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Perspective

The origin of the pseudopotential density functional method. Perspective on "Microscopic theory of phase transformation and lattice dynamics of Si"

Yin MT, Cohen ML (1980) Phys Rev Lett 45:1004–1007

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Abstract. This paper provides an overview of the title paper by Yin and Cohen. I will briefly review some of the background for this work, provide some details of the calculations and discuss how this paper has influenced the field. In particular, this paper led to the development of the first realistic calculations for the structural energies of solids. It was the origin of the pseudopotential density functional method applied to the solid state.

Key words: Pseudopotentials – Density functional theory – Structural energies

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Prior to 1975 or so, the words "ab initio" did not exist in the scientific vocabulary for methods describing the electronic structure of the solid state. At that time, a number of very powerful and successful methods had been developed to describe the electronic structure of solids, but these methods did not pretend to be first principles or "ab initio" methods. The foremost example of electronic structure methods at that time was the empirical pseudopotential method (EPM) [1]. The EPM was based on the Phillips–Kleinman cancelation theorem [2], which justified the replacement of the strong, all-electron potential with a weak pseudopotential [1]. The pseudopotential replicated only the chemically active valence electron states. Physically, the cancelation theorem is based on the orthogonality requirement of the valence states to the core states [1]. This requirement results in a repulsive part of the pseudopotential which cancels the strongly attractive part of the core potential and excludes the valence states from the core region. Because of this property, simple bases such as plane waves can be used efficiently with pseudopotentials. Plane waves also take advantage of the periodicity of the crystal by expanding the wave functions and potentials in three-dimensional Fourier series. Since the pseudopotential converges so rapidly in Fourier space only a few Fourier expansion coefficients, called form factors, are required to describe the potential. The EPM uses the form factors as parameters, fixed by experiment, to describe the potential.

This simple, but elegant, approach resulted in the first realistic description of the electronic structure and optical properties of semiconductors. The EPM also yielded the first accurate "picture" of the covalent bond in solids [3]. It demonstrated conclusively that a one-electron (band picture) of solids was correct and could be used to interpret spectroscopic results. As such, it helped create the field of optical spectroscopy in solids. But, however successful the EPM was, there were issues outside its applicability: structural energies. Extensions of the EPM were contemplated, but it was widely believed at the time that no first principles or ab initio theory could be expected to describe the solid state with sufficient accuracy to obtain any useful or predictive information.

In the late 1970s, Marvin Cohen and his student Ming-Tang Yin began to explore the possibility of using density functional theory, in particular, using the local density approximation (LDA) [4] and pseudopotentials for computing the electronic structure of solids. The LDA is a powerful tool as it maps the all-electron problem onto a one-electron problem; however, in terms of realistic calculations it was largely untested for structural energies at the time of Yin and Cohen's paper. Many people, particularly in the quantum chemistry community, felt the LDA was not a serious contender with more "rigorous" techniques. Unlike "standard" quantum chemistry approaches which use the exact Hamiltonian, the LDA ground-state energy can reside below the true experimental limit. Consequently, the LDA works only if one compares two reference states and any inherent LDA errors cancel. This “uncontrolled” cancellation of errors was thought to be serious. In contrast, other methods such as configuration interaction allow one to improve the ground-state energy in a systematic manner.

However, from a computational point of view, the LDA is much easier to implement and, relative to configuration interaction methods, is much less computationally intensive. Yin and Cohen, along with others, had used the LDA to construct pseudopotentials from first principles [5]. These ab initio pseudopotentials were very helpful in describing the electronic structure of surfaces, molecules, defects, etc., but they were not viewed as tools for computing the total energy of a solid.

In the title paper, Yin and Cohen, evaluated the total energy of various silicon polymorphs using density functional theory with the LDA and pseudopotentials: an approach we can characterize as a pseudopotential density functional method (PDFM). In particular, they evaluated

$$E_{\text{total}} = \sum_i \epsilon_i - \frac{1}{2}\int \rho(r) V_{\text{H}}(r)\mathrm{d}^3r + \int \rho(r)\{\epsilon_{\text{xc}}[\rho] - V_{\text{xc}}[\rho]\}\mathrm{d}^3r + E_{\text{ion-ion}} \ , \qquad (1)$$

where the sum is over the occupied eigenvalues, ϵ_i, $\rho(r)$ is the valence pseudocharge density, V_{H} is the Hartree or Coulomb potential, $\epsilon_{\text{xc}}[\rho]$ is the exchange–correlation energy density, V_{xc} is the exchange–correlation potential, and $E_{\text{ion-ion}}$ is the ion core repulsion energies. Evaluating the total energy for solids is a difficult task as one must be careful in handling various divergent Coulomb terms [6]. The eigenvalues, ϵ_i, and the pseudocharge density, ρ, were evaluated in the same way as in the EPM, i.e., a plane-wave basis was used resulting in an eigenvalue problem. Typically fewer than 100 plane waves were used in such calculations. Today, a personal computer could easily handle the computational load for this problem.

It is important to recognize the power of the pseudopotential in this formalism. Without pseudopotentials, one has to solve the Kohn–Sham equations for all the electrons in the system. This is a very difficult exercise as the energy and length scales for the core and valence electrons’ eigenvalues and eigenstate differ by orders of magnitude. (Only years after the Yin and Cohen paper were all-electron structural energy calculations implemented.)

Using the PDFM, Yin and Cohen looked at various real and hypothetical crystalline forms of silicon including close-packed structures such as the face-centered-cubic form and open structures such as the diamond and hexagonal diamond structures [7]. They evaluated the total energy for each structural phase and plotted the energies as a function of crystal volume. In doing so, they created a “phase diagram” for silicon at zero temperature as shown in Fig. 1.

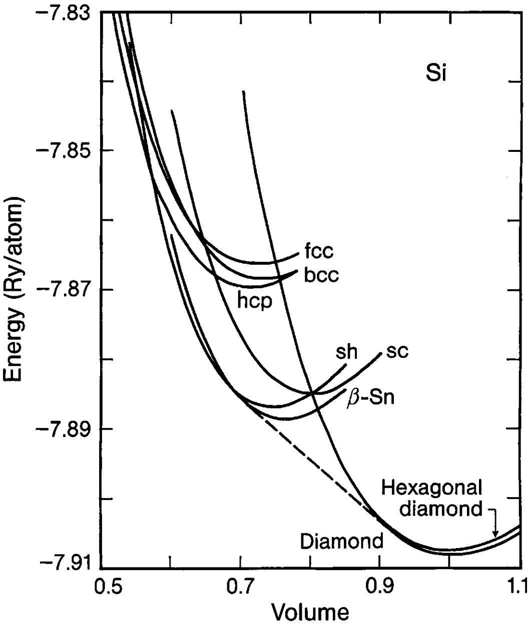

Fig. 1. The total electronic energy versus the atomic volume for several Si structures: diamond, hexagonal diamond, white tin (β-Sn), hexagonal close-packed (hcp) body-centered cubic (bcc), and face-centered cubic (fcc). The volume is normalized by the experimental value. The *dashed line* is the common tangent of the energy versus volume curves and gives the transition pressure between the diamond and white tin structures (see the title paper)

Several key points can be made about the results of Yin and Cohen. They correctly found the diamond structure to be the ground-state phase relative to the other structures. The predicted lattice constant was within 1–2% of experiment and the bulk modulus was within about 5% of experiment. The pressure to transform the diamond structure to the white tin structure (β-Sn) was also predicted to within 20%. It should also be noted that the title paper examined other structural properties such as those associated with the Grüneisen parameters and vibrational modes. Later, Cohen went on to predict a new superconducting phase of silicon on the basis of this work [8].

The impact of this paper cannot be underestimated. For the first time, it was demonstrated that accurate structural energies could be calculated and used to make predictions about the solid state. This work led to an enormous interest in utilizing pseudopotentials and density functional theory for a wide variety of systems including liquids, clusters, defects, etc. [9]. It also laid the foundation for ab initio molecular dynamics [10]. Since structural energies could be evaluated accurately, it was apparent that interatomic forces could also be calculated within this formalism and could be used in molecular dynamics simulations. It is safe to assert that this paper established the PDFM as the method of choice for the elucidation of the electronic structure of condensed matter.

References

1. Cohen ML, Chelikowsky JR (1989) Electronic structure and optical properties of semiconductors, 2nd edn. Springer, Berlin Heidelberg New York
2. Phillips JC, Kleinman L (1959) Phys Rev 116: 287
3. Cohen ML (1973) Science 179: 1189

4. (a) Hohenberg P, Kohn W (1964) Phys Rev B 136: 864; (b) Kohn W, Sham LJ (1965) Phys Rev A 140: 1133
5. Chelikowsky JR, Cohen ML (1992) In: Landsberg (ed) Handbook on semiconductors, vol 1. Elsevier, Amsterdam, p 59
6. Ihm J, Zunger A, Cohen ML (1979) J Phys C 12: 4409
7. Yin MT, Cohen ML (1980) Phys Rev Lett 45: 1004
8. Chang KJ, Dacorogna MM, Cohen ML, Mignot JM, Chouteau G, Martinez G (1985) Phys Rev Lett 54: 2375
9. Chelikowsky JR, Louie SG (eds) (1996) Quantum theory of real materials. Kluwer, Dordrecht
10. Car R, Parrinello M (1985) Phys Rev Lett 55: 2471