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Configuration interaction with Kohn–Sham orbitals and their relation to excited electronic states

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Abstract

Kohn–Sham (KS) orbitals in CH_2, formaldehyde and acetone molecules were used as reference states for configuration interaction (CI) instead of the usual Hartree–Fock (HF) orbitals. A little difference in overall accuracy of electronic excitation energies was found between these schemes. However, analysis of the wave functions indicated that Slater determinant with the KS orbitals is more suitable for construction of the electronic states. Typically, the main expansion coefficients for the CI/KS procedure were closer to unity than those for HF. The difference was most pronounced for the lowest-energy transitions, while the two methods provided more comparable results for the higher-energy states. Similar behaviour of singlet and triplet states was observed. The results justify the common practice of using the KS determinant as a wave function, for example in sum-over-states theories. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Explorations of various properties of the Kohn–Sham (KS) determinant can be justified at least by the wide range of applications of the density functional theory (DFT) [1]. Particularly, the determinant is often used in place of a true electronic wave function in order to obtain estimates of excitation energies [2–4] or in sum-over-states (SOS) expressions. For example, nuclear magnetic shifts and couplings [1,5], vibrational circular dichroism [6,7] and Raman optical activity [8,9] spectra were simulated with the SOS method using the KS orbitals. An interesting convenience appeared for the modelling of the magnetic shielding, where the SOS expression equals to the coupled-perturbed (CP) formula for pure functionals. Such functionals do not contain the Hartree–Fock (HF) exchange term and the electron density is not perturbed by the magnetic field, which eliminates the coupling. Therefore accurate values for the shifts could be obtained with a relatively modest computational effort, providing a suitable functional is used for the construction of the orbitals [10,11]. Finally, it may be of paramount interest for future development of quantum chemistry, if accurate molecular wave functions can be estimated easily within the DFT methodology. Indeed, there are indications that configuration interaction (CI) expansions can be limited even in exact limit to double excitations [12] if a good reference state is found.

A simple idea is followed in this work: usage of the KS determinant in the usual CI expansions

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instead of the traditional HF reference state. Previously, a striking similarity was quantified for ground state properties of the HF (Δ_0^{HF}) and KS (Δ_0^{KS}) Slater determinants [4] if used as wave functions. Nevertheless, rather different behaviour was indicated for cases involving excited electronic states. In this study the differences between the excited states approximated with HF and KS orbitals will be investigated more systematically.

According to the usual CI expression [13] the electronic wave function is expanded into spin-adapted determinants

$$|e\rangle = c_0^e \Delta_0 + \sum_{i=1,\ldots,N} c_i^e \Delta_i,$$

where Δ_0 is the ground state HF or KS determinant, Δ_i, $(i > 0)$ are singly, doubly, etc., excited configurations constructed from unchanged (rigid) occupied and virtual orbitals. The states $|e\rangle$ oblige the Schrödinger equation

$$H|e\rangle = E_e|e\rangle,$$

so that the electronic energies E_e can be obtained as eigenvalues of the Hamiltonian matrix with components $\langle \Delta_j|H|\Delta_i\rangle$. Note that same computer CI algorithm can be used for the HF and KS determinants, providing that the Brillouin theorem (not valid for KS [3]) is not explicitly used for the construction of the single-excited state energies.

Table 1
Formaldehyde, experimental and calculated excitation energies (eV)

Exp.[a]	TDDFT[b]		Orbital differences ($\varepsilon_\mathrm{J} - \varepsilon_\mathrm{K}$)				Rigid orbitals[c] ($\varepsilon_\mathrm{J} - \varepsilon_\mathrm{K} + J_\mathrm{JK}$ $(-2K_\mathrm{JK})$)			
	B3L	B3P86	HF	B3L	$\mathrm{B3L}_{0.05}$	B3P86	HF	B3L	$\mathrm{B3L}_{0.05}$	B3P86
(a) *Non-CI models*										
Singlets										
4.1 (3.94[d]) A_2	3.90	3.91	13.2	5.85	4.11	5.88	7.38	4.66	4.61	4.64
7.13 (7.09[d]) B_2	6.56	6.97	13.9	7.85	6.26	7.95	9.25	8.98	9.12	8.98
8.14 (7.97[d]) A_1	7.51	7.95	14.1	8.38	7.17	8.79	10.3	10.0	10.1	10.0
7.98 B_2	7.65	8.05	14.8	8.73	7.47	9.18	9.92	9.54	9.54	9.54
Triplets										
3.50 (3.50[d]) A_2	3.18	3.17	13.2	5.85	4.11	5.88	7.04	3.97	3.90	3.92
6.00 (5.53[d]) A_1	5.34	5.32	16.5	9.32	9.39	9.46	9.05	5.04	4.88	4.98
7.09 (6.83[d]) B_2	6.42	6.77	13.9	7.85	6.26	7.95	9.18	8.79	8.86	8.79
8.14 (7.79[d]) A_1	7.42	7.80	14.1	8.38	7.17	8.79	10.1	9.76	9.84	9.76
7.92 B_2	7.51	7.80	14.8	8.73	7.47	9.18	9.84	9.32	9.32	9.25

Exp.	CIS				CISD				$\mathrm{FCI}_{6\text{–}13}$	
	HF	B3L	$\mathrm{B3L}_{0.05}$	B3P86	HF	B3L	$\mathrm{B3L}_{0.05}$	B3P86	HF	B3L
(b) *Configuration interaction*										
4.1 A_2	4.52	4.90	5.10	4.86	4.81	4.13	4.11	4.13	5.21	4.40
7.13 B_2	8.67	9.05	9.25	8.92	8.10	7.70	7.70	7.75	8.86	7.95
8.14 A_1	9.76	10.1	10.3	9.76	9.32	8.79	8.86	8.86	9.76	9.12
7.98 B_2	9.54	9.84	10.1	9.76	9.39	8.79	8.79	8.86	9.92	8.92
3.50 A_2	3.71	4.08	4.29	4.03	4.52	3.85	3.81	3.84	4.75	3.99
6.00 A_1	4.77	5.02	5.19	4.96	6.46	5.82	5.82	5.82	6.39	5.66
7.09 B_2	8.27	8.61	8.86	8.55	7.95	7.51	7.47	7.51	8.79	7.85
8.14 A_1	9.39	9.76	9.92	9.61	9.25	8.67	8.61	8.67	9.61	8.86
7.92 B_2	9.12	9.46	9.69	9.39	9.32	8.67	8.61	8.67	9.69	8.92

[a] Experimental values according to [16], compiled mostly from electron impact and electron scattering data.

[b] The TDDFT calculations were repeated according to [16].

[c] The rigid orbital (also independent electron (IPA) or MP0 [4]) approximation provides energies as $E = \langle \Delta_\mathrm{JK}|H|\Delta_\mathrm{JK}\rangle$, where Δ_JK is a singly excited state K → J; J_JK is the Coulomb term; for the triplets the exchange terms $(-2K_\mathrm{JK})$ have to be added. For the limited CISD and FCI calculations orbitals 1–16 and 6–13 were active, respectively.

[d] Energies from [19], based mostly on electron energy loss spectroscopy measurements.

2. Computations

Molecular geometries for CH_2, formaldehyde and acetone were optimized at the MP2/6-311+G** level using the GAUSSIAN [14] program. Ground state occupied and virtual orbitals were calculated with the 6-311++G** basis. A set of supplementary programs 'ROA' was used for subsequent manipulation of the Gaussian orbital coefficients and for the CI computations. The basis proved to be sufficient for similar computations [15,16] and also trial calculations did not reveal a significant dependence of the results on the basis, given the properties followed in this work. Standard Becke3LYP (B3L) [17] and Becke3P86 (B3P86) [17,18] functionals were used as supplied by the GAUSSIAN, together with a modified B3L form ($B3L_{0.05}$) with 5% of the HF exchange contribution proposed recently [10,11] for calculations of the NMR shifts.

3. Results and discussion

3.1. Formaldehyde

In Table 1 excitation energies for this molecule are listed (in eV) as calculated with various models and compared to reference values. The time-dependent density functional theory (TDDFT) [2,15,16], built also in GAUSSIAN, has become a standard DFT tool for the computations of the excited electronic states. As apparent from the second and third columns in Table 1a it provides realistic estimates of experimental excitation energies, albeit with a larger error for the triplet states. The most simple model based on raw differences of orbital energies (columns 4–7 in Table 1a) obviously provides a worse agreement. However, a striking difference between HF and KS/DFT values can be observed, the latter describing experimental transitions much more faithfully. This behaviour was described in detail elsewhere [3,4]. Qualitatively similar performance can be observed for all the three (B3L, $B3L_{0.05}$ and B3P86) DFT functionals. The $B3L_{0.05}$ functional provides the HOMO–LUMO gap closest to the experimentally 'most important' lowest-energy transition, but no convincing improvement for the other energies.

The last four columns in Table 1a are dedicated to the rigid spin-adapted orbital model, which can be thought of as a zero (MP0) approximation to the CI methods. Also for this model the DFT values are much closer to experiment than HF and almost compete in accuracy with the coupled TDDFT results.

The differences between the HF and DFT results described above invoke the question whether the favourable properties of the DFT orbitals can be explored also in CI calculations behind the MP0 level. Therefore in Table 1b excitation energies of formaldehyde were calculated using a configuration interaction both with HF and DFT

Table 2
Formaldehyde, biggest CI coefficients for the states in Table 1b

$E_{\text{Exp.}}$	CIS				CISD				$FCI_{6–13}$	
(eV)	HF	B3L	$B3L_{0.05}$	B3P86	HF	B3L	$B3L_{0.05}$	B3P86	HF	B3L
0 (Ground)	1.000	0.995	0.993	0.996	0.986	0.979	0.977	0.978	0.988	0.982
4.1 A_2	0.746	0.995	9.995	0.995	0.742	0.946	0.947	0.947	0.759	0.956
7.13 B_2	0.886	0.992	0.914	0.916	0.909	0.930	0.927	0.927	0.966	0.943
8.14 A_1	0.729	0.843	0.879	0.829	0.915	0.906	0.903	0.902	0.970	0.959
7.98 B_2	0.906	0.928	0.927	0.984	0.957	0.915	0.908	0.912	0.982	0.952
3.50 A_2	0.735	0.989	0.993	0.992	0.747	0.959	0.959	0.960	0.756	0.967
6.00 A_1	0.702	0.981	0.988	0.986	0.739	0.988	0.992	0.992	0.737	0.992
7.09 B_2	0.858	0.921	0.924	0.922	0.895	0.931	0.932	0.930	0.967	0.945
8.14 A_1	0.872	0.934	0.938	0.934	0.915	0.860	0.930	0.877	0.728	0.803
7.92 B_2	0.905	0.951	0.955	0.953	0.953	0.844	0.917	0.799	0.970	0.963

Absolute values of the coefficients ($|c_i|$) are listed.

orbitals. Apparently, no unambiguous conclusion can be drawn from the CIS values (columns 2–5 in Table 1b), perhaps except of the lowest-energy singlet and triplet transitions both best described by the HF method. On the contrary, the CISD and FCI computations (restricted to orbitals 1–16 and 6–13, respectively, because of computer limitations) both provide excitation energies closer to experiment if the DFT orbitals are used instead of HF. The difference is most apparent for the lowest-energy transitions. For example, energy of the first singlet state (4.1 eV) is matched almost exactly and the first triplet state (3.50 eV) is given by about 0.3 eV higher by the CISD/DFT methods, which is even closer than if calculated by the standard TDDFT methodology. The differences between the three functionals do not appear significant, similarly as for the uncoupled calculations in Table 1a.

The better performance of DFT in the limited CISD and FCI methods suggests that the DFT reference states (Δ_i) may be closer to the true wave functions than states derived from HF Slater determinant. Indeed, this can be observed in Table 2 where absolute values of the CI leading expansion coefficients c_i are listed. Except

Table 3
Acetone, experimental and calculated excitation energies and expansion coefficients

Exp. [16]	TDDFT		Orbital differences $(\varepsilon_J - \varepsilon_K)$			Rigid orbitals $(\varepsilon_J - \varepsilon_K + J_{JK}\ (-2K_{JK}))$		
	B3L	B3P86	HF	B3L	B3P86	HF	B3L	B3P86
(a) *Energies (eV) for the non-CI models*								
Singlets								
4.41 A_2	4.37	4.38	12.9	6.23	6.23	8.16	5.49	5.39
6.36 B_2	5.82	6.23	12.3	6.63	7.04	8.92	8.73	8.67
7.41 A_1	6.74	7.17	12.8	7.42	7.85	9.76	9.76	9.69
7.36 A_2	6.93	7.38	14.9	7.75	8.16	9.61	9.54	9.54
7.49 B_2	7.17	7.61	13.3	7.95	8.38	10.1	9.84	9.84
8.09 A_2	8.32	8.32	16.3	9.76	9.76	12.8	11.3	11.3
Triplets								
4.18 A_2	3.75	3.73	12.9	6.23	6.23	7.85	4.90	4.79
5.88 A_1	5.53	5.53	14.9	8.92	8.98	11.6	6.67	6.56
6.26 A_2	6.93	7.38	14.9	7.75	8.16	9.61	9.46	9.54
7.90 A_2	8.05	8.05	16.3	9.76	9.76	12.8	11.1	11.1

Exp.	Energies (eV)						Expansion coefficients					
	CIS			CISD			CIS			CISD		
	HF	B3L	B3P86	HF	B3L	B3P86	HF	B3L	B3P86	HF	B3L	B3P86
(b) *Configuration interaction*												
0 (Ground)							1.00	0.99	0.99	0.99	0.98	0.98
4.41 A_2	5.17	5.90	5.79	4.86	5.37	5.25	0.72	0.97	0.98	0.69	0.94	0.94
6.36 B_2	8.32	8.98	8.79	7.61	7.95	7.80	0.84	0.90	0.90	0.85	0.91	0.91
7.41 A_1	9.32	10.0	9.76	8.67	8.98	8.86	0.78	0.84	0.85	0.87	0.87	0.89
7.36 A_2	9.39	10.1	9.84	8.61	8.98	8.86	0.88	0.89	0.90	0.87	0.87	0.89
7.49 B_2	9.54	10.2	10.0	8.86	9.18	9.12	0.71	0.73	0.68	0.71	0.74	0.69
8.09 A_2	12.4	11.1	11.0	9.32	9.61	9.54	0.72	0.73	0.73	0.55	0.72	0.67
4.18 A_2	4.43	5.17	5.04	4.37	4.96	4.86	0.79	0.97	0.98	0.70	0.94	0.95
5.88 A_1	11.1	5.96	5.85	5.74	6.56	6.53	0.47	0.91	0.92	0.68	0.91	0.91
6.26 A_2	9.25	9.92	9.76	7.47	7.85	7.75	0.72	0.82	0.84	0.83	0.90	0.90
7.90 A_2	12.8	10.6	10.4	8.61	8.92	8.79	0.57	0.68	0.70	0.70	0.92	0.92

CISD – active orbitals 5–32 (20 417 singlet and 28 144 triplet configurations).

for the CIS ground state where the unity value of the HF coefficient is determined by the Brillouin theorem the CI-DFT expansions yield values uniformly bigger for the lowest-energy transitions. This can be conveniently used in modelling and elucidation of molecular excited states. Note, that probabilities are determined by the square of the coefficients. For example, the first excited singlet state (at 4.1 eV) can be within the CIS model approximated by the $0.746^2 = 56\%$ contribution of the single spin-adapted HF determinant. However, a more faithful representation ($0.995^2 = 99\%$) can be constructed with corresponding KS B3L-DFT determinant. Little qualitative difference can be observed for the three functionals used. For higher-energy transitions differences between the HF and DFT CI calculations become smaller and seem to converge to a common limit. For example, for the 8.14 and 7.98 eV singlet transition and the CISD and FCI methods the HF determinant fits slightly better resultant wave functions than the DFT orbitals.

3.2. Acetone

These trends appear also for the bigger acetone molecule, as follows from its energies and the coefficients summarized in Table 3. The HF/CI energies are slightly better than those obtained with the DFT orbital basis, but both procedures lead to a large error in computed energies. The CIS and limited CISD methods are clearly not satisfactory approximations and the TDDFT methods provides better values, perhaps with the exception of the triplet transitions. Large CI expansion could not be done because of current computer limits. However, as for formaldehyde, the DFT one-determinant models of the excited states clearly better approximate the CI wave functions than those based on the HF determinants. The difference is most apparent for the second triplet 5.88 eV

Table 4
Calculated CI parameters for singlet transitions in CH_2

	FCI [20]	TDDFT	CIS		CISD		FCI_{2-16}	
	HF	B3L	HF	B3L	HF	B3L	HF	B3L
Energies (eV)								
$^1B_2$	1.79	1.45	1.65	1.79	4.15	4.13	1.83	1.76
$^1A_1$	4.66	5.88	7.17	7.17	7.85	7.90	4.38	4.23
$^1A_2$	5.85	5.51	6.05	6.17	8.10	8.05	5.71	5.64
$^1A_1$	6.53	8.38	9.46	9.12	9.18	9.18	6.56	6.33
$^1B_1$	7.70	7.04	8.38	8.43	10.5	10.5	7.75	7.61
$^1B_1$	8.00	8.79	9.92	11.4	11.2	11.4	7.90	7.80
$^1A_1$	8.49	9.39	10.7	13.2	11.7	11.7	8.86	8.73
$^1B_2$	8.92	8.00	9.12	10.0	11.2	11.3	8.43	8.21
$^1A_2$	9.46	12.3	13.9	14.8	13.9	13.8	9.84	9.61
$^1B_2$	10.60	14.3	16.5	16.8	12.7	12.7	8.61	8.43
Expansion coefficients								
A_1 (Ground)			1.000	0.998	0.967	0.967	0.975	0.972
$^1B_2$			0.891	0.995	0.874	0.975	0.889	0.978
$^1A_1$			0.921	0.981	0.771	0.965	0.780	0.946
$^1A_2$			0.892	0.998	0.853	0.967	0.875	0.970
$^1A_1$			0.883	0.997	0.883	0.947	0.906	0.951
$^1B_1$			0.928	0.973	0.885	0.936	0.659	0.829
$^1B_1$			0.958	0.976	0.765	0.957	0.771	0.837
$^1A_1$			0.938	0.971	0.939	0.942	0.945	0.938
$^1B_2$			0.883	0.980	0.833	0.943	0.802	0.873
$^1A_2$			0.966	0.994	0.685	0.892	0.729	0.911
$^1B_2$			0.918	0.992	0.710	0.916	0.702	0.868

The CIS, CISD and FCI (with active orbitals 2–16) calculations comprised 133, 8911 and 63 700 states, respectively.

transition, associated with excited state composed from $0.47^2 = 22\%$ of the HF determinant. Within the same CIS scheme the state can be much more elegantly approximated by $0.92^2 = 85\%$ with the B3P86-DFT determinant.

3.3. CH_2 singlets

Finally, a comprehensive overview of the behaviour of the CI models with the DFT orbitals can be presented for the smallest CH_2 molecule. Excitation singlet energies and corresponding biggest coefficients for this popular benchmark for ab initio computations are summarized in Table 4. An exceptionally poor performance of the TDDFT indicates possible limitations of this method for 'unusual' molecules. Also the CIS and, more surprisingly, the CISD sets of energies exhibit only approximate match of the exact (FCI) values both for the HF and DFT procedures. However, the HF expansion coefficients are consistently smaller for the HF determinants, similarly as found for formaldehyde and acetone. Satisfactory agreement for energies provides only the FCI method (limited to orbitals 2–16) both for HF and DFT. Similarly as for the two larger molecules and other models of excited states the DFT and HF values of energies converge for high energetic transitions. However, this is not true for the expansion coefficients, mostly higher for the DFT determinant throughout the whole region of energies.

The results for CH_2 also indicate that the trends obtained for formaldehyde and acetone were not biased by the limited CISD and FCI expansions that had to be used because of the computer limits. Supposedly, the extended demands of the CI computations can be reduced in the future using the special properties of the KS orbitals. For example, a combined DFT – multi-reference CI approach [21] provided already promising results for excitations limited only to singlet configurations.

4. Conclusions

The excited states derived from the KS determinant are suitable for the CI computations of excitation energies in the same way as for the usual HF determinants. Similar values of the energies were obtained with both procedures. However, despite popular believe, KS orbitals provided better one-determinantal models of the excited electronic wave functions. This finding justifies the common praxis in the DFT theory where molecular states are approximated with the KS orbitals. The results can be also explored in spectroscopic models, namely for efficient estimation of spectral intensities, as well as in SOS and other computations of molecular properties.

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