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Excitation Number: Characterizing Multiply Excited States

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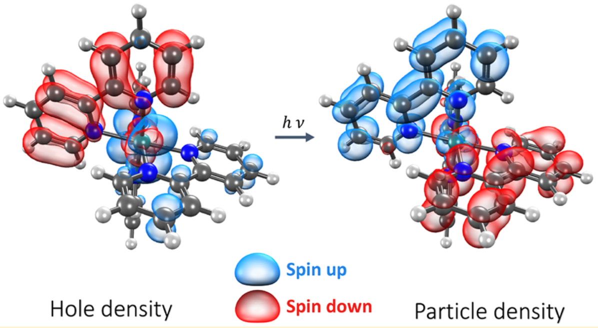
ABSTRACT: How many electrons are excited in an electronic transition? In this Letter, we introduce the excitation number η to answer this question when the initial and final states are each modeled by a single-determinant wave function. We show that calculated η values lie close to positive integers, leading to unambiguous assignments of the number of excited electrons. This contrasts with previous definitions of excitation quantities which can lead to mis-assignments. We consider several examples where η provides improved excited-state characterizations.



The electronic states of a molecular system are completely characterized by their wave functions Ψ_k which satisfy the time-independent Schrödinger wave equation

$$\hat{H}\Psi_k = E_k\Psi_k \tag{1}$$

where $\hat{H}$ is the Hamiltonian for the system and E_k is the energy corresponding to Ψ_k.

Often, however, we are less interested in individual states than in the *changes* between two states, *A* and *B*, of the system. Many of these changes, such as vertical excitation energies and oscillator strengths, can be determined both experimentally and theoretically. However, the answer to one apparently benign question remains elusive: how many electrons are excited in an electronic transition?

The issue is not trivial, for the absorption of even a single photon can excite more than one electron.[1,2] Moreover, a two-photon absorption can result in either the double excitation of a single electron or the single excitations of two electrons.[3,4]

Multiply excited states play a key role in important fields such as optoelectronics,[5] but only rarely can the number of excited electrons be measured experimentally, and there is a dearth of reliable, general theoretical methods to compute an "excitation number". In part, the reason for this theoretical deficiency can be traced to the successful modeling of excited states[6] by configuration interaction (CI) expansions

$$\Psi_k \approx c_0\Phi_0 + \sum_i^{\text{occ}}\sum_r^{\text{virt}} c_i^r\Phi_i^r + \sum_{i<j}^{\text{occ}}\sum_{r<s}^{\text{virt}} c_{ij}^{rs}\Phi_{ij}^{rs} + ... \tag{2}$$

where c_0, c_i^r, c_{ij}^{rs}, ... are the CI amplitudes. Φ_0 is the reference configuration, typically the Hartree−Fock (HF) ground-state determinant, the Φ_i^r are singly substituted determinants in which an electron has been promoted from the occupied molecular orbital (MO) $|\psi_i\rangle$ to the virtual MO $|\psi_r\rangle$, the Φ_{ij}^{rs} are doubly substituted determinants, and so forth.

Having expressed the excited state in such a way, it seems natural to define an *m*-tuply excited state as one whose CI expansion includes an *m*-tuply substituted determinant with a significant amplitude. Unfortunately, however, this definition is problematic because the resulting *m* depends on the reference configuration and the definition of "significant" is arbitrary.

In 1995, Head-Gordon *et al.* proposed[7] that the number of excited electrons be identified with the promotion number $p_n = \text{Tr}\mathbf{A} = \text{Tr}\mathbf{D}$, where $\mathbf{A}$ and $\mathbf{D}$ are the attachment and detachment densities, respectively. However, the promotion number often deviates significantly from integer values, and this complicates its interpretation.

In recent work, we[8−10] and others[11] have shown that a plausible alternative to CI-based approaches is to approximate an excited-state wave function by a *single* determinant

$$\Psi_k \approx \Phi_k = \det[\chi_i] \tag{3}$$

of spin−orbitals χ_i (Figure 1). The excited-state determinant is obtained by replacing the *aufbau* protocol with either the maximum overlap method (MOM)[8] or the initial maximum overlap method (IMOM),[10] and it can be surprisingly accurate,[9] even for challenging excited-state problems.[10] The reason for this accuracy is that the orbitals in the excited-state determinant are fully relaxed and are therefore optimal for that state.

Suppose that we have found single-determinant wave functions for states *A* and *B* and that $|a_i\rangle$ and $|b_i\rangle$ are their respective occupied spin−orbitals. Then the projection of $|b_i\rangle$ onto the occupied space of *A* is

$$|b_i^A\rangle = |a_j\rangle\langle a_j|b_i\rangle \tag{4}$$

where we have adopted the Einstein summation convention. The part of the density of state *B* that lies in the occupied space of *A* is given by

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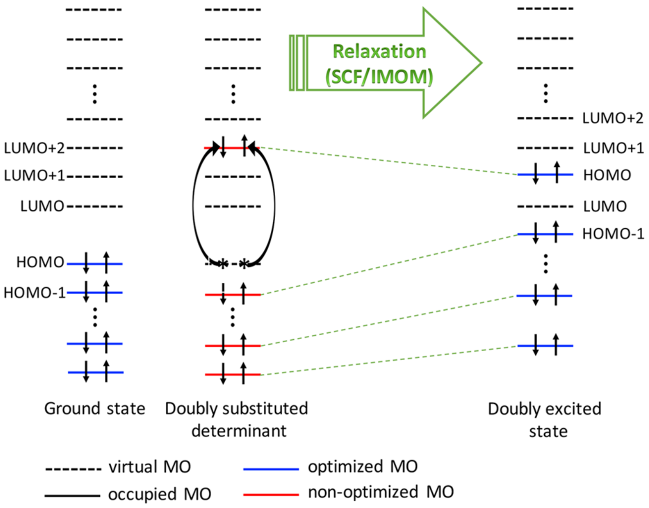

Figure 1. Formation of a single-determinant approximation to a doubly excited state. The doubly substituted determinant's orbitals are able to relax during an IMOM-mediated SCF process.

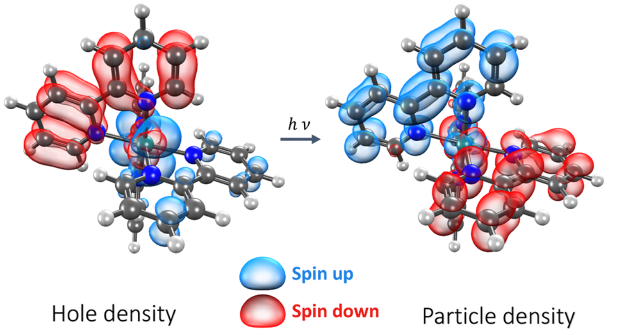

Figure 2. Hole and particle densities for a double ($\eta = 2.072$) charge-transfer state of $[\mathrm{Ru(bpy)_3}]^{2+}$ at the BLYP/3-21G level. The excitation involves metal-to-ligand (spin-up) and ligand-to-ligand (spin-down) charge transfers. The computed vertical excitation energy is 6.43 eV.

$$\rho_B^A = |b_i^A\rangle\langle b_i^A| \tag{5}$$

and integrating this gives the number of electrons in state B that lie in the occupied space of A

$$n_B^A = \langle a_j|b_i\rangle\langle b_i|a_j\rangle \tag{6}$$

The excitation number, which is the number of electrons in B that lie in the *unoccupied* space of A, is therefore

$$\eta_{AB} = n - \langle a_j|b_i\rangle\langle b_i|a_j\rangle \tag{7}$$

where n is the total number of electrons in the system.

The excitation number has four desirable properties:

(1) It is computationally trivial.

(2) It is symmetric, *i.e.*, $\eta_{AB} = \eta_{BA}$.

(3) It is an integer if orbital relaxation is not allowed.

(4) It is invariant to unitary transformations of either the occupied or virtual orbitals of either of the states.

The projected density ρ_B^A can yield additional information. Specifically, the *hole* density

$$\check{\rho}_{AB}(\mathbf{r}) = \rho_A(\mathbf{r}) - \rho_B^A(\mathbf{r}) \tag{8}$$

shows the origin of the electron(s) involved in the transition $A \rightarrow B$, and the *particle* density

$$\hat{\rho}_{AB}(\mathbf{r}) = \rho_B(\mathbf{r}) - \rho_B^A(\mathbf{r}) \tag{9}$$

shows where they go. Figure 2 shows an example of these densities for a double charge-transfer excitation in the $[\mathrm{Ru(bpy)_3}]^{2+}$ complex. For clarity, the densities are separated into their spin components.

Table 1 reports promotion numbers, excitation numbers, oscillator strengths, and vertical excitation energies for several excited states of various molecules at the BLYP/cc-pVTZ level. Calculating the oscillator strengths for multiple excitations requires going beyond the standard first-order approach and is beyond the scope of this work. The mean absolute deviation of the excitation energies from the "exact" values is less than 0.3 eV. Mean deviations for other DFT functionals are usually less than 0.5 eV; deviations for HF are larger.

The BLYP promotion numbers are usually not close to integers and, as a result, they offer unclear guidance about the number of excited electrons. The TD-BLYP promotion numbers with "relaxed" densities[7] are closer to integers, but the discrepancies are still uncomfortably large in many cases.

The η values are consistently smaller than p_n and almost invariably close to integers. Moreover, we have found that they change little when other functionals or basis sets are used. The small deviations from integers result from orbital relaxation effects (as noted above) and are usually positive. The only exception in Table 1 arises for one of the doubly excited states of LiH. The near-integer character of η encourages us to identify m-tuply excited states as being those with $\eta \approx m$.

The excitation number offers a new tool for the theoretical characterization of excited states. For example, it is clear from the η values that the 2 ^1A_g state of anthracene and the 2 $^1A_1$ state of pleiadene are low-lying doubly excited states, facts which are corroborated by strong agreement with the experimental results.[23,24]

The excitation number also reveals that certain states which have been assigned as multiply excited based on CI amplitudes may, in fact, have been mis-assigned. This appears to be the case for the controversial 2 ^1A_g state of *trans*-butadiene and the 1 $^1E_{2g}$ state of benzene.

The 2 ^1A_g state of *trans*-butadiene has been studied extensively both experimentally and theoretically (see Saha *et al.*[30] and references therein). The most accurate CI-based studies agree that the excited-state wave function includes large contributions from doubly substituted determinants. For example, Serrano-Andrés *et al.*[15] attribute only 58% of their CASSCF wave function to singly substituted configurations and hint that a large fraction of the remaining 42% is made up of doubly substituted ones. Subsequently, others[31,32] have reaffirmed the doubly excited character of the 2 ^1A_g state and a 2006 study by Starcke *et al.* concluded that "for short polyenes, the lowest excited 2 ^1A_g and 1 ^1B_u states can clearly be classified as doubly excited" and the ability of TDDFT to describe these states is ascribed to a "fortuitous cancellation of errors in the ground- and excited-state wavefunctions."[33]

However, Hsu *et al.*[34] later reported remarkably accurate excitation energies (mean deviation of 0.18 eV) using TDDFT and a variety of functionals. This was surprising since it is well-known that TDDFT is structurally incapable of describing double excitations within the commonly adopted adiabatic local density approximation.[31,32,35,36]

What does η reveal about the 2 ^1A_g state of butadiene? Our BLYP/cc-pVTZ calculations yield an excitation energy in good

Table 1. Promotion Numbers (p_n), Excitation Numbers (η), Oscillator Strengths (f), and Vertical Excitation Energies (ΔE, eV) for Various States of Molecules Using BLYP/cc-pVTZ[a]

Molecule	Point group	Primary transitions	Excited state	rTD-BLYP	BLYP				"Exact"
				p_n	p_n	η	f	ΔE	ΔE
helium atom	K	$1s \to 2s$	2 ^1S	1.105	1.170	1.027	0	20.58	20.62[12]
		$1s \to e^-_{\text{free}}$	^1S		1.182	1.033	0	24.81	24.59[13]
formaldehyde	C_{2v}	$2b_1 \to 2b_2$	1 $^1A_2$	1.208	1.378	1.024	0	3.44	4.07[14]
		$2b_1 \to 2b_2$	1 $^3A_2$	1.224	1.364	1.025	0	3.30	3.50[14]
		$(2b_1)^2 \to (2b_2)^2$	$^1A_1$		2.421	2.019	-	9.82	
trans-butadiene	C_{2h}	$1b_g \to 2a_u$	1 ^1B_u	1.424	1.150	1.001	0.486	5.54	5.92[15]
		$1b_g \to 2a_u$	1 ^3B_u	1.101	1.284	1.009	0	3.22	3.22[15]
		$1a_u \to 2a_u$	2 ^1A_g		1.393	1.022	0	6.11	6.25[16]
		$1a_u \to 2a_u$	1 ^3A_g		1.393	1.020	0	5.05	4.91[15]
		$(1b_g)^2 \to (2a_u)^2$	^1A_g		2.222	2.003	-	8.05	
benzene	D_{6h}	$1e_{1g} \to 1e_{2u}$	1 $^1B_{2u}$	1.153	1.166	1.001	0.260	5.00	4.90[17]
		$1e_{1g} \to 1e_{2u}$	1 $^3B_{2u}$	1.050	1.431	1.013	0	4.33	3.95[18]
		$1a_{2u} \to 1e_{2u}$	1 $^1E_{2g}$		1.293	1.006	0	7.66	7.80[19]
		$1a_{2u} \to 1e_{2u}$	1 $^3E_{2g}$		1.337	1.005	0	7.29	6.83[20]
		$(1e_{1g})^2 \to (1e_{2u})^2$	$^1A_{1g}$		2.279	2.004	-	10.20	
anthracene	D_{2h}	$2b_{2g} \to 2b_{1u}$	1 $^1B_{3u}$	1.064	1.578	1.015	0.668	3.36	3.45[21]
		$2b_{2g} \to 2b_{1u}$	1 $^3B_{3u}$	1.255	1.542	1.008	0	3.32	3.30[22]
		$(2b_{2g})^2 \to (2b_{1u})^2$	2 ^1A_g		2.255	2.001	-	4.60	4.71[23]
pleiadene	C_{2v}	$4a_2 \to 6b_2$	1 $^1B_1$	1.489	1.514	1.013	0.059	1.07	1.45[24]
		$4a_2 \to 6b_2$	1 $^3B_1$	1.339	1.649	1.016	0	0.84	
		$3a_2 \to 6b_2$	2 $^1B_1$		1.627	1.013	0.058	2.92	3.29[24]
		$3a_2 \to 6b_2$	2 $^3B_1$		1.666	1.013	0	2.78	
		$(4a_2)^2 \to (6b_2)^2$	2 $^1A_1$		2.681	2.012	-	2.46	2.46[24]
		$(3a_2)^2 \to (6b_2)^2$	$^1A_1$		3.012	2.033	-	6.30	
		$(4a_2)^2 \to (6b_2)^2$ $3a_2 \to 5a_2$	$^1A_1$		3.747	3.006	-	6.40	
		$(4a_2)^2 \to (6b_2)^2$ $3a_2 \to 5a_2$	$^3A_1$		3.749	3.006	-	6.23	
		$(3a_2)^2 \to (6b_2)^2$ $(4a_2)^2 \to (5a_2)^2$	$^1A_1$		4.731	4.006	-	10.69	
lithium hydride	$C_{\infty v}$	$2\sigma^+ \to 3\sigma^+$	2 $^1\Sigma^+$	1.602	1.305	1.070	0.028	3.34	3.65[25]
		$2\sigma^+ \to 3\sigma^+$	1 $^3\Sigma^+$	1.209	1.212	1.094	0	3.26	3.29[25]
		$(2\sigma^+)^2 \to (3\sigma^+)^2$	$^1\Sigma^+$		1.932	1.789	-	14.89	
		$(2\sigma^+)^2 \to (1\pi)^2$	$^1\Sigma^+$		2.030	2.000	-	14.89	
chromate	T_d	$1t_1 \to 2e$	1 $^1T_1$	1.598	1.807	1.064	0.015	2.97	2.94[26]
		$1t_1 \to 2e$	1 $^3T_1$	1.557	1.839	1.049	0	2.80	
		$(1t_1)^2 \to (2e)^2$	$^1A_1$		3.458	2.161	-	8.55	
permanganate	T_d	$1t_1 \to 2e$	1 $^1T_2$	1.434	1.654	1.053	0.078	2.23	2.27[27]
		$1t_1 \to 2e$	1 $^3T_2$	1.419	1.715	1.036		1.95	
		$(1t_1)^2 \to (2e)^2$	$^1A_1$		3.159	2.113	-	6.54	6.56[28]
ferrocene	D_{5d}	$3e_{2g} \to 4e_{1g}$	1 $^1E_{1g}$	1.255	1.581	1.021	0	2.64	2.70[29]
		$3e_{2g} \to 4e_{1g}$	1 $^3E_{1g}$	1.270	1.642	1.028	0	2.13	2.34[29]
		$(3e_{2g})^2 \to (4e_{1g})^2$	$^1A_{1g}$		2.964	2.056	-	6.61	

[a] Helium results were obtained using BLYP/aug-pc4. BLYP p_n, η, f, and ΔE values are for wave functions obtained using IMOM. rTD-BLYP/cc-pVTZ p_n values employed "relaxed" attachment and detachment densities.[7] BLYP/6-31G* geometries were used throughout. "Exact" excitation energies are either experimental or accurate *ab initio* results. References 12−29 are denoted in the final column by superscript numbers.

agreement with experiment and an η value of 1.022, leading us to conclude that the state is, in fact, only singly excited. But, if this is so, why do CI wave functions contain significant contributions from doubly substituted determinants? The answer is one of the key conclusions of this Letter.

The substituted determinants in a CI expansion describe *three* important effects, *viz.*, electron excitation, electron correlation, and orbital relaxation. The third of these reflects the fact that MOs that are optimal for the ground state are nonoptimal for the excited state.[37] We contend that the presence of large doubly substituted determinants in the CI wave function of this excited state of butadiene arises not because two electrons have been excited but, primarily, from the need to relax the MOs.

The 1 $^1E_{2g}$ state of benzene has a similar story. Benzene is one of the most studied, and most challenging, molecules in computational chemistry (see Matos *et al.*[38] and references therein). Early single-reference CI studies[39−41] yielded valence excitation energy errors exceeding 1 eV. Later multireference CI (MRCI)[42] and symmetry-adapted cluster CI (SAC−CI)[43] calculations gave better results but still produced errors of 0.5 eV. The errors can be reduced by applying perturbative corrections to the MRCI wave functions, and, in this way, Lorentzon *et al.*[44] and Hashimoto *et al.*[45] obtained a vertical excitation energy (7.73 eV) for the 1 $^1E_{2g}$ state that compares well with experiment[19] (7.80 eV). Their wave functions have strong doubly substituted character (30% and 33%, respectively) and the 1 $^1E_{2g}$ state is therefore usually described as arising from the $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ double excitation.[45]

However, our calculations reveal that the 1 $^1E_{2g}$ state has η = 1.006 and is therefore only singly excited, a result consistent with TDDFT describing this excitation well.[46] As for butadiene, we conclude that the significant doubles amplitudes are associated with orbital relaxation and correlation effects. They should not be interpreted as indicating a doubly excited state.

Finally, we draw attention to the MnO_4^- ion. The experimental spectrum[28] shows a strong absorption at 6.56 eV, but the associated transition has not been definitively assigned. Given the close agreement with one of our computed energies (6.54 eV), it is possible that this absorption may arise from the $(1t_1)^2 \rightarrow (2e)^2$ double excitation (η = 2.113).

This Letter has introduced the excitation number η, an intuitively appealing measure of the number of electrons excited in an electronic transition, and the derivation of η also leads to natural definitions of particle and hole densities. We find that η values are surprisingly close to integers, and the reasons for this warrant further study. We have used η to correct the mis-assignments of well-known excited states of butadiene and benzene.

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