Large-scale CI: Band Gaps and Excited States in EMPIRE'24

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The increasing role of quantum chemical calculations in drug and materials design has led to a demand for methods that can describe the electronic structures of large and complex systems. Semiempirical methods based on the neglect of diatomic differential overlap (NDDO) approximation (e.g., the MNDO, MNDO/d, AM1, AM1*, and PMx methods) are important representatives of such approaches. Many of these methods have been implemented in the massively parallel program EMPIRE, which makes the full quantum-mechanical treatment (electronic properties, geometry optimization, molecular dynamics) of systems containing 100,000 atoms or more on thousands of cores possible [1].

EMPIRE can, for example, be used in combination with a classical molecular dynamics (MD) code to perform electronic structure calculations on snapshots from an MD run on a periodic system. In addition, EMPIRE can perform MD calculations using semiempirical methods entirely, which enables the study of bond formation and dissociation processes [3].

Periodic boundary conditions (PBC) enable the treatment of condensed-phase systems, such as proteins in a periodic water box or solids. This allows molecular materials to be studied in their native environment. For semiempirical methods, the most practical way of implementing PBC is the cyclic-cluster approach in which the system is approximated by a supercell and by imposing Born-von Karman boundary conditions. Using a large unit cell allows the calculation to be performed entirely in real space. The main advantage of this technique is that program features like the calculation of local properties or excited states are directly transferable from nonperiodic calculations. EMPIRE is suitable for use on systems with unit cells up to 50,000 atoms (e.g., disordered and amorphous systems) [2].

Configuration interaction (CI) calculations can be used to study the properties of biradicals and excited states. In CI calculations, the MOs for the ground state are calculated and then used unchanged to construct a series of further electronic configurations (microstates) that are mixed to form new electronic states. CI calculations give not only the ground state, but also the excited states that result from mixing the microstates used. They can therefore be used for the calculation of band gaps, UV/vis spectra and second order hyperpolarizabilities etc. EMPIRE can perform CI calculations on systems containing 5,000 atoms or more.

Semiempirical UNO-CI in which unrestricted natural orbitals (UNOs) are used as the reference for CI calculations gives good results for the optical band gaps of organic semiconductors such as polyynes and polyacenes. The results of these semiempirical UNO-CI techniques are generally in better agreement with experiment than those obtained with the corresponding conventional semiempirical CI methods and often better than those obtained with far more computationally expensive methods such as time-dependent density-functional theory [4].

We now present EMPIRE'24 which uses a performance-optimized CI code, that enables the calculation of large systems at less computational cost.

[1] *EMPIRE: A highly parallel semiempirical molecular orbital program: 1: Self-Consistent Field Calculations*, M. Hennemann, T. Clark, *J. Mol. Model.* **2014**, *20*, 2331.
[2] *EMPIRE: A highly parallel semiempirical molecular orbital program: 2: Periodic boundary conditions*, J. T. Margraf, M. Hennemann, B. Meyer, T. Clark, *J. Mol. Model.* **2015**, *21*, 144.
[3] *EMPIRE: a highly parallel semiempirical molecular orbital program: 3: Born-Oppenheimer molecular dynamics*, J. T. Margraf, M. Hennemann, T. Clark, *J. Mol. Model.* **2020**, *26*, 43.
[4] *Semiempirical UNO-CAS and UNO-CI: Method and Applications in Nanoelectronics*, P. O. Dral, T. Clark, *J. Phys. Chem. A* **2011**, *115*, 11303-11312.