrow 3p_y$)	6.51	6.43	6.71	6.58[a]	6.64
2 $^1B_1$ ($1a_2 \rightarrow 3d_{yz}$)	7.19	7.11	7.41	7.26[a]	7.33
3 $^1B_1$ ($2b_1 \rightarrow 3s$)	7.29	7.24	7.55	7.46[a]	7.50
4 $^1B_1$ ($1a_2 \rightarrow 4p_y$)	7.80	7.73	8.00	7.90[b]	7.93
5 $^1B_1$ ($2b_1 \rightarrow 3p_z$)	7.88	7.85	8.15	8.07[a]	8.12
1 $^1B_2$ (V)	6.53	6.37	6.56	6.32[a]	6.40
2 $^1B_2$ ($1a_2 \rightarrow 3p_x$)	6.93	6.82	7.05	6.86[a]	6.94
3 $^1B_2$ ($1a_2 \rightarrow 3d_{xz}$)	7.63	7.54	7.83	7.66[a]	7.75
			Pyrrole		
2 $^1A_1$ (V)	6.46	6.29	6.57	6.37[c]	6.41
3 $^1A_1$ ($1a_2 \rightarrow 3d_{xy}$)	6.76	6.72	7.02	6.87[c]	6.98
1 $^1A_2$ ($1a_2 \rightarrow 3s$)	5.12	5.02	5.35	5.20[c]	5.26
2 $^1A_2$ ($1a_2 \rightarrow 3p_z$)	5.84	5.77	6.08	5.94[c]	6.00
3 $^1A_2$ ($1a_2 \rightarrow 3d_{a1}$)	6.42	6.35	6.66	6.51[c]	6.60
4 $^1A_2$ ($1a_2 \rightarrow 3d_{a1}$)	6.52	6.45	6.72	6.57[c]	6.65
5 $^1A_2$ ($1a_2 \rightarrow 4s$)	6.70	6.66	6.99	6.92[c]	6.95
6 $^1A_2$ ($2b_1 \rightarrow 3p_y$)	6.84	6.78	7.07	6.97[c]	7.01
1 $^1B_1$ ($1a_2 \rightarrow 3p_y$)	5.77	5.72	6.04	5.95[c]	6.00
2 $^1B_1$ ($2b_1 \rightarrow 3s$)	5.91	5.85	6.17	6.12[c]	6.11
3 $^1B_1$ ($1a_2 \rightarrow 3d_{yz}$)	6.41	6.36	6.68	6.55[c]	6.63
4 $^1B_1$ ($2b_1 \rightarrow 3p_z$)	6.59	6.54	6.87	6.82[c]	6.82
1 $^1B_2$ ($1a_2 \rightarrow 3p_x$, Mix.)	6.02	5.95	6.21	6.04[c]	6.14
2 $^1B_2$ (V, Mix.)	6.65	6.56	6.75	6.57[c]	6.66
3 $^1B_2$ ($1a_2 \rightarrow 3d_{xz}$, Mix.)	6.91	6.83	7.10	6.90[c]	7.02

[a] CCSD/T+7 energies plus (CC3-CCSD)/ANO triples correction from ref 19. [b] CCSD/T+7 energies from ref 19. [c] CCSD/T+7 values plus [CCSDR(3)-CCSD/D+7] triples correction from Table 3 of ref 20.

were available for comparison. Dipole moments had been obtained with CC computations including single and double excitation amplitudes (CCSD), some with a relatively modest one-electron basis set, by Christiansen, Jørgensen and co-workers[18–20] and with CASSCF by Serrano-Andrés and co-workers.[17] From this limited information, BAH were unable to evaluate the accuracy of the Tozer−Handy asymptotic correction on excited-state dipole moments. Table 1 illustrates the wildly diverging results for a few of the excited states.

The asymptotic correction, which improved the excitation energies, appeared to possibly throw the dipole moments into disarray. These results raised the question of whether even asymptotically corrected TD-DFT could be trusted to accurately describe excited-state charge distributions or electronically excited complexes with dipole−dipole or hydrogen-bonding interactions. BAH concluded, “More thorough studies are needed to be able to reliably judge the quality of the calculated dipole moments.”[14] Here, we report benchmark computations of the dipole moments for the singlet excited states of furan and pyrrole, including the effects of large one-electron basis sets and connected triple excitations on CCSD results. The importance of these effects on the accuracy of excited-state dipole moments is summarized. It is established that the Tozer−Handy asymptotic correction substantially improves excited-state dipole moments computed with TD-DFT.

Theoretical Methods

Coupled-cluster (CC) theory[23–27] provides a direct route to excited states through the equation-of-motion CC (EOM-CC) formalism.[28,29] EOM-CCSD, which includes single and double excitations in the diagonalization of the EOM-CC Hamiltonian, is a reliable method for any excited state that is dominated by one-electron excitations from a single-configuration reference function. The small effects of even higher excitations may be accounted for by the iterative inclusion of triple excitations via the CC3 method,[30,31] which has recently been implemented for closed- and open-shell molecules[32] within the PSI3[33] quantum chemistry package. Christiansen et al.[19,20] showed that the excited states treated here are dominated by single excitations from the ground state, so the results from EOM CCSD and CC3 are expected to be of high quality. In this work, ground-state geometry optimizations were performed with CCSD analytic gradients,[34] and vertical excitation energies were computed at the ground-state geometries.

The EOM-CCSD dipole moments were computed via an expectation value formula[28] involving the left- and right-hand eigenvectors of the nonsymmetric EOM-CCSD Hamiltonian,

$$\langle \Psi_L | \Theta | \Psi_R \rangle = \mathrm{Tr}(\rho\, \Theta) \qquad (1)$$

This expectation value approach is equivalent to an energy derivative with respect to an applied electric field with the orbitals and the ground-state excitation amplitudes held frozen.[28]

TABLE 3: Previous Computed Vertical Excitation Energies Compared to CC Values in eV

	HCTH[a]	PBE0[a]	B97-1[a]	LDAc[a,b]	HCTHc[a,b]	PBE0c[a,b]	B97-1c[a,b]	CASPT2[c]	CC[d]
					Furan				
2 $^1A_1$	6.39	6.83	6.75	6.40	6.42	6.86	6.76	6.16	6.69
3 $^1A_1$	6.17	6.85	6.72	7.46	7.47	7.48	7.47	7.31	7.62
1 $^1A_2$	5.12	5.70	5.62	5.91	5.97	6.02	5.97	5.92	6.08
2 $^1A_2$	5.62	6.28	6.18	6.64	6.66	6.72	6.69	6.59	6.78
3 $^1A_2$	6.04	6.65	6.55	6.97	7.01	7.07	7.03	7.00	7.12
4 $^1A_2$	6.12	6.78	6.62	7.22	7.25	7.30	7.27	7.22	7.40
5 $^1A_2$	6.18	6.81	6.69	7.55	7.56	7.59	7.58		7.72
1 $^1B_1$	5.53	6.15	6.06	6.54	6.59	6.61	6.58	6.46	6.64
2 $^1B_1$	6.04	6.70	6.59	7.16	7.18	7.24	7.21	7.15	7.33
3 $^1B_1$	6.39	7.15	7.04	7.17	7.25	7.49	7.41	7.21	7.50
5 $^1B_1$	6.88	7.70	7.57	7.87	7.92	8.13	8.07		8.12
1 $^1B_2$	6.03	6.10	6.04	6.08	6.08	6.18	6.12	6.04	6.40
2 $^1B_2$	5.68	6.46	6.38	6.83	6.84	6.85	6.83	6.48	6.94
3 $^1B_2$	6.39	6.96	6.84	7.54	7.54	7.56	7.55	7.13	7.75
rms[e]	1.16	0.55	0.66	0.21	0.18	0.11	0.13	0.34	
					Pyrrole				
2 $^1A_1$	6.01	6.63	6.54	6.30	6.31	6.67	6.58	5.92	6.41
3 $^1A_1$	5.61	6.27	6.17	6.91	6.92	6.93	6.92	6.54	6.98
1 $^1A_2$	4.34	4.91	4.83	5.05	5.11	5.23	5.17	5.08	5.26
2 $^1A_2$	4.95	5.58	5.49	5.92	5.97	6.03	5.99	5.83	6.00
3 $^1A_2$	5.42	6.07	5.96	6.50	6.53	6.60	6.57	6.42	6.60
4 $^1A_2$	5.52	6.15	6.02	6.55	6.59	6.63	6.59	6.51	6.65
5 $^1A_2$	5.61	6.20	6.08	6.92	6.93	6.96	6.95		6.95
6 $^1A_2$	5.85	6.62	6.51	6.87	6.92	7.12	7.06	6.77	7.01
1 $^1B_1$	4.98	5.59	5.50	6.01	6.05	6.07	6.04	5.85	6.00
2 $^1B_1$	5.20	5.90	5.80	5.92	5.99	6.22	6.15	5.97	6.11
3 $^1B_1$	5.45	6.10	6.00	6.57	6.60	6.65	6.62	6.40	6.63
4 $^1B_1$	5.82	6.53	6.43	6.78	6.85	6.99	6.93	6.62	6.82
1 $^1B_2$	5.14	5.73	5.64	6.04	6.07	6.10	6.07	5.78	6.14
2 $^1B_2$	6.34	6.54	6.47	6.50	6.48	6.56	6.52	6.00	6.66
3 $^1B_2$	5.61	6.24	6.14	6.92	6.92	6.95	6.94	6.53	7.02
rms[e]	1.07	0.48	0.57	0.11	0.09	0.10	0.08	0.33	

[a] From ref 14. [b] Includes Tozer–Handy asymptotic correction. [c] From ref 17. [d] From Table 2. [e] Root-mean-square difference from extrapolated CC values in last column.

When Christiansen, Koch, and Jørgensen[31] defined the CC3 model in the presence of an external perturbation, they chose to avoid explicit orbital relaxation and the corresponding Hartree–Fock poles in the response function. In that case, the triples equation without external perturbation

$$\langle \mu_3 | [\hat{F}, T_3] | \mathrm{HF} \rangle + \langle \mu_3 | [\hat{U}, T_2] | \mathrm{HF} \rangle = 0 \qquad (2)$$

becomes in the presence of a one-electron, time-independent perturbation $\beta\hat{V}$

$$\langle \mu_3 | [\hat{F} + \beta\hat{V}, T_3] | \mathrm{HF} \rangle + \langle \mu_3 | [\hat{U}, T_2] | \mathrm{HF} \rangle + \frac{1}{2} \langle \mu_3 | [[\beta\hat{V}, T_2], T_2] | \mathrm{HF} \rangle = 0 \qquad (3)$$

where HF is the Hartree–Fock reference, $\hat{F}$ is the Fock operator, the unperturbed Hamiltonian is partitioned as $\hat{H} = \hat{F} + \hat{U}$, and T_2 and T_3 are double- and triple-excitation operators. Treating the external perturbation without orbital relaxation requires the additional term in the amplitude equation. Here, we have chosen to compute dipole moments by numerical finite-differences of CC3 energies computed using an applied electric field. The SCF orbitals, T amplitudes, and excitation amplitudes are allowed to fully optimize in the presence of the field. Though not equivalent to solving eq 3, a finite-difference approach gives dipole moments corresponding to the exact linear response of the CC3 energy to an applied field and does not require substantial additional computer code. (In addition, finite differences can conveniently be used to determine a component of the polarizability of each excited state.) To emphasize this distinction, the dipole moments computed by finite-differences are denoted CC3*.

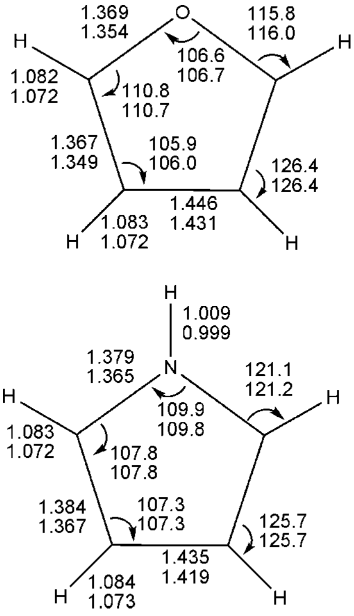

Figure 1. DZP^{++}D CCSD (top) and aug-cc-pVTZ+D CCSD optimized structures of furan and pyrrole.

TABLE 4: CC Dipole Moments of Furan and Pyrrole in Ground and Excited States in au

	DZP^{++}D CCSD	DZP^{++}D CC3*	aug-cc-pVTZ+D CCSD	previous CCSD	present extrapolated CC
			Furan		
1 $^1A_1$	0.287	0.286	0.255	0.263[a]	0.254
2 $^1A_1$	0.403	0.386	0.345	0.367[a]	0.328
3 $^1A_1$	0.518	0.488	0.495	−0.037[b]	0.466
1 $^1A_2$	−0.295	−0.191	−0.227	−0.356[b]	−0.122
2 $^1A_2$	−0.317	−0.337	−0.428	−0.471[b]	−0.448
3 $^1A_2$	0.687	0.644	0.504	0.469[b]	0.461
4 $^1A_2$	1.230	1.054	1.272	0.829[b]	1.095
5 $^1A_2$	−0.890	−0.546	−0.565	−0.806[b]	−0.221
1 $^1B_1$	−0.111	−0.074	−0.103	−0.142[a]	−0.067
2 $^1B_1$	1.263	1.223	0.854	0.694[a]	0.814
3 $^1B_1$	−0.533	−0.651	−0.551	−0.651[a]	−0.669
4 $^1B_1$	−1.582	−1.442	−1.238	−0.966[b]	−1.098
5 $^1B_1$	0.361	0.157	0.809	0.717[b]	0.606
1 $^1B_2$	1.286	1.105	0.984	0.950[a]	0.803
2 $^1B_2$	−1.772	−1.584	−1.374	−1.539[a]	−1.186
3 $^1B_2$	3.309	3.016	2.870	1.784[a]	2.577
			Pyrrole		
1 $^1A_1$	−0.755	−0.753	−0.725	−0.762[c]	−0.723
2 $^1A_1$	−0.445	−0.488	−0.465	−0.384[c]	−0.508
3 $^1A_1$	−0.065	−0.242	−0.006	−0.008[c]	−0.183
1 $^1A_2$	2.805	2.803	2.678	6.869[c]	2.676
2 $^1A_2$	−2.385	−2.464	−2.147	−5.738[c]	−2.226
3 $^1A_2$	−2.089	−2.201	−1.248	−3.752[c]	−1.359
4 $^1A_2$	−1.847	−1.682	−2.436	−4.538[c]	−2.270
5 $^1A_2$	0.956	0.932	0.993	12.557[c]	0.968
6 $^1A_2$	7.057	7.155	5.929	5.986[c]	6.027
1 $^1B_1$	2.112	1.964	1.623	0.970[c]	1.475
2 $^1B_1$	1.843	1.875	2.137	2.827[c]	2.170
3 $^1B_1$	−1.641	−1.608	−1.413	−1.184[c]	−1.380
4 $^1B_1$	−3.113	−3.113	−2.893	−3.055[c]	−2.893
1 $^1B_2$	0.716	0.695	0.746	0.759[c]	0.724
2 $^1B_2$	−3.703	−3.509	−2.653	−3.478[c]	−2.459
3 $^1B_2$	2.556	1.983	0.769	3.099[c]	0.195

[a] CCSD/T+7 value from ref 18. [b] CCSD/D+7 value from ref 18. [c] CCSD/D+7 values from ref 20.

TABLE 5: Mean (rms) Effect of Including Connected Triple Excitations and Large One-Electron Basis Sets on CC Excitation Energies and Dipole Moments of the Lowest 15 Singlet Excited States of Furan and Pyrrole (Plus the Ground State for the Dipole Moments)

	furan	pyrrole
	Excitation Energies (eV)	
connected triple excitations[a]	−0.093 (0.104)	−0.070 (0.076)
one-electron basis set[b]	0.182 (0.191)	0.225 (0.231)
	Dipole Moment (au)	
connected triple excitations[c]	−0.019 (0.157)	−0.041 (0.173)
one-electron basis set[d]	0.004 (0.261)	−0.070 (0.668)

[a] E(DZP^{++}D CC3) − E(DZP^{++}D CCSD). [b] E(aug-cc-pVTZ+D CCSD) − E(DZP^{++}D CCSD). [c] μ(DZP^{++}D CC3*) − μ(DZP^{++}D CCSD). [d] μ(aug-cc-pVTZ+D CCSD) − μ(DZP^{++}D CCSD).

A root-following algorithm was implemented which allows CC3 energies to be obtained for excited states that are not the lowest energy of their respective spin and spatial symmetries. However, CC3 eigenvectors for higher-energy states can be difficult to converge tightly. The dipole moments of furan and pyrrole are nonzero only along the z-axis running from the molecular center through the O or N atom, respectively. The electronic component was computed using the four-point formula

$$\mu = \frac{\partial E}{\partial F_z} = \frac{E_{-2h} - 8E_{-h} + 8E_{+h} - E_{+2h}}{12h} \tag{4}$$

where h is the electric field strength, and then added to the nuclear component.

Successively smaller field strengths were applied until the dipole moment of each excited state was converged to within well less than 0.1 au. The supporting evidence for this convergence is provided as Supporting Information. The diagonal electronic polarizability of each state along the z-axis was estimated using the five-point formula

$$\alpha_{zz} = \frac{\partial^2 E}{\partial F_z^{\,2}} = \frac{-E_{-2h} + 16E_{-h} + 16E_{+h} - E_{+2h} - 30E_0}{12h^2} \tag{5}$$

where $h = 0.0005$ au. The numerical convergence of the second derivatives with respect to field strength was not checked. However, even a ballpark estimate of each state's polarizability is useful, as shown in the Results and Discussion section.

Vertical excitation energies were computed with two basis sets. The DZP^{++}D basis set was composed of the Huzinaga−Dunning−Hay double-ζ set of contracted Gaussian functions,[35] augmented by sets of polarization functions [$\alpha_d(C) = 0.75$; $\alpha_d(N) = 0.80$; $\alpha_d(O) = 0.85$; $\alpha_p(H) = 0.75$], and sets of atom-centered diffuse functions[36] [$\alpha_s(C) = 0.04302$; $\alpha_p(C) = 0.03629$; $\alpha_s(N) = 0.06029$; $\alpha_p(N) = 0.05148$; $\alpha_s(O) = 0.08227$; $\alpha_p(O) = 0.06508$; $\alpha_s(H) = 0.04415$] and by two sets of s, p, and d molecule centered-diffuse functions [$\alpha_s = 0.009, 0.0018$; $\alpha_p = 0.007, 0.0014$; $\alpha_d = 0.020, 0.0040$]. The DZP^{++}D basis comprises 137 and 143 symmetry orbitals for furan and pyrrole, respectively. The molecule-centered functions were placed at the center of mass; the precise location of these functions is unlikely to significantly impact the results.[37] Throughout, "pure angular momentum" polarization functions were used. The aug-cc-pVTZ+D basis was formed by augmenting the standard aug-cc-pVTZ basis[38] with the same molecule-centered diffuse functions described above. The resulting basis set comprises 340 and 363 symmetry orbitals for furan and pyrrole, respectively. The ground-state geometries were determined using CCSD and the same basis sets as the excitation energies, excluding the molecule-centered diffuse functions. Although all orbitals were included in the ground-state CCSD geometry optimizations, the excitation energies were computed with the five core and the five highest-energy virtual orbitals frozen. The effect of the frozen-core approximation was tested at the EOM-CCSD/DZP^{++}D level and found to be on average less than 0.01 au in the excitation energies.

The "larger basis-set effect" on the computed excitation energies or dipole moments was calculated by f(aug-cc-pVTZ+D CCSD) − f(DZP^{++}D CCSD). The connected "triples effect" was calculated by f(DZP^{++}D CC3) − f(DZP^{++}D CCSD). The extrapolated values were determined by adding these effects to the DZP^{++}D CCSD value of the excitation energy or the dipole moment. Equivalently, the extrapolated CC results can be viewed as from aug-cc-pVTZ+D CCSD plus a triples correction, or as DZP^{++}D CC3 plus a basis-set correction.

Results and Discussion

The CCSD optimized geometries of C_{2v} symmetry furan and pyrrole are shown in Figure 1. There is good agreement between the computed structures. Compared to the smaller basis set, the aug-cc-pVTZ+D basis predicts ring bond lengths uniformly shorter by 0.014−0.018 Å and bond angles within 0.2°.

TABLE 6: Comparison of Computed Excited-State Dipole Moments in au

	polarizability α_{zz}	HCTH[a]	B97-1[a]	HCTHc[a]	B97-1c[a]	CASSCF[b]	CC[c]
				Furan			
2 $^1A_1$	−60	0.365	0.432	0.291	0.306	0.365	0.328
3 $^1A_1$	−227		0.423	0.539	0.550	0.515	0.466
1 $^1A_2$	−1415	−0.640	−0.365	0.235	0.321	−0.423	−0.122
2 $^1A_2$	−900	−0.191	−0.430	−0.448	−0.562	−0.490	−0.448
3 $^1A_2$	−102	1.616	1.077	0.637	0.525	0.108	0.461
4 $^1A_2$	357	0.369	0.708	1.126	1.200	−0.470	1.095
5 $^1A_2$	−24186	1.417	1.542	1.001	1.012		−0.221
1 $^1B_1$	−1115	−0.015	−0.014	0.221	0.208	−0.185	−0.067
2 $^1B_1$	−18	1.018	1.080	0.897	0.982	0.249	0.814
3 $^1B_1$	−1587	−0.466	−0.930	0.500	−0.015	−0.953	−0.669
5 $^1B_1$	3180	0.044	0.600	−0.366	0.036		0.606
1 $^1B_2$	−210	−1.898	1.348	0.663	0.767	0.123	0.803
2 $^1B_2$	−877	1.000	−2.039	−0.531	−0.652	0.418	−1.186
3 $^1B_2$	−3094	2.400	2.256	1.387	1.424	−0.564	2.577
rms[d]		1.416	0.453	0.248	0.209	0.861	
		(1.156)	(0.596)	(0.651)	(0.549)	(1.154)	
				Pyrrole			
2 $^1A_1$	−79	1.194	0.060	−0.609	−0.598	−0.451	−0.508
3 $^1A_1$	−563	−0.615	−0.617	−0.608	−0.599	0.054	−0.183
1 $^1A_2$	−820	3.157	2.906	2.687	2.609	3.671	2.676
2 $^1A_2$	−789	−3.643	−3.169	−2.753	−2.353	−2.000	−2.226
3 $^1A_2$	−1717	−2.230	−1.706	−2.878	−3.352	−1.804	−1.359
4 $^1A_2$	1553	0.313	0.391	−0.582	−0.718	−1.369	−2.270
5 $^1A_2$	−2122	0.020	−0.848	2.767	2.624	1.354	0.968
6 $^1A_2$	−16859	1.141	0.923	1.179	0.957	−1.466	6.027
1 $^1B_1$	−1690	0.913	0.908	0.924	0.942	2.012	1.475
2 $^1B_1$	−445	3.413	3.120	2.926	2.770	2.872	2.170
3 $^1B_1$	203	−2.263	−2.266	−2.194	−2.109	−1.442	−1.380
4 $^1B_1$	−556	−3.621	−3.526		−2.754	−3.062	−2.893
1 $^1B_2$	−845	1.011	1.099	0.691	0.768	0.987	0.724
2 $^1B_2$	−470	−0.148	0.341	−1.517	−1.736	−0.833	−2.459
3 $^1B_2$	−1593	−2.635	−3.247	−1.148	−0.987	−1.253	0.195
rms[d]		1.229	1.131	0.569	0.427	0.694	
		(1.900)	(2.004)	(1.617)	(1.595)	(2.066)	

[a] From ref 14. [b] From ref 17. [c] From Table 4. [d] rms difference from extrapolated values in last column excluding states whose polarizabilities are larger in magnitude than 1000 au (including all states).

Excitation energies for the 15 lowest singlet excited states of furan and pyrrole computed with CC theory are given in Table 2. The qualitative description of each state is taken from the work of Christiansen et al.,[19,20] except that (following BAH[14]) the 3 $^1A_2$ and 4 $^1A_2$ states that mix two 1a$_2$ → 3d excitations are not given unique labels. For furan, BAH omitted the 4 $^1B_1$ (1a$_2$ → 4p$_y$) state, and the state labeled in that work "(?)4 $^1B_1$(3p$_z'$)" will be compared with the 5 $^1B_1$ (2b$_1$ → 3p$_z$) state here. Also, the state denoted "(?)6 $^1A_2$(3p$_y'$)" by BAH is found to be 9 $^1A_2$ and is not further considered here.[18]

Expanding the basis set beyond DZP^{++}D *increases* the excitation energy of every state and by an average of 0.20 eV. The triples correction *reduces* the excitation energy of every state and by an average of 0.08 eV. For the Rydberg states, the effect of the triples correction is in every case to decrease the excitation energy by 0.04−0.11 eV. For the four valence excited states investigated, the triples correction is somewhat larger and more sporadic, the largest being a reduction of the 2 $^1A_1$ state of furan by 0.24 eV.

Previous CCSD values, many including triples corrections, from the work of Christiansen et al.[19,20] are also given in Table 2. Given the high level of theory and the similarity in theoretical approach, excellent agreement between the present extrapolated values and these previous CC computations is not surprising. The present values range from 0.01 eV lower to 0.12 eV higher with the largest differences found for the 2 $^1A_1$ state of furan and the 3 $^1B_2$ state of pyrrole.

Table 3 compares the extrapolated CC values with other previously computed excitation energies. The asymptotically corrected B97-1c excitation energies differ from the present extrapolated CC values by more than 0.15 eV only for the 1 $^1B_2$ and 3 $^1B_2$ states of furan and the 2$^1A_1$ state of pyrrole. The rms difference between the B97-1c and CC excitation energies for all 29 states of furan and pyrrole in Table 3 is only 0.11 eV. In this paper we do not pursue the effects of geometry relaxation and vibrational energy on the excitation energies. Christiansen et al.[20] concluded that the vertical CASPT2 energies are systematically too low and may at times compare fortuitously to experiment due to the neglect of geometry relaxation. For more detailed discussion of these effects and the experimental spectra, the reader is referred to ref 14, ref 19 and ref 20.

Table 4 shows the computed and extrapolated CC dipole moments. Also listed are values previously computed with CCSD, which due to the neglect of connected triple excitations and the use of a small basis set (particularly for pyrrole) differ significantly from the CC values here. Table 5 reports the average effect of using the larger one-electron basis and including connected triple excitations. The change in the computed dipole moments resulting from a basis set that is more complete in the valence region is greater; the rms basis set effect being 0.261 au and 0.668 au for furan and pyrrole, respectively. The smaller, corresponding rms shifts due to connected triple excitations are 0.157 and 0.173 au. For both the basis-set and triples effect, the mean change in the dipole moments is near zero. The effects are not systematic, even for states of the same molecule.

In their study of TD-DFT dipole moments of furan and pyrrole, BAH found that (1) the "dipole moments are much more sensitive to the exact form of the DFT functional than the excitation energies" and (2) the Tozer−Handy asymptotic correction brings the dipole moments predicted by the HCTH and B97-1 functionals closer together but (3) "there is little or no agreement between the asymptotically corrected values and the values obtained from quantum chemistry i.e., CCSD or CASSCF".[14] The TD-DFT dipole moments computed by BAH are compared to the present CC values in Table 6. The rms differences from the CC values for all 15 states of furan and 14 states of pyrrole are 1.598 and 1.500 au for HCTH and B97-1, respectively, with larger differences for pyrrole than for furan. With the asymptotic correction, the differences from the CC values reduce to 1.232 au (HCTHc) and 1.209 au (B97-1c). (The corresponding rms difference between the CC and CASSCF values is 1.721 au.) For a given state, the CC and asymptotically corrected TD-DFT dipole moments usually are either in good agreement or else are very different from one another. These two cases can be distinguished in a systematic fashion.

BAH suggested that the large variation in predicted dipole moments for many excited states of furan and pyrrole was due to some states having an extremely large polarizability.[14] The diagonal electronic polarizability in the same direction as the dipole moment has been computed and reported for each state in Table 6. There are six states for both furan and pyrrole with polarizabilities in excess of 1000 au; all of these are Rydberg states. These states are precisely those with the largest disparity between the TD-DFT and CC dipole moments. If these 12 states are excluded, the rms difference for the remaining 17 less-problematic states between CC and CASSCF is 0.777 au. For TD-DFT, the rms differences from the CC results become 1.314 au (HCTH), 0.880 au (B97-1), 0.536 au (HCTHc), and 0.342 au (B97-1c). The rms difference between the B97-1 and B97-1c dipole moments for this subset of states is 0.74 au, so the magnitude of the asymptotic correction is still quite large. Therefore, the Tozer−Handy asymptotic correction is seen to improve predicted excited-state dipole moments, dramatically so for states without very large polarizabilities.

Besides the theoretical limitations in the B97-1c and CC3 methods' treatment of electron correlation, differences in the predicted excited-state dipole moments may be attributed to several possible factors, such as numerical differentiation here (see Theoretical Methods), the assumed additivity of basis-set effects and correlation effects in Table 4, the neglect of the derivative of the asymptotic correction in BAH, the use of optimized geometries here and experimental geometries in BAH, as well as the use of different basis sets. Given these factors and the difficulty of the problem, the agreement achieved for dipole moments of excited states (at least without large polarizabilities) between the quite different theoretical approaches of asymptotically corrected TD-DFT with B97-1c and coupled cluster theory is remarkable.

Conclusions

The energies and dipole moments of low-lying singlet excited states of furan and pyrrole have been investigated using coupled-cluster theory. The inclusion of connected triple excitations for excited states dominated by single excitations from a reference has the predictable effect of modestly decreasing the excitation energy (rms shift is 0.09 eV). The effect on the dipole moment of the excited state is unpredictable in direction (rms shift is 0.17 au). The use of a large one-electron basis set more complete in the valence region causes a consistent increase in the excitation energy (rms shift is 0.21 eV), so that many CCSD excitation energies benefit from cancelation of errors. The basis-set effect is also larger for dipole moments of excited states (rms shift is 0.52 au). However, for dipole moments the two errors are as likely to compound as to cancel. Therefore, when computing excited-state properties such as dipole moments, it is essential to use the largest feasible one-electron basis set.

For 29 excited states of furan and pyrrole, the rms differences between the CC dipole moments computed here and the TD-DFT values computed by BAH are 1.6 au (HCTH) and 1.5 au (B97-1). The Tozer−Handy asymptotic correction reduces the difference for both functionals to about 1.2 au. Those excited states of furan and pyrrole with polarizabilities in the direction of the dipole moment with magnitude greater than 1000 au were identified. If these states are excluded, the rms differences from the CC results for the remaining 17 states become 1.31 au (HCTH) and 0.88 au (B97-1). With the inclusion of the asymptotic correction, the rms differences become only 0.54 au (HCTHc) and 0.34 au (B97-1c). Thus, the Tozer−Handy asymptotic correction for TD-DFT not only dramatically improves the excitation energies of Rydberg states but also significantly improves the prediction of excited-state dipole moments.

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Supporting Information Available: Table 1, DZP^{++}D CC3/CC3* energies of furan with and without applied electric fields. Table 2, DZP^{++}D CC3* dipole moments of furan computed by finite-differences with different field strengths. Table 3, DZP^{++}D CC3/CC3* energies of pyrrole with and without applied electric fields. Table 4, DZP^{++}D CC3* dipole moments of pyrrole computed by finite-differences with different field strengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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