

Ab-initio effective potentials in crystal Hartree-Fock theory

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Abstract. *Ab initio* effective potential technique of Ewig *et al* is applicable directly to crystal Hartree-Fock formalism provided the effective potentials are suitably defined. Corresponding to every atom or every molecule by constructing a crystal one can assign a unit species configuration. The effective potentials in the crystal can be expressed as functions of lattice parameters in terms of integrals over the orbitals of this unit species. These expressions are in a more exact form than those usually employed in molecular calculations.

Keywords. Crystal Hartree-Fock; effective potentials; species configuration.

1. Introduction

The last decade has seen the development of *ab initio* Hartree-Fock Self-Consistent-Field (HFSCF) treatment for crystalline systems (Collins *et al* 1974; Dagens and Perrot 1972; Euwema *et al* 1973, 1974; Harris and Monkhorst 1969; Kunz 1969, 1971, 1972; Kunz *et al* 1973; Mickish *et al* 1974; Surratt *et al* 1973). Various symmetry operations render such a calculation feasible in practice for crystals containing atoms of mostly upto the second row in the periodic table. For a crystal of heavier atoms the standard difficulties of an *ab-initio* HFSCF calculations of a large system are met. This leads one to look for *ab initio* effective potential techniques which translate the HFSCF theory in terms of a valence electronic Hamiltonian and mutually orthonormal valence pseudofunctions which are otherwise unconstrained in nature (Ewig *et al* 1975, 1977; Kahn and Goddard 1972; Kahn *et al* 1976; Datta *et al* 1978). The primary objective of such techniques is to make accurate calculations on a large system possible. The critical step in such a procedure is to choose a facile means of producing effective potentials in an *ab initio* fashion. This work stems from the hope that once the effective potentials are reasonably expressed for crystals, the HFSCF procedure using the effective potential technique will be a routine for crystals of heavier atoms (such as Si or Ge semiconductors).

In this work we discuss the generation of crystal effective potentials in the Ewig sense. Thus these potentials consist of two parts, one coming from the one-electronic modification of the Fock operator (Phillips-Kleinman pseudopotential) and the second one representing modifications of the two-electronic repulsions (Ewig W potentials). The core-valence interactions are grouped into W^{core} potentials whereas the change in valence-valence interactions is given by W^{val} potentials. In molecular calculations the SCF iterations give results which are very sensitive to