Modeling Molecular Electronic Properties with Semiempirical UNO-CAS

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The abbreviation UNO–CAS stands for **U**nrestricted **N**atural **O**rbitals (UNOs, **U**) – **C**omplete **A**ctive **S**pace. It is defined as full configuration interaction performed in the active space. The active space is readily defined as that of the UNOs with significant fractional occupations (between 0.02 and 1.98). The method was originally proposed by J. M. Bofill and P. Pulay as an *ab-initio* method and an inexpensive alternative to the CAS–SCF (complete active space–self-consistent field) method. [1] UNOs together with their occupation numbers **σ** can be obtained *via* diagonalization of the total UHF density matrix $\mathbf{P}^T$ (sum of α- and β-density matrices from UHF calculations), *i.e.* solving the eigenvalue problem: [2]

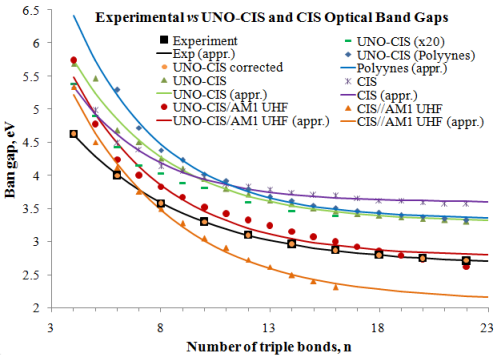
$$\mathbf{S}^{1/2}\mathbf{P}^T\mathbf{S}^{1/2}(\mathbf{S}^{1/2}\mathbf{U}) = (\mathbf{S}^{1/2}\mathbf{U})\boldsymbol{\sigma} \quad (1)$$

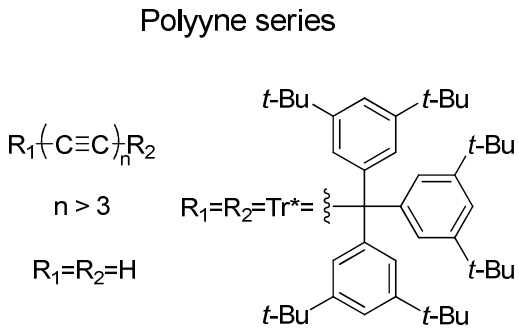
where the UNOs are the eigenvectors and the occupations are the eigenvalues of $\mathbf{P}^T$ and **S** is the atomic orbital (AO) overlap matrix. If the latter is unity, equation (1) is simplified to: [2]

$$\mathbf{P}^T\mathbf{U} = \mathbf{U}\boldsymbol{\sigma} \quad (2)$$

Here we extend formalism to obtain the semiempirical UNO–CAS method with the additional possibility of performing configuration interaction singles (CIS) as well as CI singles and doubles (CISD) in the active space, which we call semiempirical UNO–CIS and UNO–CISD, respectively. The UNO–CIS method is obviously computationally much cheaper and allows us to perform calculations for relatively large molecules with active spaces that include more than a hundred orbitals.

For instance, this method can predict the optical band gaps (E_g) of the substituted polyyne series in good agreement with available experimental data [3]. The choice of orbitals to be used in conventional semiempirical CI calculations is not obvious and it can be a significant problem to determine a reasonable number of orbitals as the number of triple bonds in the polyyne series changes. However, UNO–CIS allows this number to be determined automatically. Moreover, UNO–CIS band gaps are generally in better agreement with experiment than those calculated using conventional semiempirical CIS with the same number of orbitals. Thus, UNO–CAS can be used successfully to predict E_g values for unknown species and therefore to model new materials especially in the field of nanoelectronics.





[1] J. M. Boffil, P. Pulay, *J. Phys. Chem.*, **1989**, *90*, 3637-3646.
[2] P. Pulay, T. P. Hamilton, *J. Phys. Chem.*, **1988**, *88*, 4926-4933.
[3] W. A. Chalifoux, R. R. Tykwinski, *Nat. Chem.*, **2010**, *2*, 967-971