

AB INITIO PSEUDOPOTENTIAL STUDY

by

SHENG-YU PENG

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Approved by:

N. O. Sjolund  
Major Professor

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## Chapter I

### INTRODUCTION

It is well known that the physical and chemical properties of molecules and crystals are determined by their "valence" electrons. Valence electrons are loosely bound to the nuclei and move freely throughout the crystal. When a valence electron is near the nucleus, it is strongly affected by the nucleus and the "core" electrons which are more tightly bound to the nucleus.

Near the nuclei valence eigenfunctions are like atomic eigenfunctions. They have higher energy than the core electrons. Because valence eigenfunctions must be orthogonal to the core electron eigenfunctions they display strong oscillations in the region near the nucleus. In the region of a molecule or crystal between the cores, the valence electron will see a smooth potential and the eigenfunction is slowly varying. This suggested to Kleinman and Phillips that valence eigenfunctions  $\psi_v$  be written as a linear combination of a smooth function  $\phi_v$  and core electron eigenfunctions  $\psi_c$ .<sup>(1)</sup>

$$\psi_v = \phi_v + \sum b_c \psi_c \quad (I-1)$$

Eigenfunction  $\psi_v$  satisfies the Schrödinger equation

$$\left( \frac{p^2}{2m} + V_c \right) \psi_v = E \psi_v \quad (I-2)$$

where  $V_c$  is electrostatic potential of the nuclei, the core electrons and valence electrons of the crystal.

The valence electron wave function  $\psi_v$  is orthogonal to the core electron wave functions. Using this property and Eq. (I-1) the Schrödinger

equation may be rewritten as an eigenvalue equation for  $\phi_V$ ,

$$\left( \frac{p^2}{2m} + V_C + \sum_C (E - E_C) \Psi_C \langle \Psi_C | \right) \phi_V = E \phi_V \quad (I-3)$$

Phillips and Kleinman<sup>(1)</sup> showed that the potential in the Eq. (I-3) above is weak. It is an example of a pseudopotential called the Phillips-Kleinman pseudopotential (PKP). The objective of any pseudopotential formulation is to replace the original Schrödinger equation for an electron in the crystal by an effective equation for the physically important valence electron states which is easier to solve than the original equation. Unfortunately in the case of PKP it is not possible to solve the equation without effectively solving the original problem. However, the PKP has served to motivate various approximate pseudopotential calculation schemes.

In one such approximate scheme the pseudopotential is expressed in a parametric form and the free parameters are chosen to agree with experimental observation. This approach is called the empirical pseudopotential method.

Recently, attempts have been made to formulate pseudopotentials from a stronger theoretical base<sup>(4,5,7)</sup> than is possible with empirical pseudopotentials. The objective is to derive a pseudopotential directly from atomic models without reference to experiment or more complete electron energy band calculations. Such pseudopotentials are called *ab initio* pseudopotentials (AIPs). The principal objective of this thesis is to study AIPs both numerically and mathematically.

In Chapter II the properties of many-electron atoms are reviewed, a precise distinction is made between core electrons and valence electrons. The nodal structure of the radial function of many-electron atoms is emphasized. The concepts of empirical pseudopotential, AIPs and bare-ion

pseudopotential are introduced.

In Chapter III AIP models are discussed. First we discuss the pseudopotential for an atom. From it we introduce the concept of a bare-ion pseudopotential which can be transferred to a crystal or a system with many atoms. In order to define a pseudopotential for an atom, six conditions on the pseudo wave functions are imposed. These conditions are insufficient to completely define a pseudopotential and must be supplemented by a calculational procedure or recipe.

In Chapter IV two different recipes<sup>(4,7)</sup> for AIPs are introduced and discussed. It is shown that the six conditions are satisfied in both recipes. The result of Kerker's recipe is reproduced quite well. A comparison and discussion of these two recipes are made. The similarities and differences of these two recipes are discussed. Some properties of pseudopotentials of these two recipes are studied.

The results of the thesis are summarized and discussed in Chapter V.

## Chapter II

### ATOMS, SOLIDS, AND PSEUDOPOTENTIALS

The main objective of this work is to study pseudopotential models for atoms and solids. However to bring such models into a proper historical and conceptual perspective in this chapter, the independent particle model (IPM) or shell model of atoms will be briefly reviewed. The review will serve to introduce the language that is used to describe IPMs of atoms, leading to the conceptual basis for pseudopotential model of solids and atoms.

#### A. Hydrogen-Like Atoms

In a model of hydrogen-like atoms, we consider an electron moving in the field of a nucleus with positive charge  $Ze$ . The potential interaction energy between the nucleus and the electron is Coulombic.

$$V = - \frac{Ze^2}{r} \quad (\text{II-1})$$

The Hamiltonian for a hydrogen-like atom is

$$H = \frac{p^2}{2m} + \left( - \frac{Ze^2}{r} \right) \quad (\text{II-2})$$

The Schrödinger equation is

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right) \psi = E\psi \quad (\text{II-3})$$

The Eq. (II-3) has the meaning that the electron moves around the nucleus under the Coulomb force with the nucleus fixed.

The solution of the Schrödinger equation is separable

$$\psi = R_{nl}(r) \bar{Y}_{lm}(\vartheta, \phi) \quad (\text{II-4})$$

into a radial function times a spherical harmonic. Therefore the state of electron is characterized by the quantum numbers  $n, \ell, m$  (a spin quantum number  $m_s$  may be included).

The principal quantum number,  $n$ , has non-zero integer values. It specifies in which "energy shell" the electron is moving and it determines the energy of the state

$$E_n = -\frac{Z^2}{n^2} 13.6 \text{ eV} \quad (\text{II-5})$$

The angular momentum quantum number,  $\ell$ , can be any one of the values  $0, 1, 2, \dots, (n-1)$  for a given  $n$ . It determines the angular momentum of the electron which is equal to

$$L = \hbar \sqrt{\ell(\ell+1)} \quad (\text{II-6})$$

The magnetic quantum number,  $m$ , gives the  $Z$ - component of angular momentum.

$$L_z = m\hbar \quad (\text{II-7})$$

$m$  can take any of the following values  $-\ell, -(\ell-1), \dots, -1, 0, +1, \dots, (\ell-1), \ell$ , for a given  $\ell$ .

In classical physics the electron in a hydrogen-like atom moves in a definite orbit. In quantum mechanics the precise position and momentum can not be given simultaneously. Only the probability for finding an electron at given position and with a given momentum is found. The electron position probability density is defined by  $|\psi(\vec{r})|^2$ . When  $|\psi(\vec{r})|^2$  is large the probability of finding the electron is large.

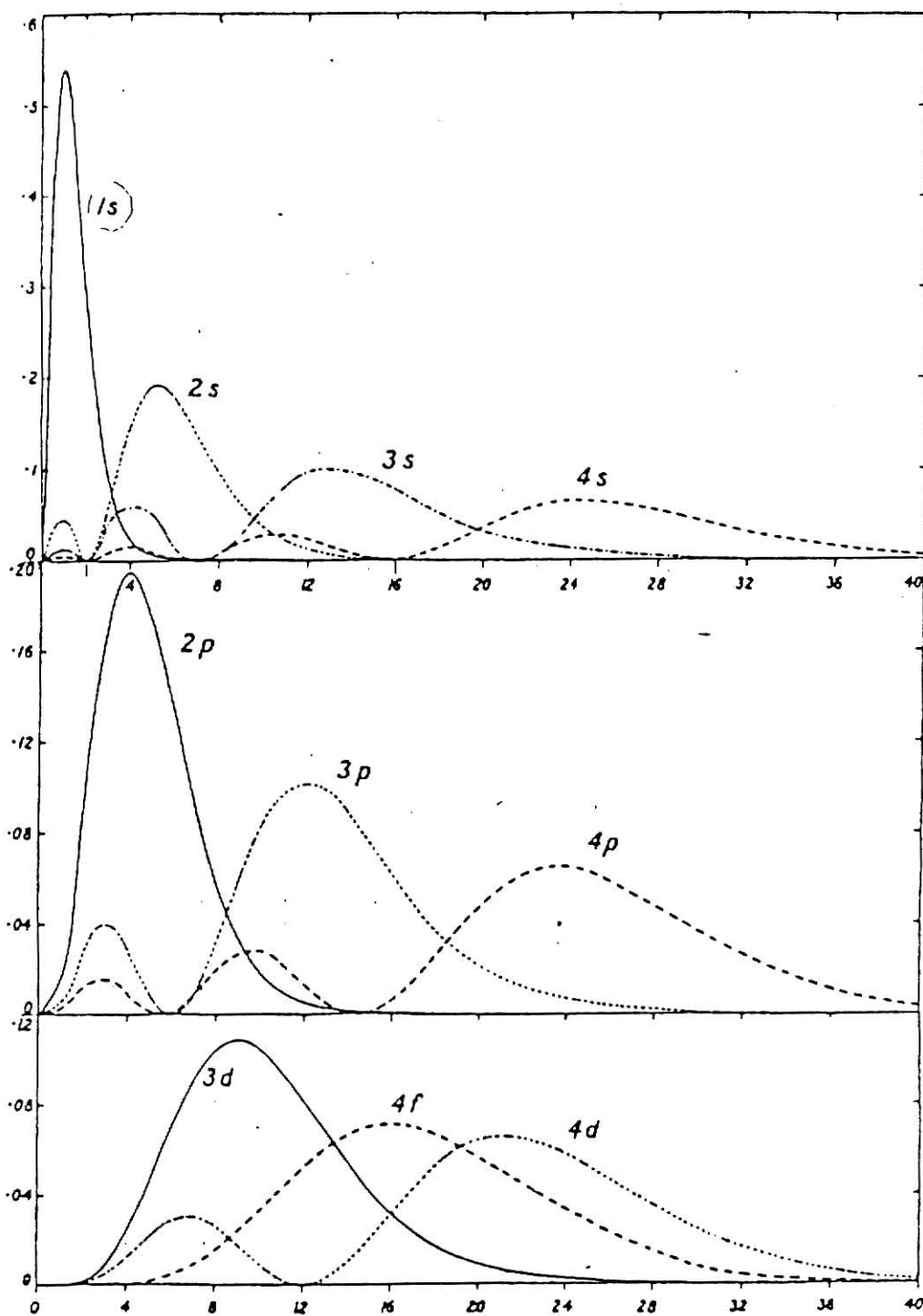
Now we will study the radial function in the eigenfunctions of hydrogen. Examples of radial eigenfunctions are shown in Fig. II-1. A physically meaningful radial solution of Eq. (II-3) is determined by boundary conditions requiring regularity at small  $r$  and that it asymptotically approaches zero

Figure II-1: The radial probability distribution  $|rR_{n\ell}|^2$  for several values of the quantum numbers,  $n$ ,  $\ell$  of the hydrogen atom. (From E.U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1953).



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The radial probability distribution function  $|rR_{n\ell}|^2$  for several values of the quantum numbers  $n, \ell$ . (From E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1953.)

at large radial distance.

The number of nodes (zeros) of a radial function  $rR_{n\ell}(r)$  is equal to  $n-(\ell+1)$ . When  $\ell = n-1$  there is no node. For a fixed  $\ell$  the energy state corresponding to the smallest  $n = \ell + 1$  has the lowest energy. Therefore for  $\ell=0$  (s states), the state 1s has the lowest energy as compared with 2s, 3s, .... states. For  $\ell = 1$  (p states), the energy state 2p has the lowest energy compared with 3p, 4p, ... states.

The average value of  $r$  for an electron in a hydrogen-like atom is calculated to be

$$\langle r \rangle = \frac{a_0 n^2}{Z} \left( 1 + \frac{1}{2} \left( 1 - \frac{\ell(\ell+1)}{n^2} \right) \right) \quad (\text{II-8})$$

This estimates the spatial extent of an electron in a state  $n, \ell$ . The electron will mainly move in the region for which  $r$  is smaller than or equal to  $\langle r \rangle$ . The higher the energy, the larger the spatial extent of the electron will be.

## B. Many Electron Atoms

In the hydrogen-like atom we have only one electron moving around the nucleus. But for many other atoms more than one electron moves near the nucleus. This is a many-body problem. Besides the interaction between the nucleus and the electrons, there are interactions between the electrons.

In an IPM

$$\left[ \frac{p^2}{2m} - \frac{Ze^2}{r} + V_H(r) + V_{xc}(r) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (\text{II-9})$$

approximates the dynamics of an electron.

The potential  $V_H(r)$  is the Coulomb potential for all electrons

$$V_H(r) = \int d\vec{r}' \frac{n(\vec{r}')e^2}{|\vec{r}-\vec{r}'|} \quad (\text{II-10})$$

where  $n(r)$  is the electrostatic average electron probability density.

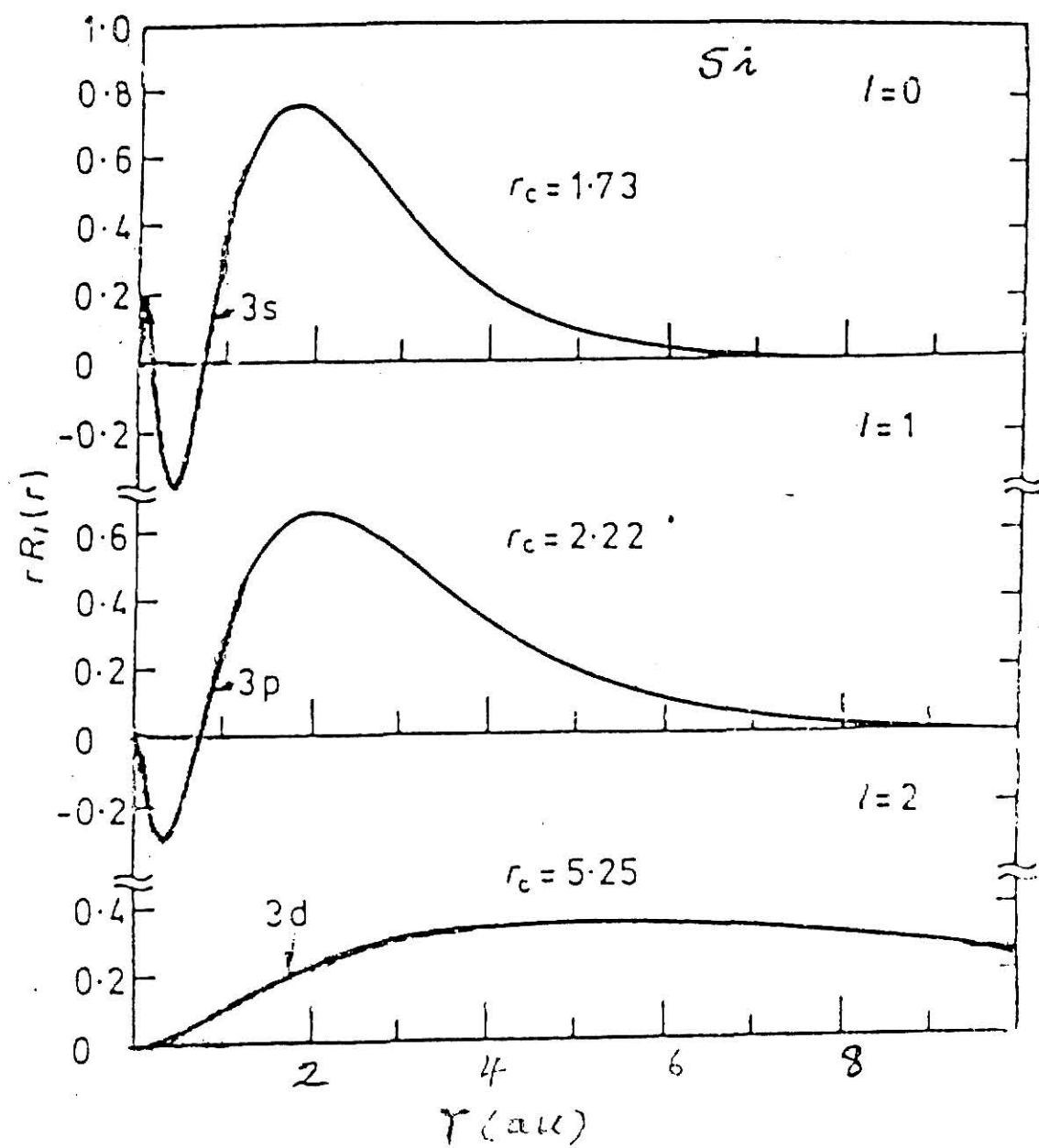
The last term  $V_{xc}(n(r))$  is the exchange correlation potential. The effect of this term is to remove an electron's interaction with itself and crudely account for correlation effects. We require the potential to be spherically symmetric and as in the hydrogen atom the solutions are separable into radial and angular factors as in Eq. (II-4). The quantum numbers  $n, \ell, m$  ( $m_s$ ) used to characterize states of the hydrogen atom retain their meaning. However, in a single-electron approximation to a many-electron atom the energy quantum number  $n$ , is not simply related to the energy as it was in the hydrogen case. The connection between quantum numbers and the nodal structure of radial eigenfunction is retained.

The energy of the electron is dependent upon  $n$  and  $\ell$ . The angular factor  $Y_{\ell m}(\theta, \phi)$  of the wave function for an electron is still the same as in hydrogen-like atoms, but the radial factor  $R_{n\ell}(r)$  may be quite different from that in a hydrogen-like atom.

But the nodal structure of the radial function is the same as in the hydrogen-like atom. That is to say the radial function  $rR_{n\ell}(r)$  has no node when  $\ell = n-1$  and has  $[n-(\ell+1)]$  nodes as  $\ell \neq n-1$ . It implies that with the same value of  $\ell$  the state corresponding to  $n = \ell + 1$  will have the lowest energy and doesn't have nodes. Several examples about the nodes in the radial functions with different  $n$  and  $\ell$  are shown in Fig. (II-2). From the figure it is seen that the 3d ( $n=3, \ell=2$ ) radial function has no node while the 3s ( $n=3, \ell=0$ ) radial function has  $3-(0+1)=2$  nodes.

The connection between the single-particle model and a many-electron atom is made by associating electrons with single-particle states. The Pauli exclusion principle requires that no more than one electron be

Figure II-2: The radial functions with different  $n$  and  $\ell$  for a Si atom.



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associated with a particular single-particle state. The total number of such states is equal to the number of electrons in the atom. A set of such states is called an electron configuration. The configuration corresponding to the lowest single particle eigenvalue is called the ground state configuration. The electron charge density in the single-particle model is the sum over ground state electron probability densities.

$$n(r) = 2 \sum_{n\ell m} |\psi_{n\ell m}(r)|^2$$

A more accurate solution of the many-electron problem may be obtained by superposing Slater determinants of single-particle configurations.

Configurations may be specified by listing the quantum numbers  $n$  and  $\ell$  along with a superscript indicating the number of electrons occupying the states. For example, the ground state of a silicon atom is

$$(1S)^2 (2S)^2 (2P)^6 (3S)^2 (3P)^2$$

and the ground state of Molybdenum is

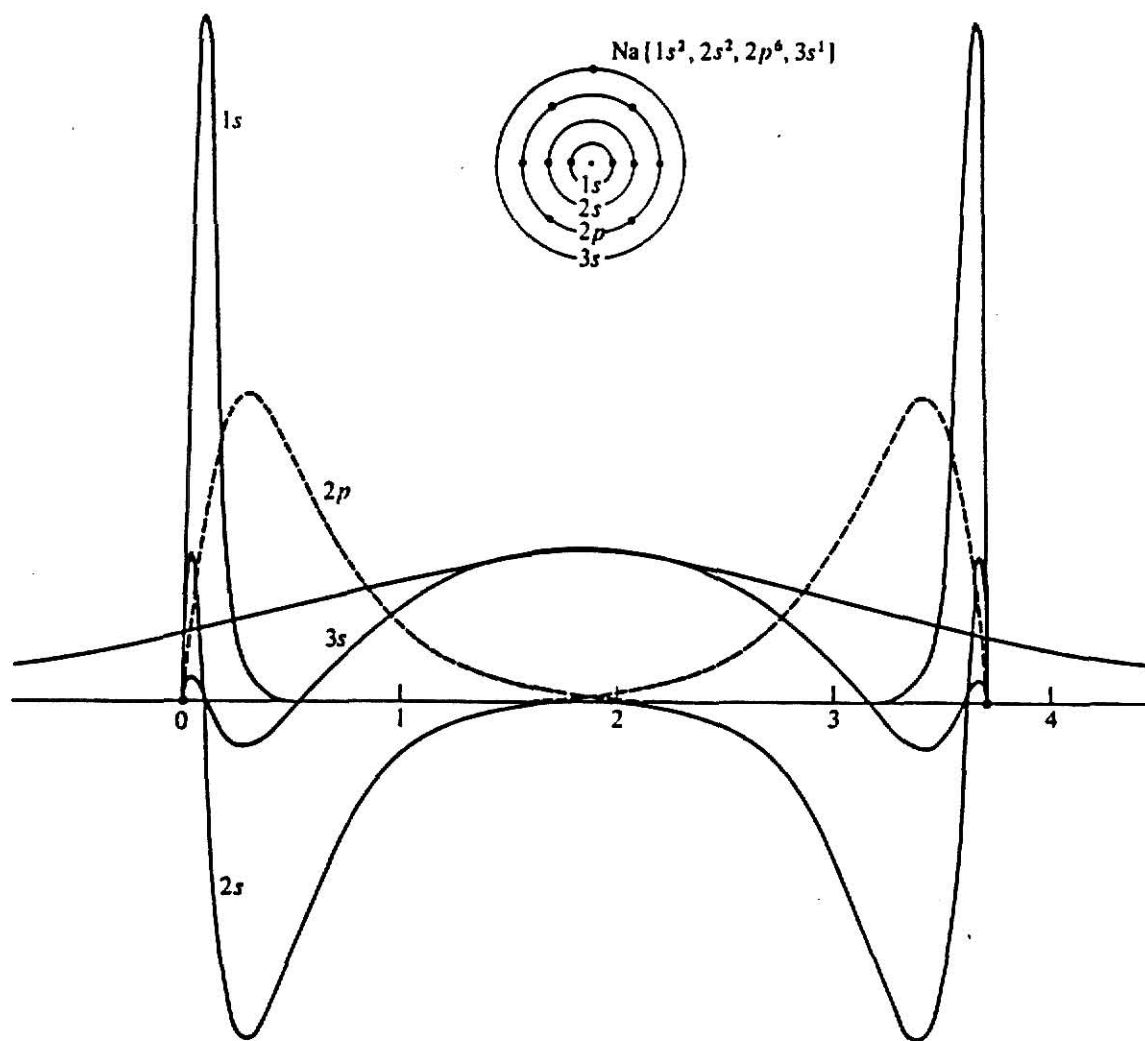
$$(1S)^2 (2S)^2 (2P)^6 (3S)^2 (3P)^6 (3d)^{10} (4S)^2 (4P)^6 (4d)^5 (5S)^1$$

### C. Forming Solids From Atoms

When the atoms come together to form a crystal, the nuclei will be regularly positioned in a crystal. The idea is schematically represented in Fig. II-3. The electron states with lower energy are bound tightly to their own nuclei. The nuclear attraction dominates the dynamics of such states and are expected to be very similar to the wave functions of an isolated atom. Those electron states are called "core" states. The spatial region in which the probability density of the core states is large is called the core region. Electron states which have higher energy are screened by the core electrons. So they are not so intensely attracted by



Figure II-3: Calculated electron wave functions for the levels of atomic sodium, plotted about two nuclei separated by the nearest neighbor distance in metallic sodium,  $3.7 \text{ \AA}$ .



Calculated electron wave functions for the levels of atomic sodium, plotted about two nuclei separated by the nearest-neighbor distance in metallic sodium, 3.7 Å. The solid curves are  $r\psi(r)$  for the 1s, 2s, and 3s levels. The dashed curve is  $r$  times the radial wave function for the 2p levels. Note how the 3s curves overlap extensively, the 2s and 2p curves overlap only a little, and the 1s curves have essentially no overlap. The curves are taken from calculations by D. R. Hartree and W. Hartree, *Proc. Roy. Soc. A* **193**, 299 (1948). The scale on the  $r$ -axis is in angstroms.

their own nuclei and can move far away. Consequently, in a crystal the atomic wave function of such electronic states will overlap those of neighboring nuclei. They are influenced as strongly by the neighboring nuclei as by their own nuclei. Such electronic states can't be associated with a definite atom. Rather, they belong to the whole crystal and wander around throughout the whole crystal. These electronic states are called valence states. Because the atomic valence wave functions from neighboring sites overlap one another, the corresponding crystal eigenfunctions will be changed. This explains why the valence electron states are so important in a crystal and why the valence electronic states determine the physical and chemical properties of a crystal.

#### D. Pseudopotential Idea

The valence eigenfunctions outside the core region are expected to be rather smooth. In the core region the valence eigenfunctions have strong oscillations. This is mainly because the valence eigenfunctions have to be orthogonal to the core electron eigenfunctions.

The idea of a pseudopotential (IPM) is to replace the effect of the nuclei and core electrons by an effective potential for the valence electrons. The valence pseudoeigenfunctions are ground state eigenfunctions in the pseudopotential model. Explicit dependence on core states has been removed. Pseudopotential models are motivated by the observation that the core electrons play an indirect role in the physics and chemistry of solids. Theoretical justification for pseudopotentials make their use plausible, but there is no rigorous derivation of a pseudopotential model from first principles.

The difficulty is that an analysis leading rigorously to a pseudopotential form can only be evaluated with the aid of a complete calculation

of the all electron problem.

There is no unique way to construct pseudopotential models. An example of a type of pseudopotential model is the empirical pseudopotential model.

A simple functional form is taken for the pseudopotential, then repeated calculations of the energy bands are used to adjust parameters in the pseudopotential until optimum agreement with experimental information is obtained. Often the choices are guided by all-electron calculation results. Thus, empirical pseudopotential models are essentially interpolation schemes for energy bands.

Many attempts have been made to devise pseudopotential models more strongly based on first-principle. The "ab initio" pseudopotential models are an attempt in this direction. One constructs from an atomic IPM an effective potential called a bare-ion potential which represents the effects of core electrons and the nucleus. Certain of these "ab initio" pseudopotentials will be studied and analyzed in detail in the next section of this thesis.

## Chapter III

### AB INITIO PSEUDOPOTENTIAL MODELS

Ab initio pseudopotentials are one kind of pseudopotential. They are a recent development in this subject.<sup>(7)(4)</sup>

The idea of an AIP is to replace the influence of nuclei and the core electrons on the valence electrons by a potential based on first-principles so that we can treat the valence states in a pseudopotential and need not consider the core states.

We first construct the pseudopotential of an atom and then find a bare-ion pseudopotential for the atom. If the approach is to be a useful one, this bare-ion potential must be insensitive to changes in the valence configuration and hence be transferable to a crystalline or molecular environment.

First we state the conditions imposed on pseudo eigenfunctions by Hamann Schlüter and Chiang (HSC), but we note that these conditions are not complete in that other conditions are imposed, but not explicitly stated. The conditions on pseudowavefunctions do not imply a unique pseudopotential. In general there will be an infinity of pseudopotentials consistent with the conditions. To completely define a pseudopotential it is also necessary to prescribe a calculational procedure or "recipe" which leads to pseudopotential. Two examples of recipes are given below.

#### A. Mathematical Requirements

The conditions for pseudowavefunctions for an atom as given by HSC are stated as conditions on radial functions for single-particle atomic model.

The dynamical equation in a single-electron model for an electron in a many-electron atom is

$$\left[ \frac{p^2}{2m} + V_n(r) + V_H(r) + V_{xc}(n(\vec{r})) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (\text{III-1})$$

where the Hamiltonian operator is spherically symmetric and the differential equation is separable in spherical coordinates,

$$\psi_i(\vec{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \quad (\text{III-2})$$

where  $Y_{\ell m}(\theta, \phi)$  is a spherical harmonic. The related radial function

$$U_{n\ell}(r) = r R_{n\ell}(r) \quad (\text{III-3})$$

satisfies the equation

$$\left[ -\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V(r) \right] U_{\ell}(r) = \epsilon_{\ell} U_{\ell}(r) \quad (\text{III-4})$$

$V(r)$  is the potential due to the nucleus, the core electrons and valence electrons of the atom.

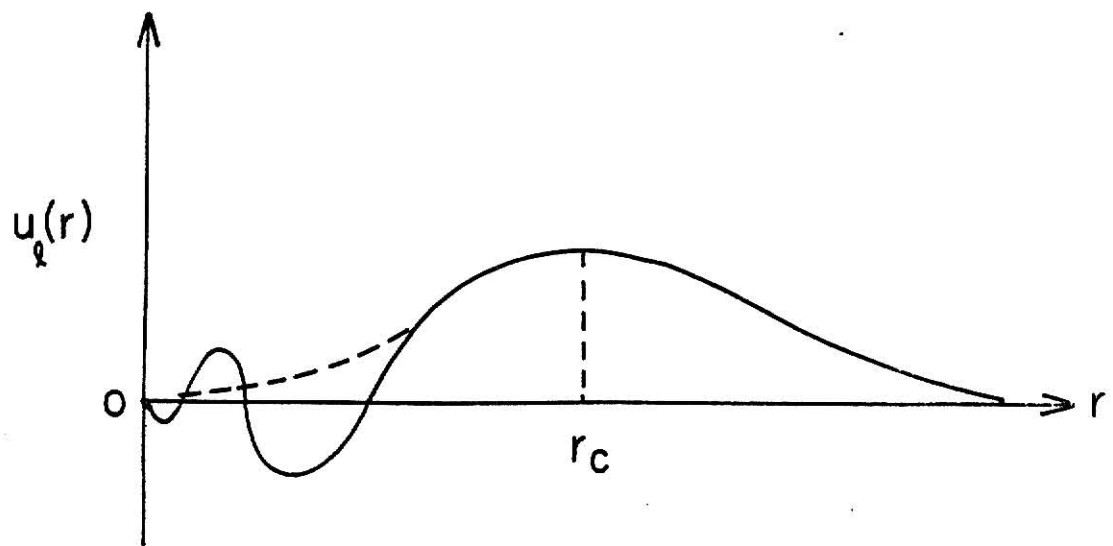
Upon replacing the potential  $V(r)$  with a pseudopotential the radial equation for valence states becomes

$$\left[ -\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} + V_{\ell}^{\text{PS}}(r) \right] U_{\ell}^{\text{PS}}(r) = \epsilon_{\ell}^{\text{PS}} U_{\ell}^{\text{PS}}(r) \quad (\text{III-5})$$

The solution  $U_{\ell}^{\text{PS}}(r)$  is the pseudo wave function. In general a pseudopotential of this type will depend on the angular momentum quantum number.

Before listing the HSC conditions a definition of a "cut-off" radius  $r_c$  is made. Such a "cut-off" radius  $r_c$  is not always precisely defined in the literature.<sup>(7)(4)</sup> Ab initio pseudopotential models are not sensitive to small changes in the cut-off radius. Here, the "cut-off" radius  $r_c$  is defined to be the radial distance from the origin to the last extremal point in the radial function  $U_{\ell}(r)$ . This is shown schematically in Fig. (III-1).

Figure III-1: The cut-off radius  $r_c$ .





The four HSC conditions are: (4)

- (1) Real and pseudo valence eigenvalues are equal for a chosen "prototype" atomic configuration.

$$\epsilon_{\ell} = \epsilon_{\ell}^{\text{PS}} \quad (\text{III-6})$$

- (2) Real and pseudo radial functions are equal at and beyond the core radius,  $r_c$ .

$$U_{\ell}^{\text{PS}}(r) = U_{\ell}(r) \text{ for } r \geq r_c \quad (\text{III-7})$$

- (3) The logarithmic derivatives of the real and pseudowavefunction are equal for  $r \geq r_c$

$$\beta_{\ell}(r) = \frac{d \ln U_{\ell}(r)}{d \ln(r)} = \beta_{\ell}^{\text{PS}}(r) = \frac{d \ln U_{\ell}^{\text{PS}}(r)}{d \ln(r)} \quad (\text{III-8})$$

- (4) The first-energy derivatives of the logarithmic derivatives are equal for  $r \geq r_c$ .

$$\frac{\partial}{\partial \epsilon_{\ell}} \beta_{\ell}(r) = \frac{\partial}{\partial \epsilon_{\ell}^{\text{PS}}} \beta_{\ell}^{\text{PS}}(r), \quad r \geq r_c \quad (\text{III-9})$$

These conditions require that the pseudo radial functions and potential be identical to the atomic radial functions and potential beyond  $r_c$ . For  $r > r_c$  the pseudopotential will have the same scattering properties as the atomic potential. One can show that condition (4) is equivalent to

$$\int_0^{r_c} U_{\ell}^2(r) dr = \int_0^{r_c} [U_{\ell}^{\text{PS}}(r)]^2 dr \quad (\text{III-10})$$

Thus, the normalization condition is kept for  $U_{\ell}^{\text{PS}}(r)$ , because

$$\begin{aligned} \int_0^{\infty} |U_{\ell}^{\text{PS}}(r)|^2 dr &= \int_0^{r_c} |U_{\ell}^{\text{PS}}(r)|^2 dr + \int_{r_c}^{\infty} |U_{\ell}^{\text{PS}}(r)|^2 dr \\ &= \int_0^{r_c} |U_{\ell}(r)|^2 dr + \int_{r_c}^{\infty} |U_{\ell}(r)|^2 dr = \int_0^{\infty} |U_{\ell}(r)|^2 dr \end{aligned}$$

HSC refer to condition (4) as the "norm-conserving" property and distinguish

pseudopotentials which satisfy this condition as "norm-conserving" pseudopotentials. Condition (4) is equivalent to requiring that the electric charge inside  $r_c$  in the pseudo and real atom be the same.

However, HSC implicitly impose additional conditions through their recipes. They require their pseudopotential to be continuous functions which have a finite value at  $r = 0$ .

Since the pseudopotential is found by inverting the radial equation (III-2) an additional condition implied is

- (5) The second derivatives of  $U_\ell^{\text{PS}}(r)$  and  $U_\ell(r)$  are equal to each other at  $r \geq r_c$ .

$$\left. \frac{d^2}{dr^2} U_\ell^{\text{PS}}(r) \right|_{r_c} = \left. \frac{d^2}{dr^2} U_\ell(r) \right|_{r_c} \quad (\text{III-11})$$

and the second derivatives of  $U_\ell^{\text{PS}}(r)$  is a continuous function for  $r \leq r_c$ . The pseudo wavefunction  $U_\ell^{\text{PS}}(r)$  is matched with  $U_\ell(r)$  very well. They are not only equal to each other at  $r = r_c$ . They will be also very close to each other in a small segment near  $r \approx r_c$ . This can be seen in Fig. III-1.

Since the pseudoradial function  $U_\ell^{\text{PS}}(r)$  is the lowest energy solution of the radial equation which is physically meaningful, the pseudo radial function  $U_\ell^{\text{PS}}(r)$  is nodeless and regular. The radial function may be written in the form

$$U_\ell^{\text{PS}}(r) = r^{\ell+1} W_\ell^{\text{PS}}(r) \quad (\text{III-12})$$

where  $W_\ell^{\text{PS}}(r)$  is regular function which is positive definite,  $W_\ell^{\text{PS}}(r) > 0$   $r \geq 0$ .

Another condition implicitly included by HSC is that the pseudopotential be finite at  $r = 0$ . This requirement may be explicitly imposed by adding the condition that

- (6) The logarithmic derivatives of the radial function evaluated at  $r = 0$  is  $\ell+1$ ,

$$\left. \frac{d \ln(U_\ell^{\text{PS}}(r))}{d \ln(r)} \right|_{r=0} = \ell + 1 \quad (\text{III-13})$$

or in terms of Eq. (III-12) that

$$\left. \frac{d}{dr} W_\ell^{\text{PS}}(r) \right|_{r=0} = 0 \quad (\text{III-14})$$

It is convenient to defer an explicit proof of this condition until after the calculation of a pseudopotential is discussed in the next subsection.

#### B. The Ab Initio Pseudopotential for an Atom

Once the pseudo wavefunction is determined then the pseudopotential can be easily determined. We need only to substitute  $U_\ell^{\text{PS}}(r)$  into the radial equation and solve it for the pseudopotential

$$V_\ell^{\text{PS}}(r) = \frac{d^2 U_\ell^{\text{PS}}(r)}{dr^2} - \left( \frac{\ell(\ell+1)}{r^2} - \epsilon_\ell \right) U_\ell^{\text{PS}}(r) \quad (\text{III-15})$$

For  $r \geq r_c$  since  $U_\ell^{\text{PS}}(r) = U_\ell(r)$  we have

$$V_\ell^{\text{PS}}(r) = V(r).$$

But the pseudopotential and real potential are different for  $r < r_c$ .

The analytic form of the pseudopotential can be more easily seen by replacing  $U_\ell^{\text{PS}}(r)$  by  $r^{\ell+1} \cdot W_\ell^{\text{PS}}(r)$  as given in Eq. (III-12). Then in terms of  $W_\ell^{\text{PS}}(r)$ .

$$V_\ell^{\text{PS}}(r) = \left( \frac{d^2}{dr^2} W_\ell^{\text{PS}}(r) + \frac{2(\ell+1)}{r} \frac{dW_\ell^{\text{PS}}(r)}{dr} \right) / W_\ell^{\text{PS}}(r) + \epsilon_\ell \quad (\text{III-16})$$

In Eq. (III-16) the centrifugal term in the potential has been eliminated.

It is also seen that if  $W_\ell^{\text{PS}}(r)$  were to have a finite first derivative at

$r=0$ , the pseudopotential would be singular. Thus, a non-singular pseudopotential must satisfy condition (6) above.

In general the pseudopotentials for each angular momentum value will be different. Some authors<sup>(14)</sup> refer to such potentials as "non-local  $\ell$ -dependent" potentials. The pseudopotential Hamiltonian may be written

$$H^{PS} = \frac{p^2}{2m} + V^{PS}(r) \quad (\text{III-17})$$

where the  $\ell$ -dependence

$$V^{PS}(r) = \sum_{\ell} V_{\ell}^{PS}(r) P_{\ell} \quad (\text{III-18})$$

is included through projection operators

$$P_{\ell} = \sum_{m=-\ell}^{\ell} |\ell m\rangle \langle \ell m| \quad (\text{III-19})$$

In principle a pseudopotential term for all  $\ell$ -values is needed. This might appear to present significant calculational difficulties. For sufficiently large values of  $\ell$  the lowest energy radial eigenfunctions of any atom will be nodeless and only condition (6) above is not immediately satisfied by the atomic radial functions themselves. In fact the pseudopotentials for these higher  $\ell$ -value terms must be very similar and a standard approximation is to simply set all higher  $\ell$ -value pseudopotential terms  $V_{\ell}^{PS}(r)$  equal to one another. For example in low  $Z$  atoms such as silicon

$$V_{\ell}^{PS}(r) = V_2^{PS}(r) \quad \text{for } \ell \geq 2 \quad (\text{III-20})$$

In this approximation the pseudopotential operator may be written as

$$V^{PS}(r) = V_2^{PS}(r) + \sum_{\ell=0}^1 (V_{\ell}^{PS}(r) - V_2^{PS}(r)) P_{\ell} \quad (\text{III-21})$$

where the "non-local" terms are restricted to the first few  $\ell$ -value.

### C. Bare-Ion Pseudopotentials

The pseudopotentials  $V_{\ell}^{\text{PS}}(r)$  include the combined effects of the nuclear core and valence charge densities. If the contribution from the valence electron charge density is subtracted from  $V_{\ell}^{\text{PS}}(r)$ , then the remainder will be the pseudopotential of the core and nuclear charges alone. Such a potential is defined by

$$V_{\ell}^{\text{PS}}(r) = V_{\ell\text{B}}^{\text{PS}}(r) + V_{\text{Coul}}(n_{\text{V}}^{\text{PS}}(r)) + V_{\text{xc}}(n_{\text{V}}^{\text{PS}}(r)) \quad (\text{III-22})$$

Because of the manner in which it is constructed the bare-ion pseudopotentials are exact potentials for the configuration upon which they are based. If the pseudopotential approach is to be a successful one, it is essential that the bare-ion pseudopotential adequately represent the effects of the core and nuclear charge densities when the valence configuration is modified. Yin and Cohen<sup>(5)</sup> have reported several numerical experiments for atomic models which test the idea. In their paper the bare-ion pseudopotential  $V_{\ell\text{B}}^{\text{PS}}(r)$  ( $n=3$ ) is originally constructed from the configuration (Ne core)  $3s^2 3p^{0.5} 3d^{0.5}$  of Si. Then they use this bare-ion pseudopotential to find the eigenvalues of Si with the valence configuration  $3s^2 3p^1 3d^1$ . The bare-ion pseudopotentials  $V_{\ell\text{B}}^{\text{PS}}(r)$  are the same ones constructed from the original configuration but the valence charge density is determined self-consistently. The result agrees well with the result from an all-electron (AE) self-consistent calculation.

For example the eigenvalues of a 3s eigenfunction in the valence configuration  $3s^2, 3p^1, 3d^1$  of Si by using the former (PS) method and the latter (AE) method are respectively -1.0794 (Ry) and -1.0784 (Ry), the percent difference is less than 0.1%. The eigenvalues of 3p are -0.5562 (Ry) and -0.5555 (Ry), the percent difference is less than 0.2%, and the eigenvalues of 3d are just the same which is equal to -0.586 (Ry) without deviation. The eigen-

values of the original configuration,  $\epsilon_{3s} = -1.4851$  Ry,  $\epsilon_{3p} = -1.9420$  Ry and  $\epsilon_{3d} = 0.3364$  Ry, are drastically altered.

The asymptotic behavior of the bare-ion pseudopotential operator is found by noting that pseudopotentials are constructed to reproduce the all-electron potential beyond the cutoff radii. For large  $r$  the all-electron potential has the form

$$V(r) = -\frac{Z_v e^2}{r} + V_{\text{Coul}}(n_v^{\text{PS}}(r)) + V_{\text{xc}}(n_v^{\text{PS}}(r)) \quad (\text{III-23})$$

where  $Z_v$  equal the number of valence charges and because  $n(v) = n_v^{\text{PS}}(r)$  for large  $r$ . Comparison with Eq. (III-22) indicates that the asymptotic form of the bare-ion potential is independent of  $\ell$ -values and literally the potential of a bare-ion

$$V_{\ell B}^{\text{PS}}(r) = -\frac{Z_v e^2}{r}. \quad (\text{III-24})$$

The bare-ion pseudopotential operator for an atom is written as

$$V_B^{\text{PS}}(r) = \sum_{\ell} V_{\ell B}^{\text{PS}}(r) P_{\ell} \quad (\text{III-25})$$

where  $P_{\ell}$  is the angular momentum projection operator defined by Eq. (III-19).

#### D. Pseudopotential in a Crystal

In a crystal, we still have the one-particle Schrödinger equation for an all-electron problem

$$\left(\frac{p^2}{2m} + V_n(\vec{r}) + V_H(\vec{r}) + V_{\text{xc}}(n)\right)\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (\text{III-26})$$

Here  $V_n(\vec{r})$ ,  $V_H(\vec{r})$  and  $V_{\text{xc}}(n)$  are the nuclei potential, Coulomb potential and the exchange-correlation potential, respectively.

The pseudopotential idea is still useful for a crystal. It will facilitate the calculation because by introducing a pseudopotential the ion core is eliminated. In an ab initio pseudopotential model the potential

is replaced by the bare-ion pseudopotentials of all the atoms located at positions  $\vec{R}_a$  plus the self-consistent Coulomb potential of the valence electrons and the exchange and correlation potential of the valence electrons

$$V^{PS}(r) = \sum_{\vec{R}_a} V_{B(a)}^{PS}(\vec{r} - \vec{R}_a) + V_{Coul}(n_v^{PS}(r)) + V_{xc}(n_v^{PS}(r)) \quad (III-27)$$

and the corresponding Schrödinger equation is

$$\left(\frac{p^2}{2m} + V^{PS}(r)\right)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \quad (III-28)$$

This may be contrasted with empirical pseudopotential calculations. The potential in the Hamiltonian operator is the empirical pseudopotential

$$V_P(r) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad (14) \quad (III-29)$$

in which the  $V(\vec{G})$ 's are parameters empirically determined by fitting to experimental data. By their construction band structures calculated from empirical pseudopotentials have excited state energies consistent with experiments. The band structure calculated from ab initio pseudopotentials generally have lower excited state energies which are less than those observed experimentally.<sup>(5)</sup> Perhaps an understanding of the differences between empirical and ab initio pseudopotential approaches can be found by comparing their respective bare-ion pseudopotentials.

## Chapter IV

### SPECIFIC AB INITIO PSEUDOPOTENTIAL MODEL (FOR AN ATOM)

In Section (III) we imposed conditions on the pseudo wavefunction. These conditions will help us to construct a pseudopotential, but they are not sufficient to uniquely construct a pseudopotential. There can be many pseudopotentials consistent with these conditions. Therefore it is necessary for us to prescribe a definite procedure to construct a pseudopotential. This procedure is called a "recipe". We can have different recipes, and they will give us different ab initio pseudopotentials. In this section we will first give the Hamann, Schlüter and Chiang recipe and Kerker's recipe and then compare and discuss them.

Before we go to these recipes, let us recollect some definitions.

The dynamical equation in the single-particle model for a many electron atom is

$$\left[ \frac{p^2}{2m} + V(\vec{r}) \right] \psi_{\ell}(\vec{r}) = \epsilon_{\ell} \psi_{\ell}(\vec{r}) \quad (\text{IV-1})$$

Here  $V(r)$  is the sum of the potential due to nuclei,  $V_N$ , the Coulomb potential of electrons,  $V_H$ , and the exchange and correlation potential  $V_{xc}(n(r))$

$$V(\vec{r}) = V_N(\vec{r}) + V_H(\vec{r}) + V_{xc}(n(\vec{r})) \quad (\text{IV-2})$$

If  $V(\vec{r})$  is spherically symmetric, then after separating variables we have a radial equation

$$\left[ -\frac{d^2}{dr^2} + V(r) + \frac{\ell(\ell+1)}{r^2} \right] U_{\ell}(r) = \epsilon_{\ell} U_{\ell}(r) \quad (\text{IV-3})$$

where

$$U_{\ell}(r) = r R_{n\ell}(r) \quad (\text{IV-4})$$



### A. HSC Recipe

We shall state this recipe step by step.

- (i) Choose an analytic function  $f(x) = e^{-x^4}$  which cuts off rapidly at large arguments.
- (ii) Choose a cutoff radius  $r_{cl} \lesssim r_{ml}$  where  $r_{ml}$  is the radius of outermost peak of  $U_\ell$  (see Fig. IV-1).
- (iii) Form a first pseudopotential

$$V_{1\ell}^{PS}(r) = [1 - f(\frac{r}{r_{cl}})] V(r) + C_\ell f(\frac{r}{r_{cl}}) \quad (IV-5)$$

and solve the radial equation, Eq. (IV-3) with this potential. Adjust  $C_\ell$  so that the eigenvalue  $\epsilon_\ell$  is the same for the first pseudopotential as the atom. Let  $w_{1\ell}(r)$  be the radial solution for the first pseudopotential problem.

Since  $V_{1\ell}^{PS}(r) \approx V(r)$  for  $r \gtrsim r_{cl}$  the normalized eigenfunction of the first pseudopotential and the atom differ by a constant factor

$$U_\ell(r) = \alpha_\ell w_{1\ell}(r) \quad (IV-6)$$

in the range  $r \gtrsim r_{cl}$ .

In general the radial eigenfunction  $w_{1\ell}(r)$  does not satisfy the pseudocharge conserving condition (4) of Chapter III. All other conditions are satisfied.

- (iv) Form a second radial eigenfunction

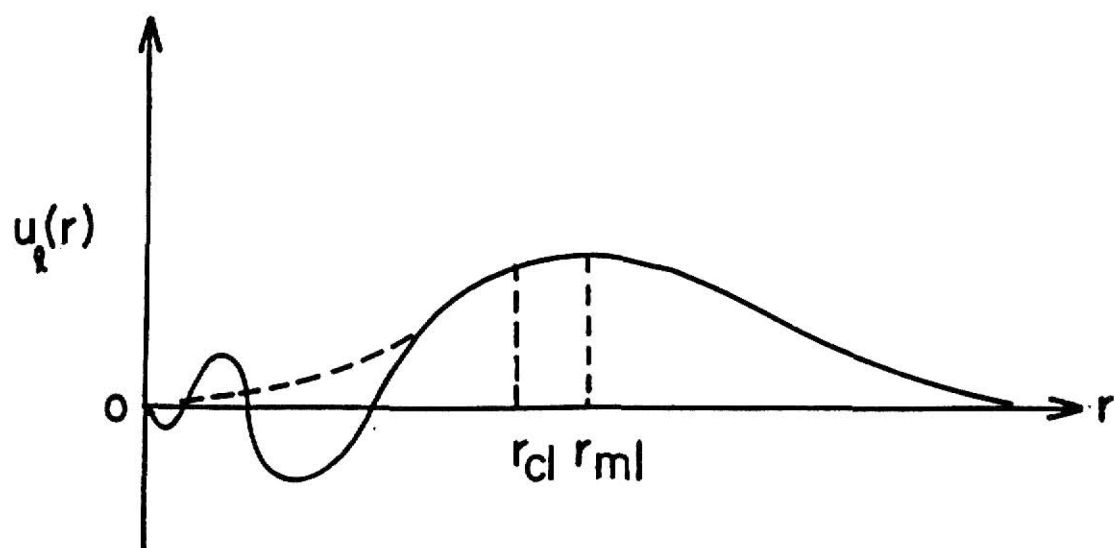
$$w_{2\ell}(r) = \alpha_\ell (w_{1\ell}(r) + \delta_\ell r^{\ell+1} f(\frac{r}{r_{cl}})) \quad (IV-7)$$

where  $\delta_\ell$  is determined by the normalization condition

$$\alpha_\ell^2 \int_0^\infty (w_{1\ell}(r) + \delta_\ell g_\ell(\frac{r}{r_{cl}}))^2 dr = 1 \quad (IV-8)$$

- (v) The final pseudopotential  $V_{2\ell}^{PS}(r)$  is found by inverting the radial

Figure IV-1: The cut-off radius  $r_{cl}$ .



equation for  $w_{2\ell}(r)$ .

Now let us verify the six conditions on the pseudo wavefunction stated in Section III.

Since  $w_{2\ell}$  satisfied the radial Eq. (IV-2) with the same eigenvalue  $\epsilon_\ell$  the first condition is satisfied.

From Eq. (IV-6 - IV-8) one can see  $w_{2\ell}(r)$  will approach very closely to  $U_\ell(r)$  for  $r$  greater than  $r_{c\ell}$  and that the charge inside  $r_{c\ell}$  is the same for the pseudo atom as for the atom. Consequently, for  $r$  greater than  $r_{c\ell}$  the first and second derivatives of  $w_{2\ell}(r)$  and  $U_\ell(r)$  are very close to each other respectively. The energy derivatives of  $\beta(r)$  and  $\beta_\ell^{PS}(r)$  are equal to each other as discussed in Chapter III. Since  $V_{1\ell}^{PS}(v)$  is equal to  $C_\ell$  at  $r=0$ , and if we write  $w_{2\ell}(r) = r^{\ell+1} W_{1\ell}(r)$ , we must have  $W_{1\ell}'(r) = 0$  at  $r=0$ , as shown in Chapter III. If we write  $w_{2\ell}(r) = r^{\ell+1} W_{2\ell}(r)$ , then from Eq. (IV-7) we know  $W_{2\ell}'(r) = 0$  at  $r=0$ . Therefore the six conditions on pseudo wavefunction  $w_{2\ell}(r)$  are all satisfied.

#### B. Kerker's Recipe

The following is another recipe due to Kerker.<sup>(7)</sup> We first introduce Kerker's recipe and then reproduce the results from Kerker's paper.

##### (a) Kerker's Recipe

A cutoff radius is defined as in Chapter III. The pseudowavefunction in the region  $r \leq r_c$  is parametrized as

$$F_\ell(r) = r^{\ell+1} W_\ell(r), \quad W_\ell(r) = e^{ar^4} + br^3 + cr^2 + d \quad (IV-9)$$

in terms of constants  $a$ ,  $b$ ,  $c$ , and  $d$ . The Kerker form assures that the pseudoeigenfunction is nodeless and satisfies condition (6). The four constants are chosen to satisfy conditions (2-5) in Chapter III. Thus,

the six conditions on pseudoeigenfunctions are all satisfied. The pseudopotential is found by inverting the radial equations for Kerker's pseudo-radial function.

(b) To Reproduce  $V_B^{PS}(r)$  in Kerker's Paper

Kerker<sup>(6)</sup> wrote a paper to explain his recipe for pseudopotential. In his paper he gave two numerical examples using Si and Mo. He calculated  $U_\ell(r) = rR_\ell(r)$ ,  $U_\ell^{PS}(r)$  and  $V_B^{PS}(r)$  for different  $n, \ell$  in a configuration for Si and Mo separately. Kerker's results are shown in Fig. IV-2 and Fig. IV-3.

We shall reproduce the results in these two figures by using Kerker's recipe. The result will show that our understanding of the recipe is correct and allow us to analyze contributions to a pseudopotential.

The results in Kerker's paper are reproduced quite well. Now we want to analyze the pseudopotential to see if there is something we can learn from it.

As we stated in Section II, there are similarities between hydrogen-like atoms and single-particle models of many-electron atoms. Hydrogen-like atoms may be viewed as the simplest many-electron atom. Hence we will first analyze hydrogen-like atoms, and hope we can learn something which is useful for the analysis of the many-electron atom.

For a hydrogen-like atom the potential is equal

$$-\frac{2Z}{r} = \frac{\frac{d^2}{dr^2} U_{n\ell}(r)}{U_{n\ell}(r)} - \frac{\ell(\ell+1)}{r^2} + \epsilon_{n\ell} \quad (IV-10)$$

where

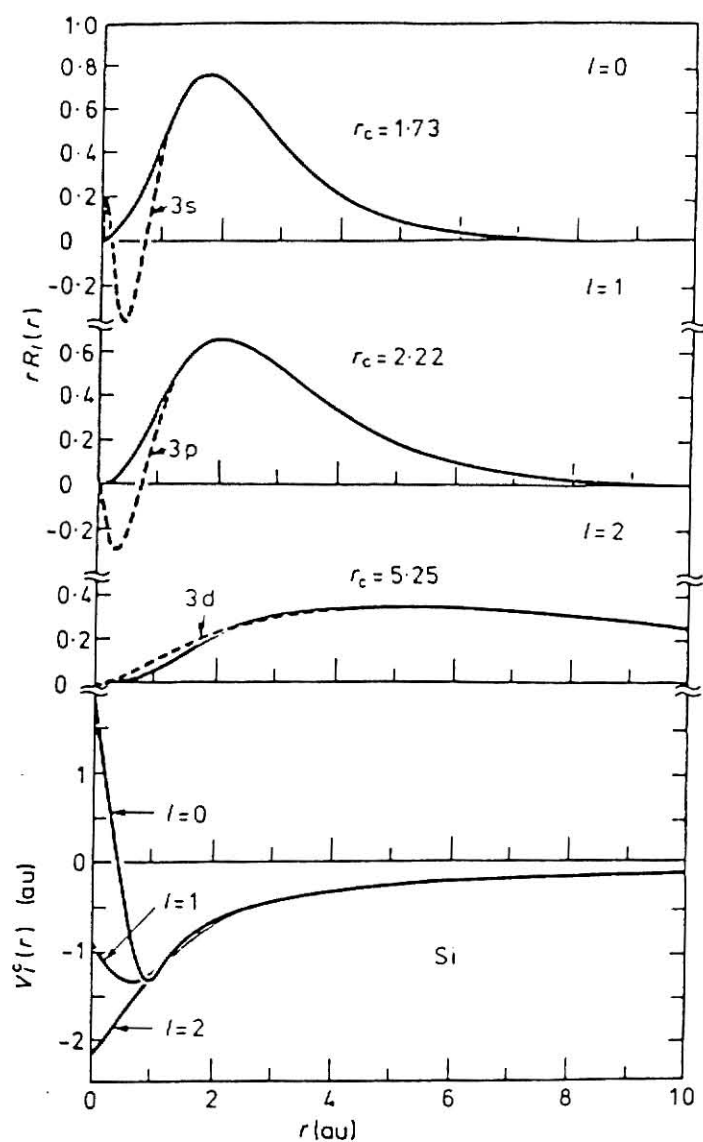
$$\epsilon_{n\ell} = -\frac{Z^2}{n^2} \text{ (Ry)} \quad (IV-11)$$

let

$$U_{n\ell}(r) = r^{\ell+1} w_{n\ell}(r) \quad (IV-12)$$

Figure IV-2: Comparison of real radial functions and Kerker's pseudo radial functions and bare-ion pseudopotentials for Si.

(From G. P. Kerker, J. Phys. C: Solid St. Phys., 13 (1980) L189-94 printed in Great Britain).

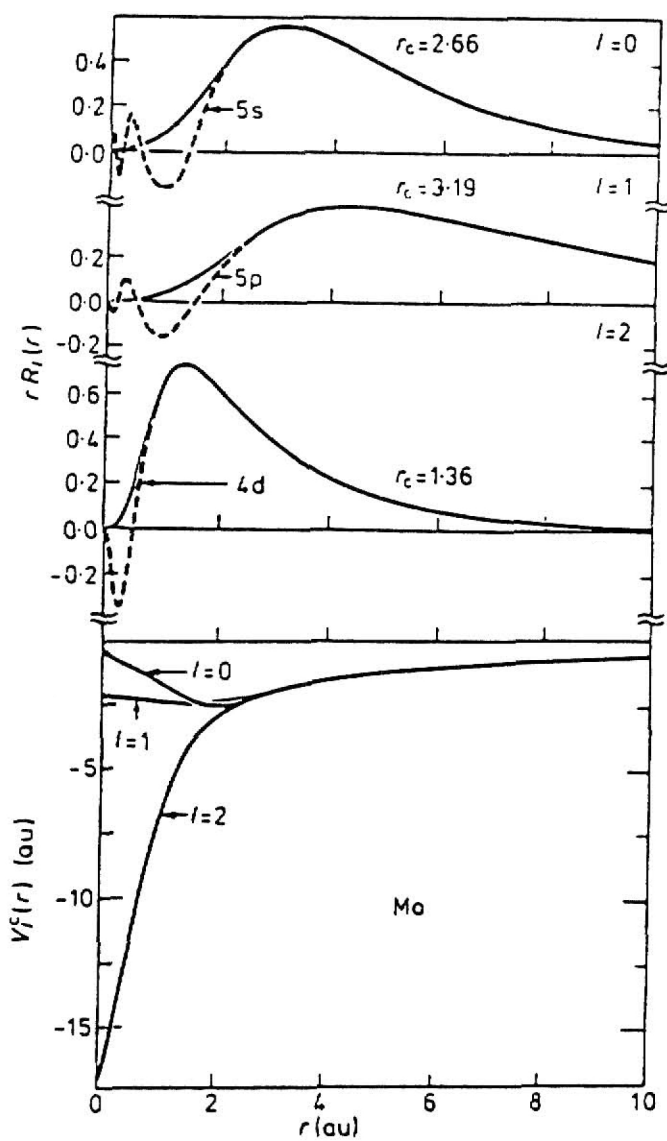


Real (broken curves) and pseudo- (full curves) radial wavefunctions for Si in the configuration  $3s^2 3p^1 3d^1$ . The angular components of the corresponding core pseudo-potential are also plotted. Note that the repulsive centrifugal potential is not included.

Figure IV-3: Comparison of real radial functions and Kerker's pseudo radial functions and bare-ion pseudopotentials for Mo.

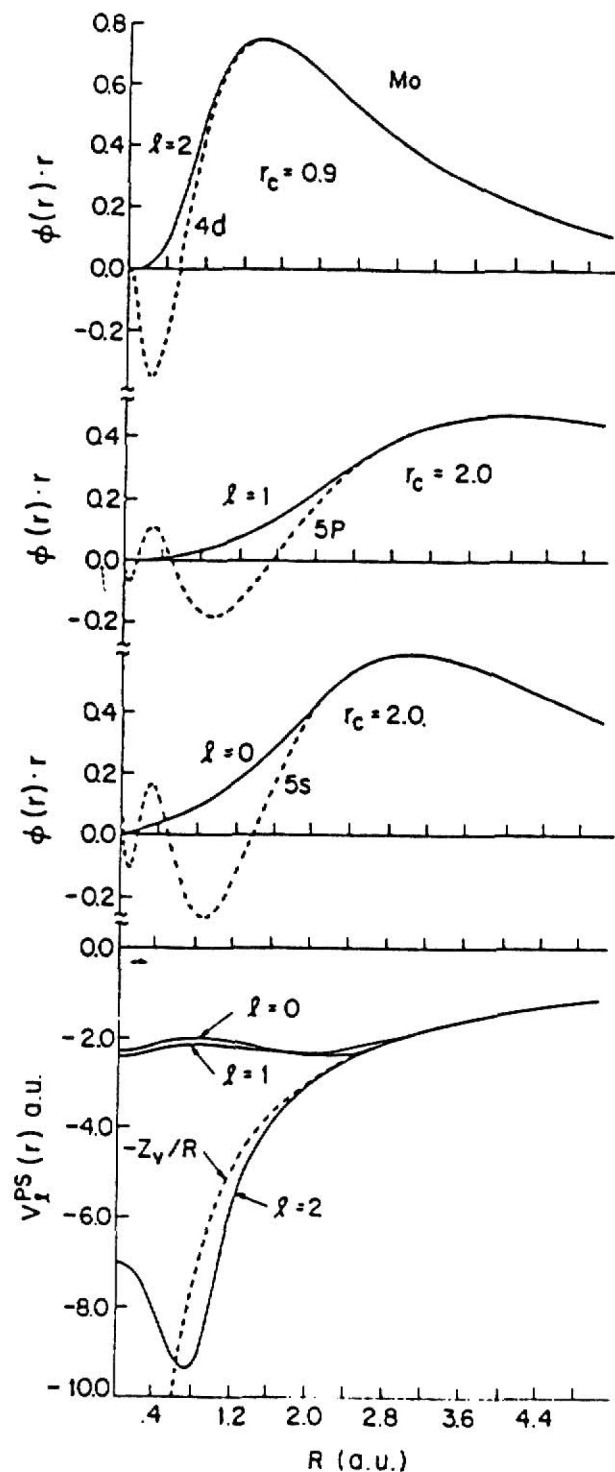
(From G. P. Kerker, J. Phys. C: Solid St. Phys., 13 (1980) L189-94 printed in Great Britain).





Real and pseudo-radial wavefunctions for Mo  $5s^1 4d^5 5p^0$  and the core pseudopotential.

Figure IV-4: Comparison of real radial functions and Hermann, Schlüter and Chiang's pseudo radial functions and bare-ion pseudopotentials for Mo.  
(From Hamann, D. R., Schlüter, M. and Chiang, C., 1979, Phys. Rev. Lett. 43, 1494).



Comparison of pseudo wave functions (solid lines) and *ab initio* full-core atomic valence wave functions (broken lines) for Mo. The lower panel shows the corresponding bare-ion pseudopotentials.

Replace  $U_{n\ell}$  in Eq. (IV-10) and it becomes

$$-\frac{2Z}{r} = \frac{W_{n\ell}''(r)}{W_{n\ell}(r)} + \frac{2(\ell+1)}{r} \frac{W_{n\ell}'(r)}{W_{n\ell}(r)} + \epsilon_{n\ell} \quad (\text{IV-13})$$

For a hydrogen-like atom the lowest energy radial function for a given angular momentum  $\ell$  is nodeless and has the form

$$U_{n\ell}(r) = C r^{\ell+1} \exp(-Zr/n) \quad (\text{IV-14})$$

where

$$n = \ell+1$$

For such states

$$W_{n\ell}(r) = C e^{-\frac{Z}{n}r}$$

The first term in Eq. (IV-13)  $W_{n\ell}''(r)/W_{n\ell}(r) = -\epsilon_{n\ell}$  exactly cancels the eigenvalue term. The second term  $2(\ell+1) W_{n\ell}'(r)/(rW_{n\ell}(r))$  reproduces the hydrogen-like potential.

Since  $F_{\ell}^{\text{PS}}(r)$  is nodeless, we conjecture that for  $n = \ell+1$ ,  $F_{\ell}^{\text{PS}}(r)$  may have the same property. This is that the first and second terms in a pseudopotential may approximate the pseudopotential and the energy of the state, respectively. To investigate this idea the terms

$$V_{\phi} = W_{n\ell}''(r)/W_{n\ell}(r) + \epsilon_{n\ell} \quad (\text{IV-15})$$

and

$$V_1 = 2(\ell+1)W_{n\ell}'(r)/(rW_{n\ell}(r)) \quad (\text{IV-16})$$

are calculated. For a hydrogen-like atom  $V_{\phi}$  is identically zero and  $V_1$  reproduces the potential. The plots using Kerker's pseudo radial functions are shown in Figs. (IV-5 - IV-10) for Mo and Si. Also plotted is the total pseudopotential

$$V_{\ell}^{\text{PS}}(r) = V_{\phi}(r) + V_1(r) \quad (\text{IV-17})$$

Figure IV-5: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 3s state of Si

$$V_{\ell}^{\text{PS}}(r) = V_{\phi}(r) + V_1(r)$$

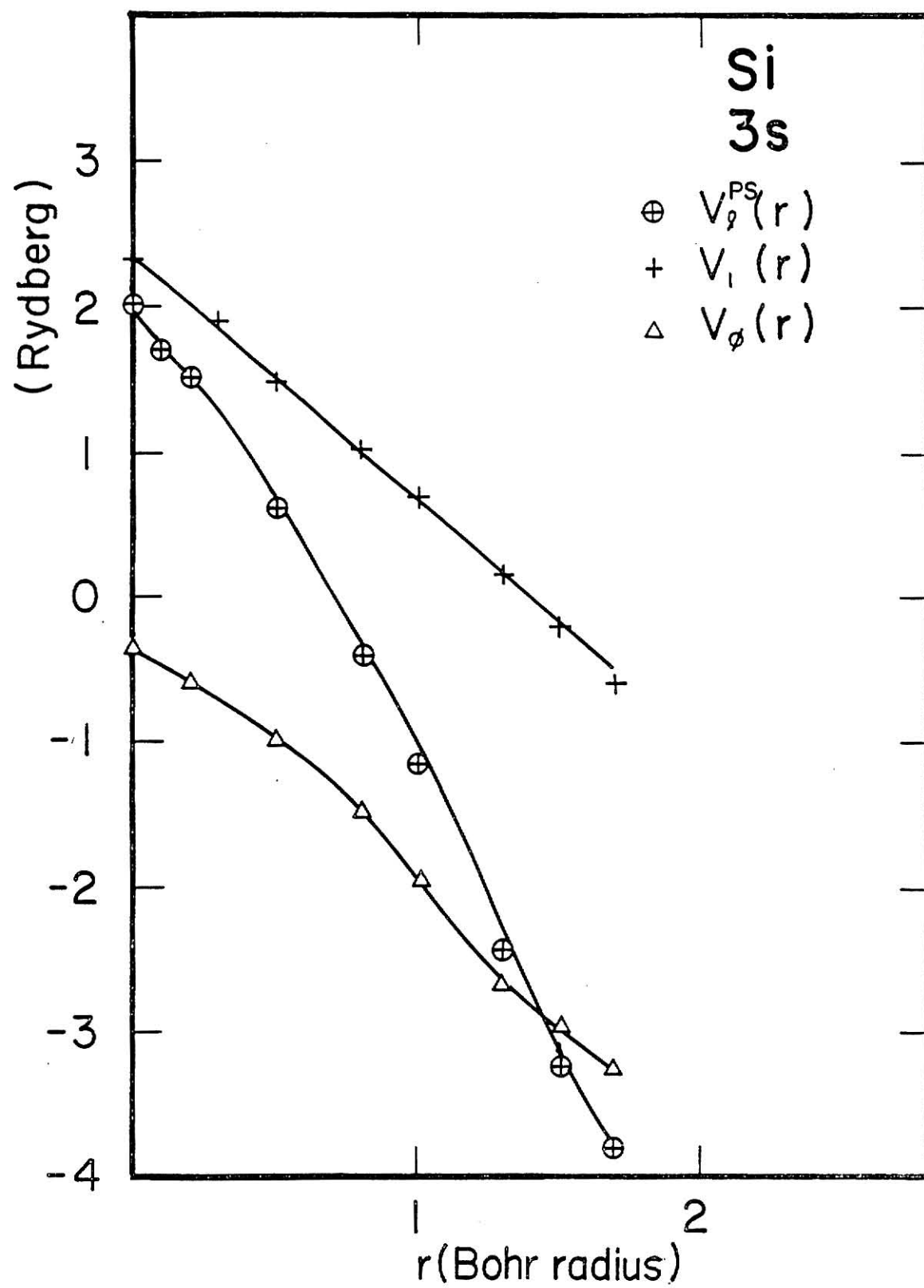


Figure IV-6: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 3p state of Si

$$V_{\ell}^{\text{PS}}(r) = V_{\phi}(r) + V_1(r)$$

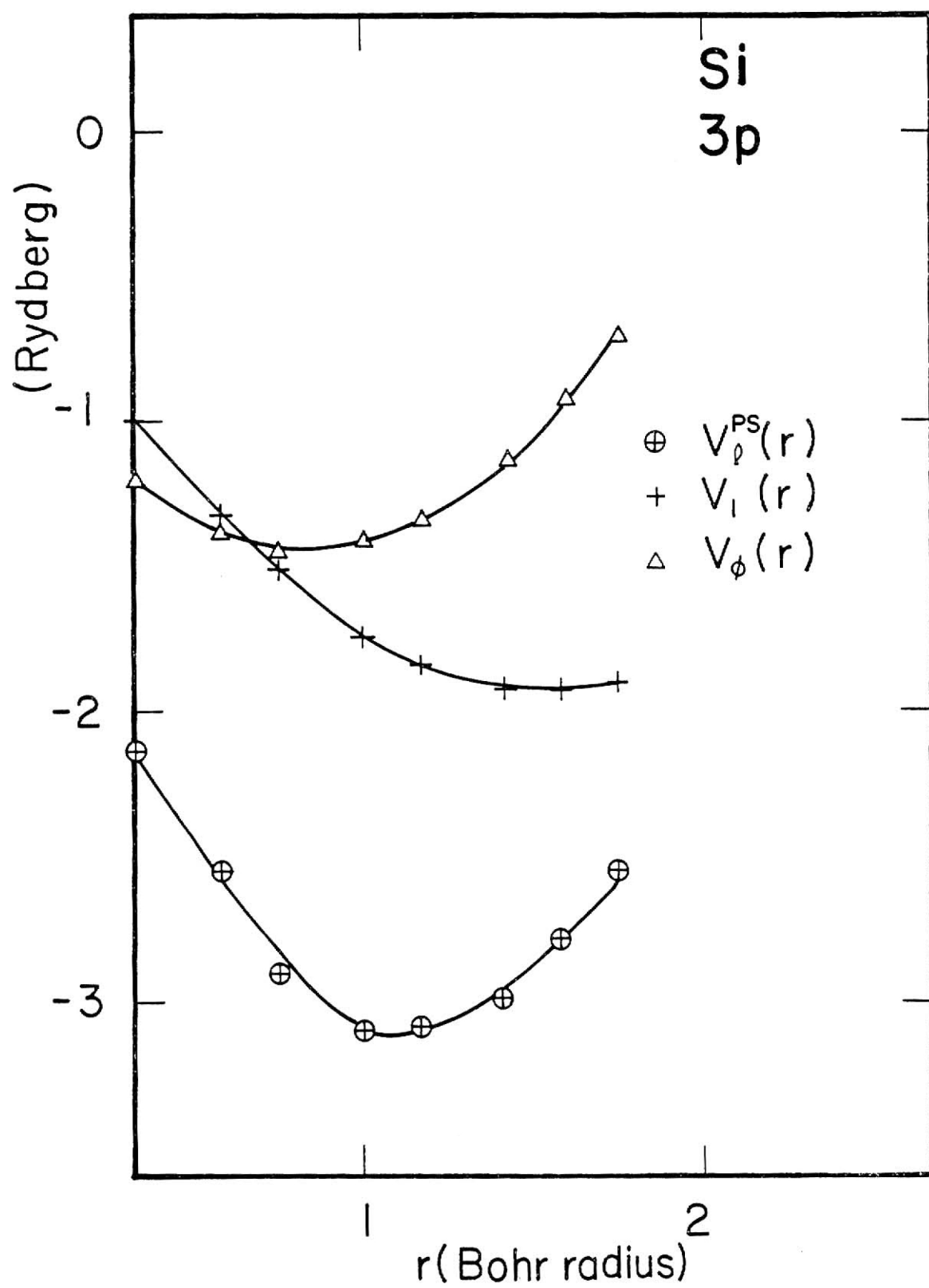




Figure IV-7: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 3d state of Si

$$V_{\ell}^{\text{PS}}(r) = V_{\phi}(r) + V_1(r)$$

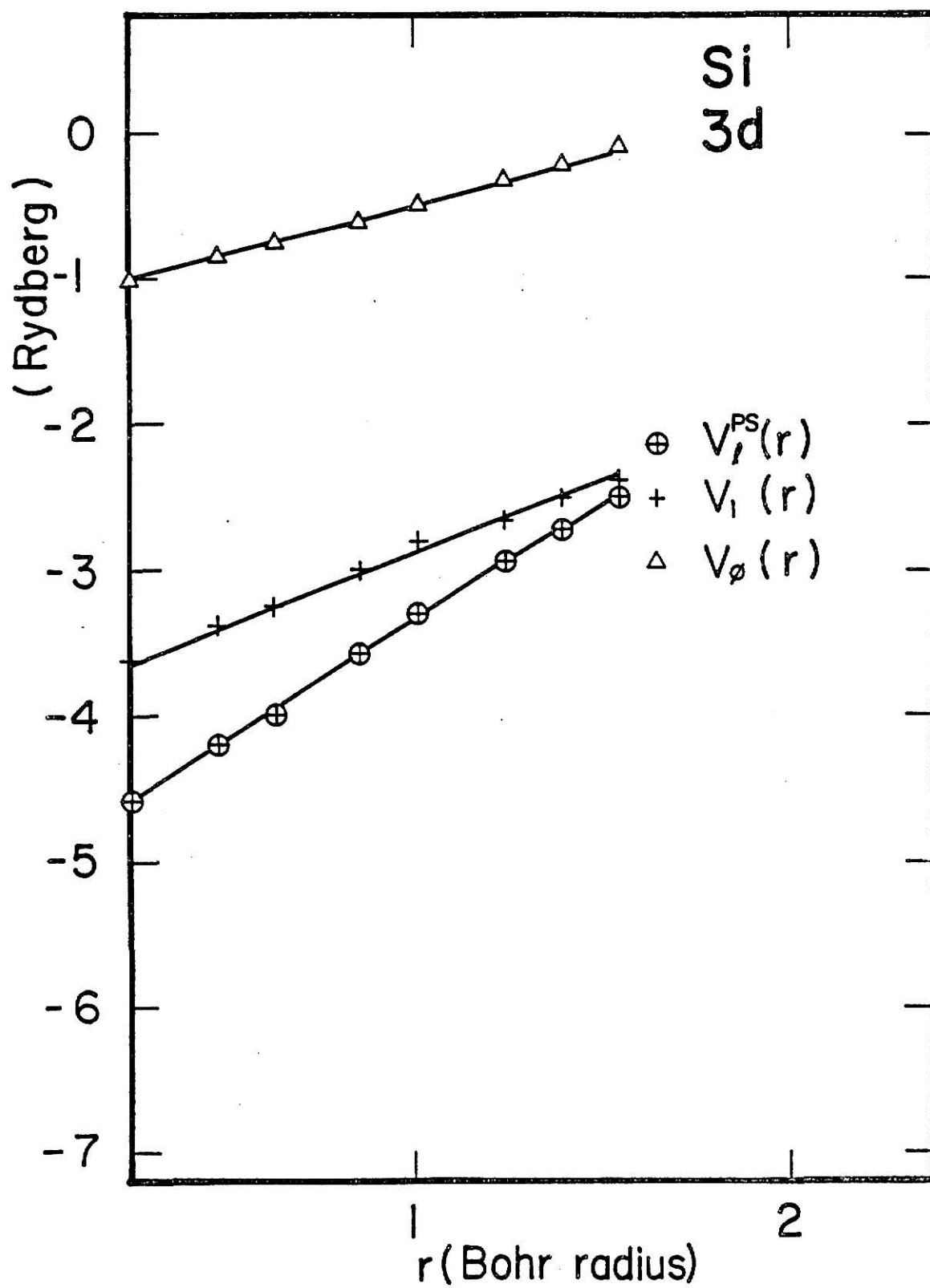


Figure IV-8: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 5s state of Mo

$$V_{\ell}^{\text{PS}}(r) = V_1(r) + V_{\phi}(r)$$

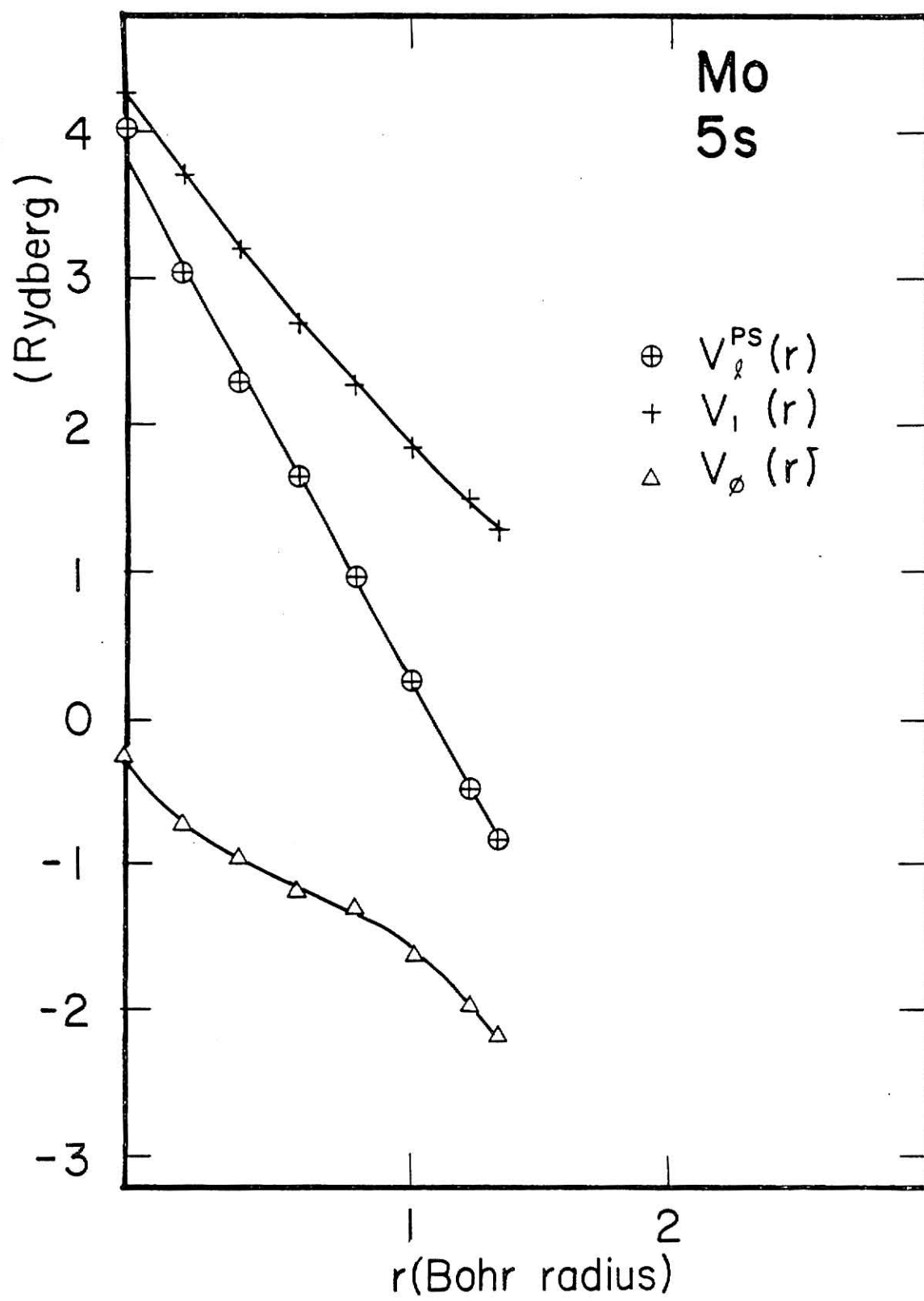


Figure IV-9: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 5p state of Mo

$$V_{\ell}^{\text{PS}}(r) = V_{\text{l}}(r) + V_{\phi}(r)$$

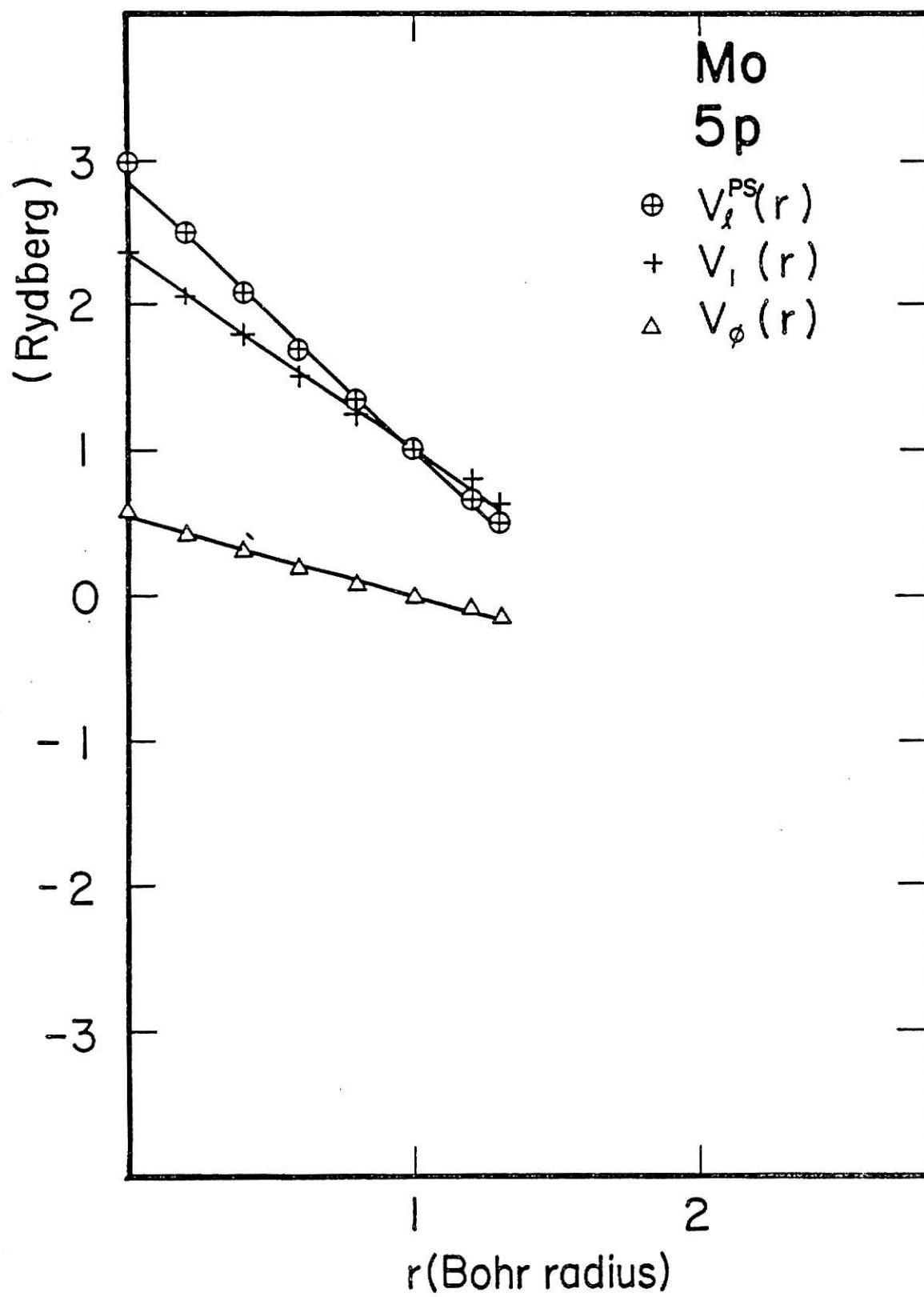
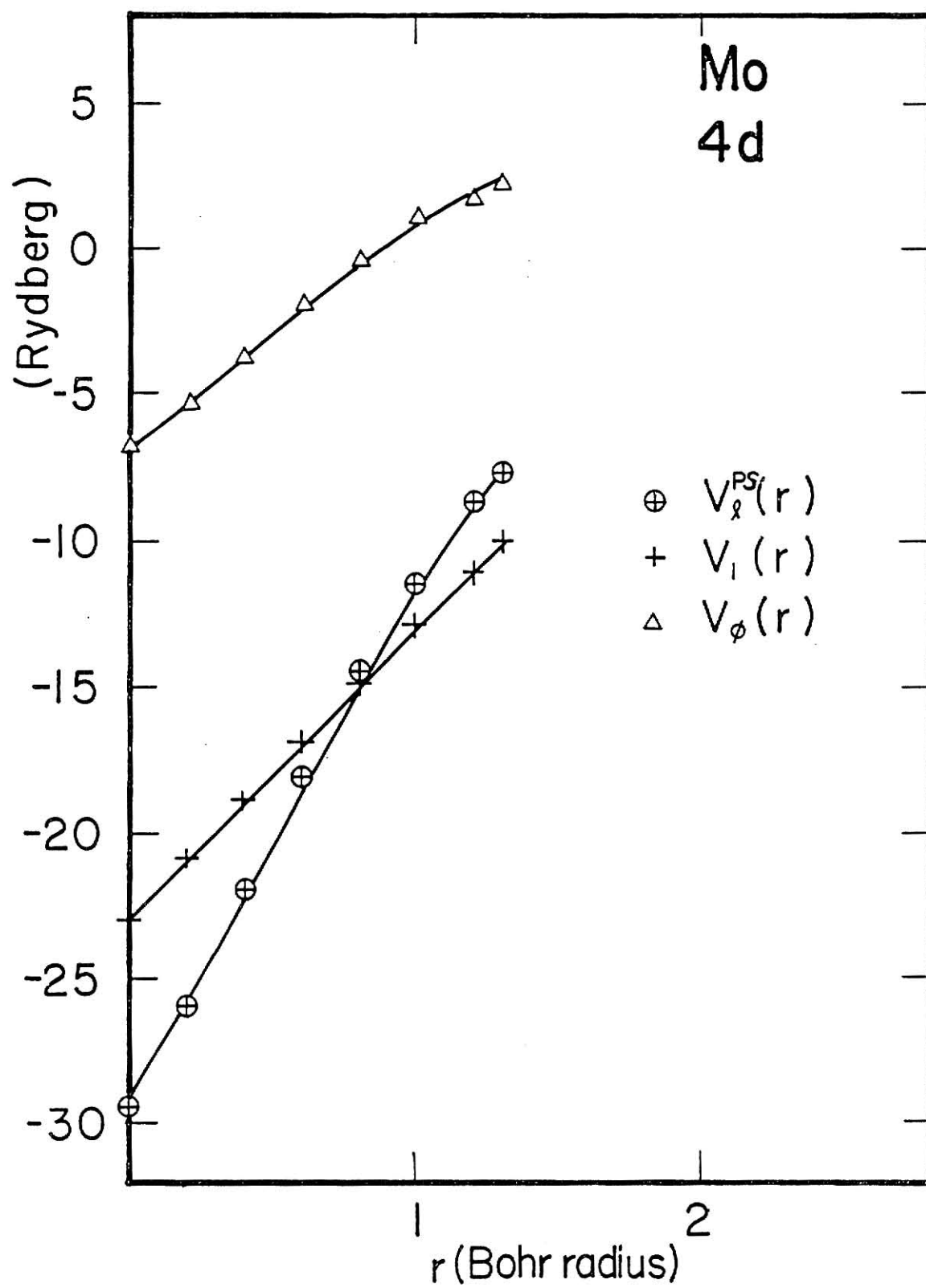


Figure IV-10: Decomposition of the pseudopotential ( $V_{\ell}^{\text{PS}}$ ) versus radial distance  $r$  for the 4d state of Mo

$$V_{\ell}^{\text{PS}}(r) = V_1(r) + V_{\phi}(r)$$





From these figures we find that the 3d state of Si is the only case for which  $n$  is equal to  $\ell+1$  and for this case the terms  $V_\phi(r)$  and  $V_1(r)$  do behave similarly to the hydrogen-like atom case. That is  $V_\phi$  is approximately zero and  $V_1(r)$  is the main contribution to the pseudopotential. The Mo 4d and 5p states behave similarly although for these states  $n$  is not equal to  $\ell+1$ .

Another interesting thing is that in all six figures there is a common character. For small  $r$  the pseudopotentials produced by Kerker's recipe are linear in  $r$ . Is it true that the pseudopotentials from HSC recipe will also have this same property? This question motivates us to compare and discuss these two recipes. This will be the topic for the next section.

### C. Comparison and Discussion

At first we will compare these two recipes to see the similarities and differences between them, then we will discuss some properties of the pseudopotentials.

#### (i) Comparison of the Recipes

The similarities and differences between these two recipes are explained below.

Both of them are ab initio pseudopotential recipes, based on atomic structure information. Each can provide pseudo eigenfunctions, pseudopotentials and bare-ion pseudopotentials of an atom which can be used to get the pseudopotential of a crystal as stated in Chapter III-IV.

The pseudowavefunctions from these two recipes satisfy all the six conditions stated in Chapter III. But there are some differences between them.

Kerker's recipe starts with the construction of pseudo wave

function with undetermined constants and a definite cutoff radius. By using the condition which the pseudo wave functions have to satisfy we can find the pseudowavefunctions and then find the pseudopotential and bare-ion pseudopotential by inversion.

The HSC recipe starts with the construction of the first approximate pseudopotential  $V_{1\ell}^{\text{PS}}(r)$ . Then from the radial equation we get the first approximate pseudo eigenfunction  $w_{1\ell}$ . After improving  $w_{1\ell}$  we get the pseudo eigenfunction  $w_{2\ell}$ . Finally by means of inversion we get the pseudopotential.

They are two different recipes. Therefore, they will give different pseudo wave functions, pseudopotential and bare-ion pseudopotential. The difference between bare-ion pseudopotentials can be seen in Fig. IV-3 and Fig. IV-4. But from these two figures it is not very easy to see the difference between the pseudo wave functions of the two recipes. In order to see the difference between the two pseudo wave functions we shall study the behavior of these two pseudo wave functions as  $r$  approaches zero and we shall see these two pseudo wave functions are different from each other, as  $r$  approaches zero.

In Kerker's recipe the pseudo wave function

$$F_{\ell}(r) = r^{\ell+1} e^d(1+cr^2+br^3+(a+\frac{1}{2}c^2)r^4+ \dots) \quad (\text{IV-18})$$

for small  $r$ .

The HSC recipe proceeds in two steps. The real potential  $V(r)$  has the form

$$V(r) = \frac{-Z}{r} + V_{\ell 0} + V_{\ell 1}r + V_{\ell 2}r^2 + \dots \quad (\text{IV-19})$$

for small values of  $r$ .

Then we have from Eq. (IV-5)

$$V_{1\ell}^{PS}(r) = c - \frac{Z}{r_c^4} r^3 + \frac{V_{\ell 0} - c_\ell}{r_c^4} r^4 + \dots \quad (IV-20)$$

for small  $r$ .

It follows from the radial equation, Eq. (IV-3) that leading terms in  $r$  are

$$w_{1\ell}(r) = r^{\ell+1} \left( 1 + \frac{(c_\ell - \epsilon_\ell)}{(4\ell+6)} r^2 + \frac{(c_\ell - \epsilon_\ell)^2}{4(2\ell+5)(4\ell+6)} r^4 + \dots \right) \quad (IV-21)$$

In the "norm-conserving" second step of the HSC recipe

$$\begin{aligned} w_{2\ell} &= \alpha_\ell (w_{1\ell} + \delta_\ell g_\ell(x)) \\ &= r^{\ell+1} \delta_\ell \left[ (1+\delta_\ell) + \frac{(c_\ell - \epsilon_\ell)}{(4\ell+6)} r^2 \right. \\ &\quad \left. + \left( \frac{(c_\ell - \epsilon_\ell)^2}{4(2\ell+5)(4\ell+6)} - \frac{w_\ell}{r_c^4} \right) r^4 + \dots \right] \end{aligned} \quad (IV-22)$$

The coefficient of  $r^3$  is equal to zero for the pseudoeigenfunction in the HSC recipe. The corresponding term using Kerker's recipe is  $e^d b$  which is not equal to zero in general. The pseudo wave functions are different from each other in these two recipes. From the result above we can find the pseudopotentials in two different recipes for small  $r$  and shall see what different behaviors they will have.

From Eq. (IV-18) and Eq. (IV-15 - IV-17) the pseudopotential in Kerker's recipe for small  $r$  is

$$V_{\ell(K)}^{PS}(r) = 2c(2\ell+3) + 3b(2\ell+4)r + \epsilon_\ell \quad (IV-23)$$

and the pseudopotential in HSC recipe for small  $r$  is

$$V_{\ell(H)}^{PS}(r) = \frac{2(\ell+2)(c_\ell - \epsilon_\ell)}{(4\ell+6)(1+\delta_\ell)} + \frac{3(c_\ell - \epsilon_\ell)^2}{(2\ell+5)(4\ell+6)(1+\delta_\ell)} r^2 + \epsilon_\ell \quad (IV-24)$$

Hence, for small  $r$  the leading term in Kerker's recipe is linear in  $r$  while in HSC recipe the leading term is quadratic in  $r$ . This gives the answer to the question raised in the end of the previous section.

## (ii) Discussion

From Fig. IV-2 we see that the Kerker bare-ion pseudopotentials of Mo for  $\ell=0$ ,  $\ell=1$  are very flat and close to each other. But the bare-ion pseudopotential of Mo for  $\ell=2$  is very steep, and is far below that of  $\ell=0$  and  $\ell=1$ .

The following will give an explanation for this fact.

From the diagram we know as  $r$  approaches a large value then all three  $V_{B\ell}^{PS}(r)$ 's for  $\ell=0$ ,  $\ell=1$ , and  $\ell=2$  will coincide. So we see if two  $V_{B\ell}^{PS}(r)$ 's differ very much at  $r=0$  then these two  $V_{B\ell}^{PS}(r)$ 's will differ very much. Otherwise if two  $V_{B\ell}^{PS}(r)$ 's differ not too much at  $r=0$ , then these two  $V_{B\ell}^{PS}(r)$  will be close to each other. Therefore, to determine whether two  $V_{B\ell}^{PS}(r)$  differ very much or not, we need only to see the values of these two  $V_{B\ell}^{PS}(r)$  at  $r=0$ . This is the key point.

From Eq. (IV-23) we have the pseudopotential at  $r=0$  in Kerker's recipe as follows

$$V_{\ell}^{PS}(0) = 2C(2\ell + 3) + \epsilon_{\ell} \quad (IV-25)$$

In general there is no large difference between  $\epsilon_{\ell}$  for different  $\ell$ . Then the constant  $C$  will determine the magnitude of  $V_{\ell}^{PS}(0)$ . Since  $V_{\ell}^{PS}(0)$  and  $V_{\ell B}^{PS}(0)$  differ by the same constant for different  $\ell$ , so the value of  $C$  will determine the magnitude of  $V_{\ell B}^{PS}(0)$ . If  $C$  is large, then  $V_{\ell B}^{PS}(0)$  is large, otherwise  $V_{\ell B}^{PS}(0)$  is small.

The values of  $C$ 's for different  $\ell$  for atom Mo and atom Si are given in Table IV-1.

For atom Mo the constant  $C$  for  $\ell=0$  and  $\ell=1$  are close to each other and they are quite different from that for  $\ell=2$ . Therefore it accounts for the fact that the bare-ion pseudopotentials of Mo for  $\ell=0$  and  $\ell=1$  are close to each other while they are far apart from that for  $\ell=2$ .

As for atom Si, we see the constant  $C$  for  $\ell=1$  and  $\ell=2$  are close to

each other, and they are quite different comparatively from the constant  $C$  for  $\ell=0$ . Therefore we have an idea that the  $V_{\ell B}^{\text{PS}}(r)$ 's for  $\ell=1$ , and  $\ell=2$  will be close to each other while they will be separated from  $V_{\ell B}^{\text{PS}}(r)$  for  $\ell=0$ . This happens to be the case.

Table IV-1: The value of  $c$  for different  $\ell$  for Mo and Si atoms.

Table IV-1

Mo

$\ell = 0$	$c = 0.74950$
$\ell = 1$	$c = 0.09085$
$\ell = 2$	$c = -2.03135$

Si

$\ell = 0$	$c = 0.5836$
$\ell = 1$	$c = -0.1197$
$\ell = 2$	$c = -0.3019$

## Chapter V

### SUMMARY

Ab initio pseudopotential method is an important method developed recently. It is an efficient method, because it only needs to consider a few valence electrons and ignores the core. This makes calculations relatively much easier. It is very useful because we can construct a bare-ion pseudopotential from the pseudopotential for an atom. This bare-ion pseudopotential will replace the influence of the core on the valence electrons, therefore it can be used for different valence configurations, and can be used in a crystal.

For ab initio pseudopotentials we study all the conditions imposed on the pseudowavefunction for an atom. Some of them are implicit and are ignored by HSC. These conditions are not sufficient to uniquely determine a pseudowavefunction. Many different pseudowavefunctions can satisfy these conditions. In order to uniquely determine a pseudowavefunction and then a pseudopotential we need a definite procedure to prescribe the calculation which will lead to a definite pseudo wave function. This procedure is called a "recipe". Once the pseudo wave function is determined, then by inverting the radial equation, we get the pseudopotential and by subtracting the influence of the valence electrons from the pseudopotential, the bare-ion pseudopotential is obtained.

Two ab initio pseudopotential recipes, HSC recipe and Kerker's recipe are studied in this thesis. The pseudo wave functions and the bare-ion pseudopotentials are calculated by Kerker's recipe. The results are reproduced. They are in good agreement with Kerker's results.



These two recipes are compared and discussed. The similarities and differences of these two recipes are discussed. These two recipes produce different pseudo wave functions, pseudopotentials, and bare-ion pseudopotentials. It is interesting to note that while eigenfunctions produced by two recipes are definitely different from each other for small  $r$ , they look very similar to each other for small  $r$  in the diagram of the two recipes given by HSC and Kerker in their papers. The decomposition of the pseudopotential is made. The differences between the bare-ion pseudopotential of Mo and Si for different  $\ell$  are explained.

We have studied two different ab initio recipes. The question is how to use these two recipes for crystals and determine the properties of the crystals. From the results we can judge which recipe is better and we can try to get another recipe better than these two.

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AB INITIO PSEUDOPOTENTIAL STUDY

by

SHENG-YU PENG

B.S., Tsing Hua University, 1952

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AN ABSTRACT OF A MASTER'S THESIS

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## ABSTRACT

In a crystal, two different kinds of electrons may be distinguished. Electrons which are tightly bound by nuclei are core electrons. Less tightly bound valence electrons move throughout the crystal. Valence electrons determine the physical and chemical properties of a crystal. The idea of a pseudopotential is to replace the influence of the nuclei and core electrons and other valence electrons by an effective potential for valence electrons. Elimination of explicit dependence on core electrons facilitates calculation.

To obtain an ab initio pseudopotential in a crystal, an ab initio pseudopotential is first constructed for an atom. Subtracting the valence electron contributions leaves a bare-ion pseudopotential. Bare-ion pseudopotentials attempt to replace the effect of the nucleus and the core electrons by an effective potential. Thus bare-ion pseudopotential is then used for different valence configurations of atoms and for crystals.

To find an ab initio pseudopotential for an atom general mathematical conditions are imposed on the pseudo eigenfunctions. However, these conditions are insufficient to uniquely determine a pseudoeigenfunction. In addition, a definite calculation procedure or "recipe" must be prescribed. Different recipes will lead to different pseudo eigenfunctions. The Hamann, Schlüter and Chiang mathematical conditions with two alternative recipes are analyzed in this thesis. Pseudopotentials for an atom are obtained by inverting the radial equation for the pseudo eigenfunctions. It is found that besides the mathematical conditions given by Hamann, Schlüter and Chiang, implicit conditions are also implied by their calculational

procedure. The consequences of these implicit conditions are discussed  
ab initio pseudopotential recipe due to Kerker is reproduced.

A decomposition of the Kerker pseudopotential is studied. The  
Kerker recipe is compared and contrasted to the Hamann, Schlüter and  
Chiang recipe. The pseudoeigenfunctions and the pseudopotential of those  
two recipes are analytically different. Although the pseudo eigenfunctions  
produced by two recipes appear very similar to each other when plotted.