

**Analytical energy gradients for dynamical simulations of trans polyacetylene chains within the Pariser-Parr-Pople Hamiltonian.** Foerner, W

**Abstract**

Exact anal. energy gradients for the PPP (PPP) Hamiltonian are derived. A comparison of computer times for dynamical simulations of trans-Polyacetylene (t-PA) using anal. and numerical gradients is given. The numerical method is shown to lead to serious difficulties both computationally and from the point of view of numerical accuracy. In fact, using the anal. method, it turned out that the computational effort for the gradient calcn. is negligible compared to that for the SCF iteration in each time step of a simulation. On the other hand, using the numerical method the gradient calcn. is the time consuming bottle-neck of a simulation. A previously presented method for the gradient calcn. in the Hueckel type Su-Schrieffer-Heeger (SSH) Hamiltonian which was thought to be approx., is shown to be exact.