

The use of the Fourier Transform in the Calculation of Electronic Properties of One-Dimensional Periodic Systems

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The implementation of the HF-LCAO or DFT methods for the study of the electronic structure of stereoregular polymers needs to take into account the existence and the convergence of one-dimensional infinite lattice summations appearing in the Coulomb and exchange terms.

Generally, the multipolar expansion is used in order to handle the lattice series appearing in the classical Coulomb terms while the convergence of lattice summations in the exchange is usually controlled by the rate of decay of the density matrix elements with respect to the cell indexes. This approach has the difficulty that the lattice sums involved may converge rather slowly and in some cases it is not possible to achieve satisfactory convergence, not only due to the large number of integrals that enter in the computation, but also because of numerical instabilities.

A way out of this dilemma is suggested by the Poisson transformation, which permits a lattice sum in direct space (*DS*) to be converted into an equivalent summation in reciprocal (also called Fourier) space (*FS*). In general, the more slowly a *DS* sum converges, the more rapid will be its convergence in *FS*. However, the *FS* approach alone only transfers the regions of slowest convergence to other parts of the parameter space, so the problem is altered but not eliminated. But these lattice sums can be partitioned, using the Ewald-type procedure, in a *DS* and a *FS* part, both characterized with exponential (rather than inverse-power) convergence.

This Ewald-type partitioning leads, in the *DS* partition, to integrals similar to those encountered in the usual molecular computations using gaussian type atomic orbitals. However, the *FS* partition produces expressions that can be identified as incomplete Bessel functions. Reasonable methods for the evaluation of these functions [1] are now available and it has become practical to evaluate all the quantities arising when stereoregular polymers are treated with gaussian type basis sets of arbitrary angular symmetry.

This technique [2, 3] is implemented in a code called FT-1D . It also takes full advantage of all line-group symmetries to calculate only the minimal set of two-electron integrals and to optimize the computation of the Fock matrix.

The present communication reports some benchmark studies of this code. Our results not only confirm the algorithmic correctness of the code through agreement with other studies where they are applicable, but also show that the use of convergence acceleration enables accurate results to be obtained in situations where other codes fail. It is also found that full attention to the line-group symmetry leads to an increase of between one and two orders of magnitude in the speed of computation.

This work would not have made possible without the decisive contribution of Professor F.E. Harris to the field. He is, with Professor Joseph Delhalle of University of Namur, who recognized the importance of lattice sums, the difficulty in computing them accurately. It was for me a rare privilege and a chance of having the opportunity to collaborate with him over the years.

References

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