Application of Semiempirical UNO–CI and CI Methods in Nanoelectronics

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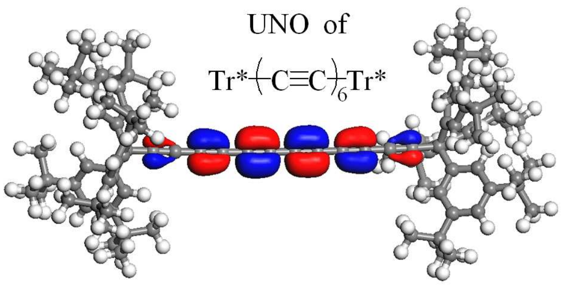
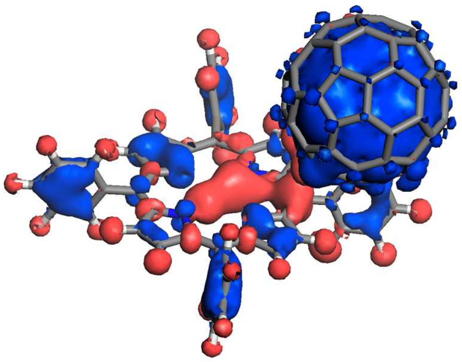
MNDO-like semiempirical configuration interaction (CI) methods have been applied successfully for calculating excited states (ES) of large systems. The inclusion of dynamic and static electron correlations in these methods provides the accuracy of the determination of ES energies comparable with that of time-dependent density functional theory (TDDFT) methods. [1]

We recently introduced semiempirical UNO–CI methods that perform CI calculations using unrestricted natural orbitals (UNOs). [2] UNOs and their occupation numbers ($\boldsymbol{\sigma}$) are the eigenvectors and the eigenvalues of the total unrestricted Hartree–Fock (UHF) density matrix $\mathbf{P}^{\mathrm{T}}$, respectively. [2, 3] One of the advantages of UNO–CI methods is that orbitals (active space) for CI calculations are determined automatically by choosing orbitals with physically meaningful significant fractional occupation numbers (SFONs). Using SFONs between 0.02 and 1.98 to choose UNOs is sufficient in most cases, though sometimes using a broader range of SFONs may improve results. Moreover, occupations of frontier semiempirical UNOs predict diradical characters of singlet ground state PAHs better than those of *ab initio* and DFT UNOs. [2]

We have demonstrated that optical band gaps (E_{g}) of polyynes and polycyclic aromatic hydrocarbons (PAHs) calculated using semiempirical UNO–configuration interaction singles (UNO–CIS) are in good agreement with experimental values. Generally E_{g} values calculated using UNO–CIS are better than those calculated using conventional semiempirical CIS and comparable or better than those calculated by TDDFT. Noteworthy, UNO–CIS calculations are faster by one or several orders of magnitude than TDDFT calculations. The accuracy of UNO–CIS calculations can be improved further by performing full CI in the active space. Nevertheless, the latter approach, called UNO–CAS (UNO–complete active space), is much more computationally expensive than UNO–CIS. [2]

More recently semiempirical CI and UNO–CI methods have been used successfully to calculate absorption UV/vis spectra of cumulenes. Furthermore, experimental band gaps of polymers consisting of metal centers and heterocycles were reproduced well by the title methods. Another application of semiempirical CI methods is revealing the nature of charge separated (CS) states of porphyrin-fullerene dyads. In summary, semiempirical CI and UNO–CI methods are very reliable and fast approaches for predicting and explaining electronic properties of nanomaterials.





[1] MNDO-like Semiempirical Molecular Orbital Theory and its Application to Large Systems, T. Clark and J. J. P. Stewart, in Computational Methods for Large Systems, J. J. Reimers (ed.), Wiley, Chichester, **2011**, *Chapter 8*, pp. 259-286.
[2] P. O. Dral, T. Clark, *J. Phys. Chem. A*, **2011**, *115*, 11303-11312.
[3] J. M. Bofill, P. Pulay, *J. Chem. Phys.* **1989**, *90*, 3637-3646.