CHAPTER 1

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Transition metals have attracted continuous attention of both physicists and chemists because of their unusual electronic and structural properties, which have their origin in the dominant influence of \(d\)-electrons on the electronic structure. This group of metals often exhibit pronounced phonon anomalies as a result of complex Fermi-surface geometries in conjunction with strong electron phonon coupling (EPC), whose consistent description still provides a challenge for theoretical approaches.

The pseudopotential theory, in its different forms (local, non-local and first principles) has done tremendous job in giving the understanding of large number of metallic properties of simple metals over the last 40 years. However, the applicability of local model pseudopotential to \(d\)-band metals is a long standing problem and it still remains a problem of interest.

The goal of pseudopotential theory is to obtain the physical properties of atoms, molecules, solids, liquid metals and alloys by dealing only with the valence electrons [Harrison (1966, 1999), Cohen and Heine (1970), Pickett (1989), Szasz (1989), Akinlade et al. (1996)].
To avoid a complicated all electron problem, an effective weaker potential between the valence electrons and the atomic core is introduced. The interactions among the valence electrons are often described by density functional theory [Dreizler and Gross (1990)].

It may seen that the use of a simple pseudopotential model for calculating physical properties does not correspond to the current state of the quantitative theory of metals, when completely *ab initio* methods for calculations of phonon spectra have been developed [Maksimov and Savrasov (1995)]. However, the description of a wide range of lattice properties, including temperature and pressure or volume variation of different physical properties is still beyond the capabilities of completely *ab initio* approaches. Moreover, if it is taken into account that pseudopotential approach also gives the pairwise defects, diffusion processes, radiation effects, for the description of the liquid phase properties (for example, maximum value of the structure factor, thermodynamics of liquids, etc.), then the importance of development of pseudopotential theory for the metals for which it is valid appears indisputable. Until recently, use has been virtually made of solely empirical pairwise potentials, the overwhelming majority of which are short-range ones [Kuchhal and Dass (1999)]. These do not correspond to the real functional dependence in metals, because of the presence of Friedel oscillations. Significantly, eventhough an appropriate empirical pairwise potential can be chosen to simulate a particular defect type, there are, generally speaking, no ground to expect it to be adequate for simulating defects of a different type, or even to describe the properties of an ideal lattice. For the list of such properties, see Mohammed et al. [1984]. Therefore, it is important to construct “theoretical pairwise potentials” that are derived from the realistic model of the metals. In rigorous terms, such pairwise potentials would have to be obtained from *ab initio*
band calculations. However, we do not know any successful attempt to meet the challenge.

Not only simple $s-p$ banded metal, but transition elements may also be described by a local pseudopotential, provided that valence is chosen appropriately [Akinlade et al. (1996), Starkloff and Joannopoulos (1977), Vanderbilt and Joannopolos (1983), Katsnelson et al. (1997), Greenberg et al. (1990), Eichler et al. (1998), Singh (1999), Antonov et al. (1990)].

For transition metals, unlike what happens for simple metals, there are not yet large number of local model potentials which could account for a broad spectrum of lattice properties. In a few recent efforts [Animalu-Heine (1965)], local model potentil has been tried for transition metals [Greenberg et al. (1990), Antonov et al. (1990), Vaks et al. (1989)]. For simple metals also recently some sophisticated model local pseudopotentials have been constructed [Fiolhais et al. (1995, 1996), Pollack et al. (1997)].

For transition metals, one of the most popular psedopotentials is that based on the first principles studies made by Wills and Harrison (1983). This approach uses separate treatments for $s-p$ and $d$-states leading to an effective pair potential that takes into account the effect of $s-d$ hybridization. Despite the success of the theory in solid state, the results for the structure factors of liquid $3d$ transition metals using molecular dynamics and other liquid state theories have not been that reliable [Hausleitner et al. (1991), Regnaut (1989)].

Essentially, for transition metals, one has to consider the fact that the
tightly bound $d$-electrons hybridize with the nearly free electrons resulting in a partially filled $d$-band, crossing the Fermi energy. The presence of $d$-band has been a serious impediment to the construction of local pseudopotential for such systems.

It is true that non-local pseudopotentials are to be preferred for accurate predictions of the properties of real materials, and the use of the non-local potentials is not a serious hindrance in most pseudopotential calculations. Nevertheless, local pseudopotentials have some advantages over non-local ones:

1. Their relative simplicity is an aid to conceptual understanding.

2. They are more convenient and present practical advantages in complex calculations such as quantum Monte Carlo [Mitas and Martin (1994), Fled et al. (1992, 1994), or in extensive studies of cohesion involving many structures or materials [Robertson et al. (1993, 1994)].

3. The Kohn-Sham scheme of density functional theory requires that the external potential be local [Hohenberg and Kohn (1964), Dreizler and Gross (1990), Kohn and Sham (1965)]. When external potential in this theory is non-local, the exchange correlation energy is a functional of the non-interacting density matrix, $\rho(\vec{r}, \vec{r}')$, and not just of the density $n(\vec{r})$.

Naturally enough, many of today's material scientists are skeptical of the pseudopotential method and consider its predictions unreliable or at least difficult to interpret. Some physicists avoid the use of the method in their work and some use the technique without properly understanding it (which is not an error-proof attitude). The pseudopotential method was first put forward in the framework of the nearly free-electron model and it
is in this term that it is mostly discussed. However, the method extends far beyond one particular model, indeed it provides insights into virtually every aspect of the behaviour of electrons in a crystal. Today, a knowledge of pseudism is mandatory for anyone interested in a thorough understanding of the properties of solids and their dependence on external conditions and composition.

The purpose of the present work is three-fold:

1. To extend the applications of local pseudopotential scheme proposed by Antonov et al. [1990] with a view to see as to how far this scheme is useful in predicting the physical properties which have not been used in fitting the parameters of the model.

2. We, for the first time, study the suitability of the model due to Bretonnet and Silbert [1992] for the calculations of solid state properties. This model has been previously used for liquid state properties.

3. We construct a model pseudopotential from first principles approach due to Harrison [1969] and examine its applicability. For this purpose, we make a comprehensive study of lattice properties of f.c.c. transition metals $Ni$, $Pd$, $Pt$, $Co$, $Fe$, $Ir$ and $Rh$. It may be noted that such comprehensive studies are quite rare in the literature.

The plan of the thesis is as follows:
In Chapter-2, we survey the literature which deals with various approaches to study the physical properties of transition metals and then formulate the problem of the present thesis. In Chapter-3, we compile various expressions to compute the physical properties. Finally, in Chapter-4, we present the results of the present calculations along with discussion and conclusion. Lastly, we present some ideas regarding future work.
References


