Indian Streams Research Journal
ISSN 2230-7850
Volume-3, Issue-8, Sept-2013 Available online at www.aygrt.isrj.net

# Density of State And Effective Mass From Pseudo Potential Theory

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**ABSTRACT:** The empirical pseudopotential method was developed in the 1960's [1-3] as a way to solve Schrodinger's equation for bulk crystals without knowing exactly the potential experienced by an electron in the lattice. Since electrons are interacting with the crystal lattice, an electronic band structure calculation is a many body problem (unlike the situation in photonic crystal calculations, for example [4]). Although other methods existed at the time for approximating electronic band structures, the pseudopotential method gives surprisingly accurate results considering the computing time and effort involved.

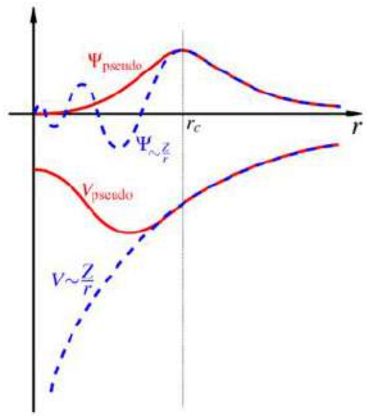
**KEYWORDS:** Pseudo Potential Theory, Science, Physics, Density of State, Effective Mass.

## INTRODUCTION:

The basic scheme is to assume that the core electrons are tightly bound to their nuclei, and the valence and conduction band electrons are influenced only by the remaining potential. Since the potential can be Fourier expanded in plane waves, an eigenvalue equation for determining an E-k relationship can be established. Although the Fourier coefficients for the potentials are not known, they can be empirically determined for a given crystal by fitting calculated crystal parameters to known measurements. Cohen and Bergstresser followed these steps to determine band structures of several diamond and III-V zincblende structures [5].

In this term paper, I repeat the original steps taken by Cohen and Bergstresser in formulating the pseudopotential method, then carry out calculations using a computer program I wrote to construct the electronic band diagrams of Si and GaAs using their form factors. Then, I apply the method to AlAs, for which form factors are essentially unavailable, and construct a plausible E-k diagram for the compound using known parameters. Limitations on the method used are discussed, as well as more powerful methods of determining accurate band structures.

In physics, a **pseudo potential** or **effective potential** is used as an approximation for the simplified description of complex systems. Applications include atomic physics andneutron scattering.



Comparison of a wavefunction in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red). The real and the pseudo wavefunction and potentials match above a certain cutoff radius .

## ATOMIC PHYSICS

The pseudopotential is an attempt to replace the complicated effects of the motion of the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, or pseudopotential, so that the Schrödinger equation contains a modified effective potential term instead of the Coulombic potential term for core electrons normally found in the Schrödinger equation. The pseudopotential approximation was first introduced by Hans Hellmann in the 1934.[1] By construction of this pseudopotential, the valence wavefunctiongenerated is also guaranteed to be orthogonal to all the core states.

The pseudopotential is an effective potential constructed to replace the atomic all-electron potential (Full-potential) such that core states are eliminated and the valence electrons are described by nodeless pseudo-wavefunctions. In this approach only the chemically active valence electrons are dealt with explicitly, while the core electrons are 'frozen', being considered together with the nuclei as rigid non-polarizable ion cores. Norm-conserving pseudopotentials are derived from an atomic reference state, requiring that the pseudo- and all-electron valence eigenstates have the same energies and amplitude (and thus density) outside a chosen core cutoff radius $r_c$. Pseudopotentials with larger cutoff radius are said to be *softer*, that is more rapidly convergent, but at the same time less *transferable*, that is less accurate to reproduce realistic features in different environments.

MOTIVATION:

1. Reduction of basis set size
2. Reduction of number of electrons
3. Inclusion of relativistic and other effects

## APPROXIMATIONS:

1. One-electron picture.
2. The small-core approximation assumes that there is no significant overlap between core and valence wave-function.

Nonlinear core corrections or "semicore" electron inclusion deal with situations where overlap is non-negligible. *Norm-conserving* pseudopotentials enforce the condition that, outside of a cutoff radius, the norm of each pseudo-wavefunction be identical to its corresponding all-electron wavefunction. *Ultrasoft* pseudopotentials relax the norm-conserving constraint to reduce the basis-set size further. Another related technique is the projector augmented wave (PAW) method.

Early applications of pseudopotentials to atoms and solids based on attempts to fit atomic spectra achieved only limited success. Solid-state pseudopotentials achieved their present popularity largely because of the successful fits by Walter Harrison to the nearly free electron Fermi surface of Aluminum (1958) and by James C. Phillips to the covalent energy gaps of Silicon and Germanium (1958). Phillips and coworkers (notably Marvin L. Cohen and coworkers) later extended this work to many other semiconductors, in what they called "semiempirical pseudopotentials". The very high accuracy of these "semiempirical pseudopotentials" in fitting optical and photoemission spectra of many semiconductors has never been equaled, not even by the most elaborate "first principles" calculations; this very high accuracy of simple single-electron models remains a puzzle today.

## FERMI PSEUDOPOTENTIAL

Enrico Fermi introduced a pseudopotential, $V$, to describe the scattering of a free neutron by a nucleus.[7] The scattering is assumed to be *s*-wave scattering, and therefore spherically symmetric. Therefore, the potential is given as a function of radius, $r$:

$$V(r) = \frac{2\pi\hbar^2}{m} b\,\delta(r),$$

where $\hbar$ is the Planck constant divided by $2\pi$, $m$ is the mass, $\delta(r)$ is the Dirac delta function, $b$ is the neutron scattering length, and $r = 0$ the center of mass of the nucleus.[8] The Fourier transform of this $\delta$-function leads to the constant neutron form factor.

## PHILLIPS PSEUDOPOTENTIAL

James C Phillips developed a simplified pseudopotential while at Bell Labs useful for describing silicon and germanium.

**BASIC PSEUDO POTENTIAL THEORY**

Consider a single isolated atom, with atomic number $Z$. There are $N$ ($= Z$) electrons, moving in an external potential given by

$$v_{ext}(r) = \frac{Z}{r}. \tag{1.138}$$

Applying Kohn-Sham DFT to this system will result in a set of $N$ Kohn-Sham orbitals, $\psi_i(\mathbf{r})$, a corresponding density, $\rho(\mathbf{r})$, and a Kohn-Sham potential, $\mu_{KS}(\mathbf{r})$.

In order to create a pseudopotential for this atom, we must first specify which orbitals are to be considered core, and which are to be considered valence, and also specify the cut-off radius, $r_c$. In most cases, all the electrons that are in ``closed shells" are considered core, while the remainder are considered valence. In general, the pseudopotential $\hat{v}_{PS}$ is *non-local*, in that there is a separate local potential, $v_{PS}^{(l)}(r)$, acting on each angular momentum component, $l$, of a given orbital.

If we apply Kohn-Sham DFT to the atom, with the external potential, $v_{ext}(r)$, now replaced with the pseudopotential, $\hat{v}_{PS}$, and with only valence electrons present, the resulting pseudo-orbitals, $\psi_{PS}(\mathbf{r})$, must satisfy the following requirements:

1. Each pseudo-orbital, $\psi_{PS}(\mathbf{r})$, must equal the corresponding orbital from the all-electron calculation, $\psi_{AE}(\mathbf{r})$, for all points $\mathbf{r}$ that lie outside the cut-off radius.
2. The eigenvalue of each pseudo-orbital must equal the eigenvalue of the corresponding all-electron orbital.
3. The first and second derivatives of each $\psi_{PS}(\mathbf{r})$ must equal those of the corresponding $\psi_{AE}(\mathbf{r})$ at the cut-off radius.
4. There must be no radial nodes of the pseudo-orbitals inside the cut-off radius.

Implicit in above is the requirement that the total electronic charge of the valence electrons inside the cut-off radius is equal for both the pseudo- and all-electron orbitals. This is because in standard Kohn-Sham theory, each orbital is normalised to $1$. Pseudopotentials in which this condition is respected are referred to as *norm-conserving* pseudopotentials. A class of pseudopotentials, called *ultrasoft* pseudopotentials, also exist in which this condition is relaxed, allowing a lower plane wave cut-off energy, but such potentials will not be used in this work. Now, any pseudopotential can be chosen so long as it satisfies the above conditions, and the particular form is usually chosen so as to make the pseudo-orbitals as smooth as possible to minimise the required plane wave cut-off energy. In the basic non-local form described above, in which there is a separate local potential for each angular momentum component, the pseudopotential acts on an orbital as follows:

$$\hat{v}_{PS}\psi(\mathbf{r}) = \sum_{lm} v_{PS}^{(l)}(r) Y_{lm}(\theta,\phi)\langle Y_{lm}|\psi(\mathbf{r})\rangle, \tag{1.139}$$

where the $Y_{lm}(\theta,\phi)$ are spherical harmonics. When implemented within a plane wave basis, applying such a pseudopotential would require a double-loop over $\mathbf{G}$-vectors of the general form

$$\hat{v}_{PS} c_{i\mathbf{k}}(\mathbf{G}) = \sum_{\mathbf{G}'} v_{PS}(\mathbf{G},\mathbf{G}') c_{i\mathbf{k}}(\mathbf{G}'), \tag{1.140}$$

which would lead to unfavourable scaling with system size. This problem can be overcome by using *Kleinman-Bylander* pseudopotentials [37], in which each angular component of the pseudopotential is separated into a local and a non-local component as follows:

$$v_{PS}^{(l)}(r) = v_{PS}^{LOC}(r) + \delta v_{PS}^{(l)}(r). \tag{1.141}$$

The non-local component, $\delta v_{PS}^{(l)}$, is then approximated as

$$\delta v_{PS}^{(l)}(r) = \frac{|\delta v_{PS}^{(l)}(r)\psi_l^0(r)\rangle\,\langle\psi_l^0(r)\delta v_{PS}^{(l)}(r)|}{\langle\psi_l^0(r)|\delta v_{PS}^{(l)}(r)\psi_l^0(r)\rangle}, \tag{1.142}$$

where the $\psi_l^0(r)$ are the pseudo-orbitals for the atomic system. Constructing the pseudopotentials in this way reduces the computational costs so this part of the calculation scales linearly with the number of plane waves.

**REFERANCE:**

- Schwerdtfeger, P. (August 2011), "The Pseudopotential Approximation in Electronic Structure Theory", *ChemPhysChem*, doi:10.1002/cphc.201100387
- Louie, Steven G.; Froyen, Sverre; Cohen, Marvin L. (August 1982), "Nonlinear ionic pseudopotentials in spin-density-functional calculations", *Physical Rev. B* (American Physical Society) **26** (4): 1738–1742, Bibcode:1982PhRvB..26.1738L,doi:10.1103/PhysRevB.26.1738
- Reis, Carlos L.; Pacheco, J. M.; Martins, José Luís (October 2003), "First-principles norm-conserving pseudopotential with explicit incorporation of semicore states", *Physical Review B* (American Physical Society) **68** (15): 155111,Bibcode:2003PhRvB..68o5111R, doi:10.1103/PhysRevB.68.155111
- Bachelet, G. B.; Hamann, D. R.; Schlüter, M. (October 1982), "Pseudopotentials that work: From H to Pu", *Physical Review B* (American Physical Society) **26** (8): 4199–4228, Bibcode: 1982PhRvB..26.4199B, doi:10.1103/Phys RevB.26.4199

- Vanderbilt, David (April 1990), "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism", *Physical Review B* (American Physical Society) **41** (11): 7892–7895, Bibcode:1990PhRvB..41.7892V,doi:10.1103/PhysRevB.41.7892
- M. L. Cohen, J. R. Chelikowsky, "Electronic Structure and Optical Spectra of Semiconductors", (Springer Verlag, Berlin 1988)
- E. Fermi (July 1936), "Motion of neutrons in hydrogenous substances", *Ricerca Scientifica* **7**: 13–52
- Squires, *Introduction to the Theory of Thermal Neutron Scattering*, Dover Publications (1996) ISBN 0-486-69447-X
- http://en.wikipedia.org/wiki/Pseudopotential
- J.C. Phillips, “Energy-Band Interpolation Scheme Based on a Pseudopotential,” Phys. Rev. 112, 685 (1958).
- J.C. Phillips and L. Kleinman, “New Method for Calculating Wave Functions in Crystals and Molecules,” Phys. Rev. 116, 287 (1959).