

**Derivatives of eigenvalues from ab initio Hartree-Fock crystal orbital calculations with respect to the quasimomentum and the iterative solution of the inverse Dyson equation in the correlation problem.** Foerner, Wolfgang

**Abstract**

We derive an anal. formula for the calcn. of densities of states from ab initio Hartree-Fock Crystal Orbital (HF-CO) results, using an exact expression for the derivs. of the eigenvalues with respect to the quasimomentum  $k$  following from first-order perturbation theory. The result is completely equiv. to that reported previously by Delhalle. Derivs. of the CO-coeffs. with respect to  $k$  cannot be derived from first-order perturbation theory, because one coeff. in the wavefunction is not defined. Further, due to the arbitrary phase factors at each CO, the form of such derivs. is not unique, but depends on the actual phase. Second derivs. of eigenvalues, and thus effective masses, are also obtained in this way, because for this purpose the unknown coeff. in the first order wavefunction is not necessary. In principle, perturbation theory can also yield expressions for higher-order derivs. We develop a CO formalism based on real quantities only and show that with this approach well defined phases are obtained. There are no more artificial numerical discontinuities in the phases and in this way the matrixes introduced by Ladik to avoid complex calculus can be related directly to a basis set transformation. Further we discuss the use of phase factors for the construction of Wannier functions in correlation calcns. on polymers, as well as the properties for the iterative soln. of the inverse Dyson equation. Finally we describe the exploitation of helical symmetry without rotating two-electron integrals but instead with rotations on d. matrixes.