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COMMUNICATIONS

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A means of finding a compact orbital representation for the electronic transition density matrix is described. The technique utilizes the corresponding orbital transformation of Amos and Hall and allows a dramatic simplification in the qualitative description of an electronic transition. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1558471]

The description of electronically excited states is often couched in terms of excitation amplitudes based on a set of ground state orbitals. For example, in the configuration interaction singles (CIS) approach to excited states, the many-electron space consists of all single particle-hole excitations (singles) from the ground state. In *ab initio* approaches utilizing the Hartree–Fock ground state this is often a fairly crude approximation, but it can be effective when used with semi-empirical Hamiltonians.[1–4] A similar expansion is used in linear response approaches to excited states such as the random-phase approximation (RPA). The RPA can be applied to reference states derived from either Hartree–Fock or density functional theory (DFT). The latter approximation also goes by the name of time-dependent DFT (TDDFT).[5–11] It is becoming increasingly popular as it appears to be significantly more accurate than the analogous approach applied to Hartree–Fock reference states.[3,4]

The end result of such a calculation is an excitation energy and a set of coefficients describing the contribution that each particle-hole pair makes to the excited state (excitation amplitudes). Oftentimes, there is no dominant configuration in the list of excitation amplitudes, thereby making a straightforward interpretation of the excited state difficult. This is particularly unsatisfactory when attempting to determine the qualitative nature of an excited state. An additional complication in the DFT case is that in principle all orbitals in DFT but the HOMO are devoid of physical significance. However, chemical intuition is built on the orbital construct, and a simple orbital interpretation of "what got excited to where" is important.

In this communication I describe an approach to this problem which relies on finding a compact orbital representation for the electronic transition density matrix. By applying separate unitary transformations to the occupied and the virtual orbitals, a maximal correspondence between the excited "particle" and the empty "hole" can be obtained, without changing the physically relevant quantity, the transition density. This is accomplished using the corresponding orbital transformation of Amos and Hall.[12] This transformation has been used extensively in quantum chemistry, but to my knowledge it has not been applied in the present context previously,[13] and therefore merits a brief review.

For the sake of having a specific example, let us consider the CIS approximation, which is equivalent to the Tamm–Dancoff approximation of TDDFT. The result of a self-consistent-field (SCF) calculation on the ground state is an orthogonal set of N_o occupied spin orbitals, ψ_i, and a set of N_v unoccupied spin orbitals, ψ'_a. Assume that $N_v \geq N_o$, as is usually the case. The relevant quantity associated with the electronic excitation is the single particle transition density matrix $\mathbf{T}$, a rectangular $N_o \times N_v$ matrix coupling the ground state Ψ_0 with the excited state Ψ_{ex},

$$T_{ia} = \sum_\sigma \langle \Psi_{ex} | c_{i\sigma}^\dagger c_{a\sigma} | \Psi_0 \rangle. \tag{1}$$

The index i labels occupied orbitals in the set ψ and the index a labels the virtuals in set ψ'. σ is the spin index.

We construct two new sets of orbitals, defined by the unitary transformations

$$(\phi_1, \phi_2, \ldots, \phi_{N_o}) = (\psi_1, \psi_2, \ldots, \psi_{N_o}) \mathbf{U}, \tag{2}$$

and

$$(\phi'_1, \phi'_2, \ldots, \phi'_{N_v}) = (\psi'_1, \psi'_2, \ldots, \psi'_{N_v}) \mathbf{V}. \tag{3}$$

The matrices $\mathbf{U}$ and $\mathbf{V}$ are determined by solving the eigenvalue equation

$$\mathbf{TT}^\dagger u_i = \lambda_i u_i, \quad i = 1 \ldots N_o \tag{4}$$

$$\mathbf{T}^\dagger \mathbf{T} v_i = \lambda'_i v_i, \quad i = 1 \ldots N_v \tag{5}$$

with

$$\mathbf{U} = (u_1, u_2, \ldots, u_{N_o}), \tag{6}$$

$$\mathbf{V} = (v_1, v_2, \ldots, v_{N_v}). \tag{7}$$

The new orbitals ϕ and ϕ' have the following useful properties:

(a) If the λ_i and λ'_i are separately numbered in order of decreasing magnitude, then

$$1 \geq \lambda_i \equiv \lambda'_i \geq 0, \quad i = 1 \ldots N_o, \tag{8}$$

and

$$\sum_{i}^{N_o} \lambda_i = 1. \tag{9}$$

(b) The eigenvectors $v_{N_o+1}...v_{N_v}$ will have eigenvalues zero.

(c) The transition density matrix expressed in terms of the new orbitals is diagonal,

$$|[\mathbf{U}^\dagger\mathbf{TV}]_{ij}| = \sqrt{\lambda_i}\delta_{ij}. \tag{10}$$

Note what has been accomplished with this transformation. The N_oN_v transition amplitudes which previously served to define the excitation have been reduced to a set of N_o particle-hole amplitudes. With each hole in the occupied space, one can associate a single corresponding particle in the virtual space. The importance of a particular particle-hole excitation to the overall transition is reflected in the associated eigenvalue λ_i.

The application of this transformation to RPA or TDDFT transition densities follows along the same lines. However, due to the presence of the de-excitation operators the eigenvalue sum $\Sigma_i^{N_o}\lambda_i$ will not be identically one, but will deviate from that to the extent that the de-excitation operators are significant. These de-excitation terms are usually small, as witnessed by the success of the Tamm–Dancoff approximation (which ignores them) in reproducing TDDFT.[11] Extension to spin-unrestricted cases is straightforward, as separate transformations may be applied to each spin index in turn, rendering the $\alpha\alpha$ and $\beta\beta$ components of the transition density individually diagonal.

This procedure has been implemented in a local version of the GAUSSIAN 98 suite of programs[14] and utilized with the TDDFT implementation of Stratmann, Scuseria and Frisch.[10] As an example of the approach we consider the excited states of a d^6 Re complex recently studied by Dattelbaum and coworkers[15] shown in Fig. 1. The molecule is the pseudo-octahedral Re(bipyridyl)(CO)$_3$(4-ethylpyridine)$^+$ ion. The calculations utilized the LANL2 relativistic effective core potential for Re. The associated double-zeta basis set[17] was completely uncontracted. Note, however, that when the LANL2DZ basis is uncontracted, two nearly linearly dependent p functions result. One function ($\alpha = 0.4644$) was retained, and one deleted ($\alpha = 0.4900$). The 6-31G* basis set was utilized for the ligands. A geometry optimization using the B3LYP DFT approximation[16] was followed by a TDDFT calculation of the lowest singlet states employing the same functional.

The TDDFT calculation provides excitation energies and oscillator strengths to the lowest singlet states reported in Table I. The lowest excitation carries little oscillator strength, and is fairly cleanly described as $\psi_{homo}\rightarrow\psi'_{lumo}$. The next two excited states also involve excitation into ψ'_{lumo}, but the
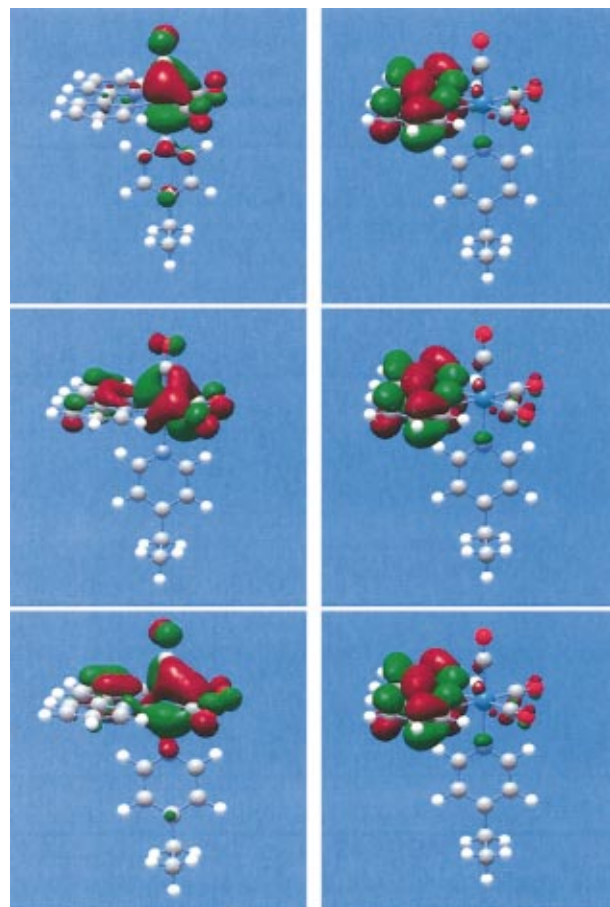

FIG. 1. (Color) The dominant natural transition orbital pairs for the first three excited singlet states of $[\mathrm{Re(bpy)(CO)_3(4\text{-}Etpy)}]^+$. The first excited state is at the top of the figure; for each state, the "hole" is on the left, the "particle" on the right. The associated eigenvalues λ are 0.9962, 0.9967, and 0.9809, respectively.

associated hole involves significant contributions from both ψ_{homo-1} and ψ_{homo-2}. For example, from the amplitudes in Table I the second excited state is approximately described as $0.7973\ (\psi_{homo-2}\rightarrow\psi'_{lumo}) + 0.5886\ (\psi_{homo-1}\rightarrow\psi_{lumo})$. The third excited state differs primarily in the phase of the configuration mixing. This leads to one weak transition and a higher energy, more intense one. The last column reports the largest natural transition orbital eigenvalue, λ_{max}, for each state. This eigenvalue is ≥ 0.98 for all the states, signifying that even the heavily mixed second and third states can be quite well described in terms of a dominant excitation pair accounting for over 98% of the transition. Stated another way, if the calculation were repeated for a specific excited state using the transition natural orbitals appropriate for it, the leading term would be $\sqrt{\lambda_{max}}(\phi_{max}\rightarrow\phi'_{max})$. This coefficient is ≥ 0.99 for all three states in their respective transition natural orbital basis. Plots of the pairs are given in the Fig. 1.

TABLE I. TDDFT results for the low lying excited states in $[\mathrm{(bpy)Re(CO)_3(4\text{-}Etpy)}]^+$.

Excited State	ΔE(eV)	f	Description	λ_{max}
1	2.65	0.0031	$0.9894\ (\psi_{homo}\rightarrow\psi'_{lumo})$	0.9962
2	2.91	0.0079	$0.7973\ (\psi_{homo-2}\rightarrow\psi'_{lumo}) + 0.5886\ (\psi_{homo-1}\rightarrow\psi_{lumo})$	0.9967
3	3.02	0.0658	$-0.5883\ (\psi_{homo-2}\rightarrow\psi'_{lumo}) + 0.7642\ (\psi_{homo-1}\rightarrow\psi_{lumo})$	0.9809

Note that all three states are metal-to-ligand charge transfer in character, the excitation promoting an electron from an orbital that is dominantly on the Re center to one that is localized on the bipyridyl group. The three states differ only in the particular d_π Re orbital involved.

In summary, I have described an orbital transformation which should be quite helpful in providing a qualitative description of an electronic excitation. In addition to providing a simple orbital interpretation of the excitation, all one-electron properties associated with the transition, such as the transition dipole, may be interpreted in a transparent way as a sum over the occupied natural transition orbitals, each orbital being paired with a single unoccupied orbital, weighted with the appropriate eigenvalue λ.

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