CHAPTER I

INTRODUCTION

To determine the wave functions and energies of the possible states of a solid,we need to solve many-body Schrödinger equation describing the interaction between the electrons and the nuclei. A popular method to solve this problem is to use the Hartree-Fock equations. Many approximation methods have to be introduced, because of the difficulties in solving these equations. Some of these methods are the nearly-free electron model, the tight-binding method, the cellular method, the orthogonalized plane wave, the augmented plane wave, the Green function method,and the pseudopotential method (Ziman, 1972). In the Hartree-Fock approach, it is assumed that the N electrons move in the field of a nucleus of charge Ze (N of course equals Z for a neutral atom, but would be different for a positively or negatively charged ion). The electrons themselves, of course, produce a space charge, this space charge being approximately spherically symmetrical. The total field acting on an electron arises not only from the nucleus but also from the other electrons. The other electrons have the effect of partially shielding the nuclear field, since they are oppositely charged. Thus we find that the electrons move in a resultant central field, and it is the motions of the electrons in this central field that must be determined.

The cellular method (Wigner and Seitz,1933,1934), the most successful one , was first applied to metallic sodium. The assumptions used in this method are

a) An atomic cell is replaced by a sphere of equal volume

b) Crystal potential is spherically symmetric within a cell out to the boundary

c) The crystal potential is replaced by potential due to core of a free ion with all valence electrons removed

d) Exchange and correlation energies are taken to be that of a free-electron gas having density appropriate to uniform distribution of valence electrons over an atomic cell

If the spherically symmetric field (or effective potential) has been found, wave functions and their associated energy levels of a metal and of the free atom can be easily obtained by solving Schrödinger radial wave equation . Physical quantities such as cohesive energy, lattice constant, thermal expansion coefficient, compressibility, etc., of that metal can then be determined. As an inverse problem, the potential can be determined from the experimental atomic energy levels which have been found from spectroscopy.

We shall consider monovalent atoms such as alkali metals since they have lesser complexity than other types of atoms. The alkali metals are in the first column of the periodic table and are Li, Na, K, Rb, and Cs. The Na potential was first constructed semiempirically by Prokofjew(1929) who used the WKB approximation, and it could give energy levels for the free atom which were in agreement with the corresponding observed spectra. This potential was later employed to calculate the cohesive energy and the lattice constant by Wigner and Seitz(1933,1934). The Na potential given in Prokofjew's paper contained several misprints. The corrected one was published in the first paper of Wigner and Seitz. The Na potential was reconstructed by Dumrongsak(1976) using the same method as that used by Prokofjew. The same result was found. An attempt was made by Seitz(1935) to find the Li effective potential, in the same fashion as that used by Prokofjew, in order to be used in a calculation of the cohesive energy of Li. He found that the potential could not reproduce energy levels to good accuracy. He therefore introduced a new technique to create the Li potential. In the new technique, the potential could be adjusted at any point along the radius. The proper readjustment was that which caused the calculated energy levels to be in agreement with the experimental spectra. This meant that the potential created by Seitz could not be expressed in an analytical form as the Prokofjew's Na potential could be. The resulting Li potential was employed to solve Schrödinger equation in various works. The corrected potential was published in Kohn and Rostoker(1953). Gorin(1936) attempted the same thing for K and also found that the potential could not reproduce energylevels to good accuracy.

The first aim in our work is to recalculate the Prokofjew's Na potential in order to reproduce the energy levels to better accuracy. Our second aim is to reconstruct the Li potential in the fashion of Prokofjew in order to obtain an analytical form of potential which would be easier to use in solving Schrödinger equation. We shall take into consideration the correction term due to ion-core polarization. An attempt to find a new potential is then carried out. Finally, all of the constructed potentials are tested by comparing the predicted energy levels with the experimental data.

In chapters II and III , some theoretical background using in our work are reviewed. A new technique to find out quantum defects semiempirically which was previously suggested by Jaffé and Reinhardt (1977) is also reviewed. Their applications in our work are refered in chapter IV. In chapter V, the results of construction the potentials are presented and the results of our testing all of the potentials are compared. Some discussions of our work are given in the last chapter.