

CHAPTER V

DISCUSSIONS



In this chapter a summary of the three methods used for calculating of the cohesive energy of the alkali metals is given. The results obtained by these methods are then compared with the experimental values. Some useful suggestions are also given.

The first method to be mentioned was that of Fröhlich. He used the cellular method to obtain the wave function near $r = r_0$ of the valence electron in the atomic sphere. By imposing certain boundary condition the lowest state energy could be expressed analytically in terms of the constant r_0 and the atomic sphere radius r_s . The value of r_0 was determined by the matching of the wave function near $r = r_0$ and the free atom wave function. The expression of the latter wave function, obtained by Fröhlich, kept terms up to the order of $\frac{1}{r}$ while we allowed for one more term. Knowing the value of r_0 allowed us to find the lowest state energy. This inturn allowed us to determine the average energy per electron when the Fermi energy was added. The cohesive energy was then obtained. We present in table 2.1 the values of r_0 which we calculated using the form of the

free atom wave function which contained terms up to $\frac{1}{r^2}$ along with the values obtained by Fröhlich. It can be seen that these two values are close together. The $\frac{1}{r^2}$ - extended wave function does not have much effect on the values of r_0 . We expect that if the wave function (2.20) is used instead of (2.15), the values of r_0 will be better since (2.15) is an approximated form of (2.20). Table 2.2 shows that the calculated values of ρ are in fairly good agreement with the experimental values. The difference between the calculated cohesive energy and the experimental values agree to within 20 % except for Li for which its values is rather low. After we add the correction terms, the results become better for Li and Na for which the differences are within 15 % . The agreement is poor for the case of K, Rb and Cs. This due to fact that the valence electron in the alkali metals are not really free electron. This assumption is only the approximation used for finding the correction terms and the Fermi energy. The effective mass has also been omitted in the expression for Fermi energy. Even after the correction terms have been added, the results are still unsatisfied as can be seen from the table. There is another expression of the lowest state energy $E_{II}(r_s)$ (from (2.7), (2.11) and (2.21)) which hasn't been calculated. It is expected that the value of $E_{II}(r_s)$ will be better if r_0 suggested above is used. Another

way for improving the calculation of the lowest state energy is to include the polarization potential $-\frac{\alpha}{r^4}$ with the hydrogenic potential. However, inclusion of this term will make the calculations more difficult.

In chapter III, Imai's wave function about the origin was used as the wave function in the neighbourhood of the turning points. This wave function is expressible in terms of three parameters P_h, z, ξ and the arbitrary constants η_1 . Since two turning points have to be considered, only η_1 and η_2 were taken into account. The constant η_1 was determined by the behavior of the wave function at the origin. η_2 was determined by the matching of the expanded wave function to the asymptotic wave function at the two turning points. The three parameters P_h, z and ξ are specified by the nature of the potential. Applying the boundary condition at the surface of the atomic sphere, an equation which connected the quantum defect δ , the energy and a function $F_\gamma(x_s)$ was obtained. The function $F_\gamma(x_s)$ was then expanded about x_{sm} and the minimum energy E_{om} and substituted into the equation. Values for E_{om} were obtained from this equation by using the interpolation formula for δ with the known coefficients given in table 3.1. The value of x_{sm} leads to r_{om} which corresponds to r_o of chapter II. To obtain the lowest state energy, Fröhlich's expression was used. The Fermi energy for free

electron was added to give the total energy which was then minimized. Thus r_s was obtained along with the average energy per electron. The ionization energy was then subtracted from the average energy per electron to get the cohesive energy. The values of the latter and the atomic sphere radius for cases of neglecting the correction terms and of including these terms are shown in table 3.2 for comparison. In the first case, the cohesive energy for Li, Na and K are in better agreement than those for Rb and Cs. For Li especially the difference from the observed values is about 3 % while Na and K are corrected within 15 % . The remaining values are not satisfactory when compare with the observed values. Looking at the table, we see that the cohesive energy and the atomic sphere radius in the former case are better than the latter case. One possibility for improving the cohesive energy calculation is to consider the effective mass dependence of the Fermi energy term.

We presented in chapter IV, Wigner and Seitz's method. They obtained the lowest state energy by first rewriting the Schrödinger equation into a simple form. In doing this, the explicit form of potential had to be known. The Prokofjew's potential was employed. With the guess at values of energy, the equation was ready to be solved numerically. The trial energies were restricted to certain values by the boundary condition at the atomic sphere radius.

We follow Wigner and Seitz's method except that the potential introduced by Cowley, et al. is used. The new potential has been written as the sum of the Coulomb and the screened Coulomb potential which is characterized by a parameter α_l . The values of α_l are shown in table 4.1. The technique of calculating the lowest state energy has been given in chapter IV. The average energy per atom can be obtained by taking into account the $E_2 k^2$ and $E_4 k^4$ energy terms where the coefficients E_2 and E_4 are listed in table 4.2. In this table we compare the lowest state energy obtained by the use of Cowley, et al.'s potential given by (4.13) and by Callaway's calculation. The two values seem very close to each other. It appears that the potential used by Callaway and Cowley, et al. yield almost identical values. Only the lowest state energy and the cohesive energy of Callaway are presented here. Our calculation of the Fermi energy was to the k^4 -term. The values of E_2 for Li, Na, K and Rb which we used differ from Callaway's by about 10%. For Cs the difference is within 20%. For E_4 , our values for Na, K and Cs deviate by more than 30% from those used by Callaway. For the rest, the deviation is small. The difference is the least for the case of r_s . After the ionization energy was subtracted from the average energy per electron, the cohesive energy was obtained. With the exclusion of the correction

terms, our calculated cohesive energy are close to the values obtained by Callaway and are agreement with the observed values especially those for Na, Rb and Cs. For Li and K, its cohesive energy agree to within 20 %. When the correction terms are included, the agreement between our values and the observed values are not as satisfactory as Callaway's values. This rises from the fact that the correlation energy term used by Callaway is that of Wigner while we have used that of Bohm and Pines. One of the correlation term as a function of $\frac{1}{r_s}$ while the other is a logarithmic function of r_s .

From table 2.2, 3.2 and 4.2, we see that the cohesive energy which calculated by the last method but does not into account the correction energy are in better agreement with the observed values than other methods.