

Harrison W A. *Pseudopotentials in the theory of metals*.  
New York: Benjamin. 1966. 336 p.  
[General Electric Research Laboratory, Schenectady, NY]

Methods were developed for calculating the properties of metals using pseudopotential perturbation theory. Optimized first-principles pseudopotentials were derived and used to calculate energy bands, Fermi surfaces, electron scattering, and other electronic and bonding properties of simple metals. [The *SCI*<sup>9</sup> indicates that this book has been cited in over 1,560 publications.]

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Pseudopotentials provide a way to make approximate calculations much more simply than one could achieve the solution of the original problem. This is accomplished by removing an unneeded part of the complete problem, such as, in the case of solids, the core states of the constituent atoms. The first significant use in solids was by J.C. Phillips and L. Kleinman,<sup>1</sup> in which they made two approximations to simplify semiconductor band calculations. They approximated the true pseudopotential operator (which would have given an exact solution for the bands) by a local potential, and they drastically reduced the number of waves used to expand the electronic state. For metals, I wanted to calculate properties, rather than bands, and it was not necessary to make either of the approximations used by Phillips and Kleinman. However, I did all calculations to the lowest order in the pseudopotential operator, an approximation that they did not make. Thus it was a completely different theory, which should be appropriately called pseudopotential perturbation theory, though the distinction has been largely lost in contemporary terminology.

In the early 1960s I developed these methods for calculating the vibration spectrum, the electron-phonon interaction, the relative energies of different crystal structures, and the resistivity of alloys and of liquid metals.<sup>2-4</sup> It seemed to me that pseudopotential perturbation theory would be widely used and that I had the opportunity, before others began using it, to design all of the terminology and notation for

the methods as we all wish other areas of physics had been designed, with care and consistency. I worked for "Generous Electric," as we all called the GE Research Laboratory, which would let me undertake such a project essentially full time. It isn't often that one finds out how long it takes, full time, to write a book; this one took about a year.

As it turned out, most of the notation and terminology did stick. That may be one of the reasons that the book has been so widely cited. However, I think another reason is that it may be convenient to give it as a general reference whenever any worker wants to use some piece of pseudopotential theory that he understands well enough to apply but doesn't want to read the earlier literature to find a similar application. I can sympathize with that, but it has had an amusing effect. My theory had been based upon first-principles pseudopotential operators, with the only approximation on the starting one-electron theory being the perturbation expansion. I had also noted that one could obtain almost as accurate results more simply with much simpler local model pseudopotentials. These, and some introduced by others,<sup>5</sup> were much more popular than the full theory and became the standard approach for treating the properties of simple metals. Contemporary theory marched down the ladder to simpler and simpler calculations. Subsequent generations then wanted to improve upon their elders and began marching back up the same ladder, still referring to my book but never realizing that the first-principles theories they were developing were already there.

In order to help maintain enthusiasm during such a long project I decided to treat stacking faults in the crystal structure as I proceeded, doing each part at the time that I was writing the chapter where that part belonged. I also promised myself not to look up the experimental energy of formation until I had completed the prediction, which would be near the end of the book. It turned out that I was able to carry out all of the parts and complete the calculation, obtaining 50 ergs/cm<sup>2</sup> for magnesium, the metal for which I could have the most confidence. Thus I finally went to the library to track down the experimental value. The closest I could come was from a study much earlier by P. Buford Price.<sup>6</sup> He gave a value of 30 ergs/cm<sup>2</sup> for zinc and said that it was more difficult to measure for magnesium, but that it appeared to be somewhat higher than that for zinc. That was good enough agreement for me, but the surprise was the source; Buford and I shared a car pool every day at that time and for some reason the question had never come up.

1. Phillips J C & Kleinman L. New method for calculating wave functions in crystals and molecules. *Phys. Rev.* 116:287-94. 1959. (Cited 540 times.)
2. Harrison W A. Electronic structure and the properties of metals. I. Formulation. *Phys. Rev.* 129:2503-11. 1963. (Cited 115 times.)
3. ———. Electronic structure and the properties of metals. II. Application to zinc. *Phys. Rev.* 129:2512-24. 1963. (Cited 120 times.)
4. ———. Theory of sodium, magnesium and aluminum. *Phys. Rev.* 136:A1107-19. 1964. (Cited 105 times.)
5. Ashcroft N W. Electron-ion pseudopotentials in metals. *Phys. Lett.* 23:48-50. 1966. (Cited 560 times.) [A complete and simple analysis of the properties of metals using Ashcroft's empty-core pseudopotential, with Fermi-Thomas screening, is given in Harrison W A. *Electronic structure and the properties of solids*. New York: Freeman. 1980. 565 p. (Cited 505 times.)]
6. Price P B. Direct observations of glide, climb, and twinning in hexagonal metal crystals. (Thomas G & Washburn J, eds.) *Electron microscopy and the strength of crystals*. New York: Interscience. 1963. p. 41-130. (Cited 75 times.)