The empirical pseudopotential method

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1 Background

In 1934, Fermi [1] proposed a method to describe high lying atomic states by replacing the complex effects of the core electrons with an effective potential described by the pseudo-wavefunctions of the valence electrons. Shortly after, this pseudopotential (PSP), was realized by Hellmann [2] who implemented it to describe the energy levels of alkali atoms. Despite his initial success, further exploration of the PSP and its application in efficiently solving the Hamiltonian of periodic systems did not reach its zenith until the middle of the twentieth century when Herring [3] proposed the orthogonalized plane wave (OPW) method to calculate the wave functions of metals and semiconductors. Using the OPW, Phillips and Kleinman [4] showed that the orthogonality of the valence electrons' wave functions relative to that of the core electrons leads to a cancellation of the attractive and repulsive potentials of the core electrons (with the repulsive potentials being approximated either analytically or empirically), allowing for a rapid convergence of the OPW calculations.

Subsequently in the 60s, Marvin Cohen expanded and improved upon the pseudopotential method by using the crystalline energy levels of several semiconductor materials [6, 7, 8] to empirically obtain the potentials needed to compute the atomic wave functions, developing what is now known as the empirical pseudopotential method (EPM). Although more advanced PSPs such as the ab-initio pseudopotentials exist, the EPM still provides an incredibly accurate method for calculating optical properties and band structures, especially for metals and semiconductors, with a less computationally taxing method. Such calculations are even efficient enough that EPM calculations can be performed on personal computers.

Cohen's development of the EPM was key to understanding the optical response function of solids and has led to breakthroughs in the study of semiconductor materials. This is partly the reason why semiconductors are one of the most well understood class of materials today. This achievement and its profound impact in the field of solid state physics earned Cohen the Buckley Prize in 1979.

2 Building up to the empirical pseudopotential

We begin with Herring's development of the orthogonalized plane-wave (OPW) method for solving the eigenfucntions and energy values for an electron in the periodic field of a crystal. In his method, if the crystal wave functions are expanded in plane waves, the periodic boundary conditions at the surface of the unit cell are automatically satisfied such that a good crystal wave function is obtained with enough plane waves are used. But to include the radial nodes of the valence wave functions in the core, calculations become impractical as many plane waves are needed. To resolve this issue, the wave function of the valence electron is orthogonalized to the actual core electron wave function which adds a linear combination of core orbitals to each plane wave, thus giving us a plane wave that allows for rapid convergence, the orthogonalized plane-wave:

$$\psi_\alpha = \phi_\alpha + \sum_n a_n^\alpha \phi_\alpha^n \tag{1}$$

Here, ψ_α is the true wave function, ϕ_α is a basis function resembling the combinations of plane waves, ϕ_α^n is a sum of the smooth wave function and occupied core states, the superscript n refers to the core electron levels and a_n^α is a constant that ensures orthogonality at every core level, i.e.:

$$\int d\mathbf{r}\phi_\alpha^{n*}\psi_\alpha = 0 \tag{2}$$

and hence:

$$a_n^\alpha = -\int d\mathbf{r}\phi_\alpha^{n*} e^{i\dot{\mathbf{k}}\mathbf{r}} \tag{3}$$

For brevity, we will define two orthogonal wave functions with the following convention: $-(\phi_\alpha, \phi_\alpha^n)$.

As Phillips and Kleinman [4] later pointed out, orthogonalization will lead to a loss in spherical symmetry for the core wave functions, making the solution to Herring's equation overly complicated and difficult to calculate. As a solution, ϕ_α was orthogonalized to the core wave functions instead, allowing for a more simple solution to the eigenfunctions and energy. ϕ_α describes the smooth part of the symmetrized combinations of the Bloch functions and contains the repulsive potential and depends on the core wave functions and valence wave functions in the core region. ϕ_α can be used to derive the repulsive portion of the core potential which consequentially, the orthogonality of the valence wave function leads to a cancellation of the core repulsive and attractive potentials. As a result, the orthogonal part of the OPW equation is simplified, leading to rapid convergence. To obtain this repulsive potential, we substitute Equation 1 into Schroedinger's general equation:

$$H\psi_\alpha = E\psi_\alpha \tag{4}$$

to obtain:

$$H\phi_\alpha + \sum_n a_n^\alpha H\phi_\alpha^n = E\phi_\alpha + E\sum_n a_n^\alpha \phi_\alpha^n \tag{5}$$

and solve for $E\phi_\alpha$ (where $H\phi_\alpha^n = E^n\phi_\alpha^n$) to get:

$$H\phi_\alpha + \sum_n a_n^\alpha (E^n - E)\phi_\alpha^n = E\phi_\alpha \tag{6}$$

If we define the repulsive potential of the core electrons as:

$$V_r^\alpha = \sum_n a_n^\alpha (E^n - E)\phi_\alpha^n/\phi_\alpha \tag{7}$$

and substitute the repulsive potential back into Equation 6, we will obtain:

$$(H + V_r^\alpha)\phi_\alpha = E\phi_\alpha \tag{8}$$

which is the new wave function for ϕ_α, the pseudowavefunction, where E is still the true energy eigenvalue of the true wave function. This equation is equivalent to the OPW equations when ϕ_α is used in V_r. In addition, under the condition of OPW we can substitute 3 into 7 to write the repulsive core potential more explicitly as:

$$V_r^\alpha = \sum_n (E - E^n)(\phi_\alpha, \phi_\alpha^n)\phi_\alpha^n/\phi_\alpha \tag{9}$$

Furthermore, if we separate the Hamiltonian into kinetic energy and a long range attractive potential (V_c^α):

$$H = p^2/2m + V_c^\alpha \tag{10}$$

we can rewrite 8 as:

$$(p^2/2m + V_c^\alpha + V_r^\alpha)\phi_\alpha = (p^2/2m + V^\alpha)\phi_\alpha = E\phi_\alpha \tag{11}$$

where V^α is the pseudopotential with a weak potential that is almost cancelled out near the core and a weak attractive region further away from the core. The cancellation of repulsive and attractive core potentials is more explicitly proven by Cohen and Heine [5] in a publication following the work of Phillips and Kleinman. This simplified OPW solution to the wave function was not only applicable to crystals, but to molecules as well.

Despite its success, the OPW based pseudopotential developed by Phillips and Kleinman does not have wider applications as a computational tool for obtaining properties such as electronic band structures of materials. However, because the empirical pseudopotential method fits observed properties from experiments, it is able to incorporate implicitly complex many body interactions via the fitting process, allowing for accurate determination of electronic band structures. We shall see that by qualitatively estimating this repulsive potential by empirical means, Cohen was able to produce an incredibly accurate and efficient pseudopotential.

3 The empirical pseudopotential

The repulsive potential described by Phillips and Kleinman can be obtained empirically by fitting the pseudopotential atomic form factor with observed properties such as atomic energy levels, optical properties or Coulomb potentials. Cohen's most important contribution in the field of computational chemistry and semiconductors stems from the development of EPMs using form factors fitted from experimentally observed band splitting values. The majority of this paper will primarily focus on this aspect of Cohen's work. The potential can then be used to solve a host of problems such as the band structure of semiconductors.

Since the purpose of Cohen's derivation of the EPM was to obtain the band structures of semiconductors. In this context, the pseudopotential V^{α} will be a crystal potential represented by a linear superposition of atomic potentials:

$$V(\mathbf{r}) = \sum_{\mathbf{R},\tau} V_a(\mathbf{r} - \mathbf{R} - \tau) \tag{12}$$

with $\mathbf{R}$ and τ being the lattice vector and basis vector respectively. Using the reciprocal lattice vector ($\mathbf{G}$), Equation 12 can be rewritten as:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_a(\mathbf{G})\mathbf{S}(\mathbf{G})\mathbf{e}^{\mathbf{i}\mathbf{G}\dot{}\mathbf{r}} \tag{13}$$

where $S(\mathbf{G})$ is the structure factor, the descriptor for the crystal structure:

$$S(\mathbf{G}) = \frac{1}{N_a} \sum_{\tau} e^{-i\mathbf{G}\dot{\tau}} \tag{14}$$

and $V(\mathbf{G})$ is the pseudopotential atomic form factor, the primary property to fit using experimental quantities which has the following equation:

$$V(\mathbf{G}) = \frac{\mathbf{1}}{\mathbf{\Omega_a}} \int \mathbf{V_a(r)exp(-iG\dot{}r)d^3r} \tag{15}$$

From Bloch theorem, we can use $\mathbf{k}$ as a quantum number and Equation 12 to write the pseudowavefunction ϕ_{α} which is now $\psi_{n,\mathbf{k}}$ and the band energy $E_n(\mathbf{k})$ as a solution to Schrodinger's equation:

$$[\frac{p^2}{2m} + V(\mathbf{r})]\psi_{\mathbf{n},\mathbf{k}}(\mathbf{r}) = \mathbf{E_n}(\mathbf{k})\psi_{\mathbf{n},\mathbf{k}}(\mathbf{r}) \tag{16}$$

It is important to note that the pseudopotential should be modeled as a nonlocal potential to account for the difference in a potential's strength for electrons with a different quantum number l. A much deeper discussion of this issue is tackled by Chelikowsky and Cohen [9] in a later publication that resolved some discrepancies found in the local potential discussed here. Amazingly, the nonlocal pseudopotential was even able to predict bonding properties from the calculated charge density of various semiconductors years prior to experimental confirmation. However, for most semiconductors, only l=0,1,2 are significant and electrons with these angular momentums are not as affected if nonlocality is not taken into account and so for our purposes, the nonlocal pseudopotentials will not be discussed here in detail.

4 The empirical pseudopotential method for semiconductors

We will demonstrate Cohen's method for deriving the EPM with a binary crystalline semiconductor material, GaAs, and afterwards, we will simplify the derived pseudopotential for the case of an elemental crystalline system. We begin by defining the terms from Equation 13 and split the product of the structure and form factor into a symmetric and antisymmetric form for convenience:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} (V_G^S(\mathbf{G}) \cos \mathbf{G}\dot{\tau} + \mathbf{V_G^A}(\mathbf{G})\mathbf{i} \sin \mathbf{G}\dot{\tau}) e^{i\mathbf{G}\dot{\mathbf{r}}} \tag{17}$$

with the form factors V_G^S and V_G^A simply being the sum and differences of the atomic pseudopotential form factors respectively:

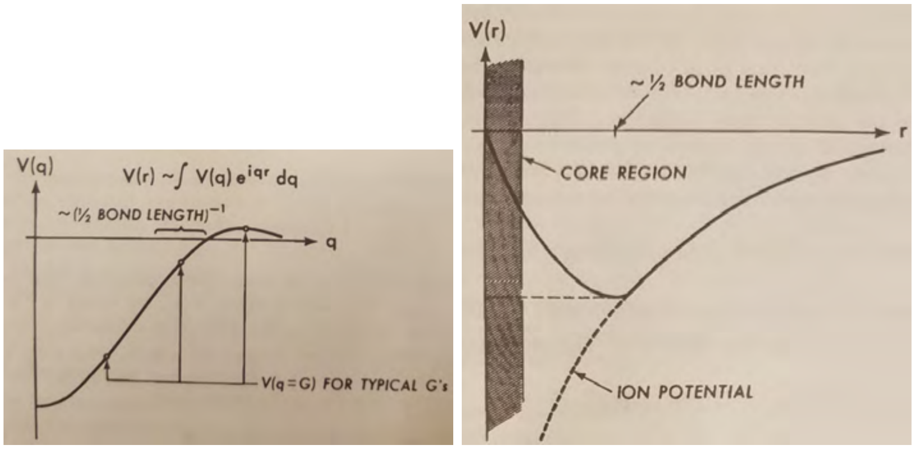
$$V_G^S = \frac{V_{Ga}(G) + V_{As}(G)}{2}, V_G^A = \frac{V_{Ga}(G) - V_{As}(G)}{2} \tag{18}$$

where the atomic pseudopotentials can be described by Equation 15. Note that for an elemental crystalline solid, the antisymmetric form factor becomes 0 and as such, Equation 17 becomes:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} (V_G^S(\mathbf{G}) \cos \mathbf{G}\dot{\tau}) e^{i\mathbf{G}\dot{\mathbf{r}}} \tag{19}$$

The basis vectors τ if defined for a binary crystal of the $Fd\bar{3}m$ spacegroup which is composed of two fcc crystals shifted by (1/4, 1/4, 1/4)a with a being the lattice constant. For convenience, we set the origin of the crystal between the two fcc structures at $\tau = (1/8, 1/8, 1/8)a$.

Next we select a number of symmetric and antisymmetric $V_i(G)$ with $G \neq 0$ to describe the form factor for each type of atom. Figure 1(a) (which is just Figure 1(b) after a Fourier transform is applied), will show that $V(q)$ dissipates relatively quickly, typically with $q = G$ for the first three values of G. As such we will select three $V(G)$ with $G^2 = 3, 8, 11$ (in units of $(2\pi/a)^2$) to describe the pseudopotential of our semiconductor (however, many of the symmetric and antisymmetric form factors will just become 0 in the end).



(a) Reciprocal space

(b) Real space

Figure 1: Plot of the pseudopotantial in reciprocal space (1(a)) and real space (1(b))

There are a few methods of selecting the initial form factors. For example, a model pseudopotential can be used to make an initial guess of $V(\mathbf{G})$. Alternatively, one can estimate $V(\mathbf{G})$ by extrapolating from known form factors. For example, one can estimate the form factor of Sn ($V_{Sn}(\mathbf{G})$) by average $V_{In}(\mathbf{G})$ and $V_{Sb}(\mathbf{G})$ if their atomic form factor are known. In the study of interest, Cohen obtained his initial guest using using previously known form functions. As $V_{Ge}(\mathbf{G})$ has already been calculated, $V_{Ga}(\mathbf{G})$ and $V_{As}(\mathbf{G})$ can be extrapolated to make an initial guess of the atomic form functions for GaAs. Once the optimally fitted form functions for GaAs are obtained, $V_{Zn}(\mathbf{G})$ and $V_{Se}(\mathbf{G})$ can be extrapolated to make an initial guess for the form function of ZnSe. This is repeated for the next row in the periodic table where from $V_{Sn}(\mathbf{G})$, one can extrapolate the form functions needed for InSb and CdTe. This process of extrapolation is repeated for compounds such as InAs, GaSb and ZnTe where both $V_{Ge}(\mathbf{G})$ and $V_{Sb}(\mathbf{G})$ are used to determine an initial guess. Similarly for InP and AlSb, the form functions can be extrapolated using the known form functions of Si and Sb.

We note that prior to this current work, Cohen and his colleagues had implemented this method by using the reflectance, photoemission and density of states of Si [6] to fit his EPM. Similarly, the EPM of Ge and Sb were also obtained using these experimental parameters. The form factors used to extrapolate the initial guess of other elements discussed here used the form factors from these studies. Examples of other calculated parameters used for fitting include the electron effective mass, optical gaps, modulated reflectivity and full dielectric function.

With an initial estimate of the form factors, we can determine a solution for Equation 17 for GaAs and subsequently the eigenvalues and wavefunctions,

$\psi_{n,k}$ and $E_n(k)$, using Equation 11. The eigenvalues and wavefunctions can then be used to calculate our chosen response function (in this case the energy band splitting). The fitting of the form function with experimental observations comes from comparing our calculated energy band splitting to an experimental value. Exact agreement with values of energy band splitting must be limited in order to obtain an exact fit with the form factor. As such, only values near the band gap and splittings of less than 1 eV were used in the fitting process. These particular values are the most important in a band structure. If we are unsatisfied with the accuracy of the calculated response functions when compared to experiments, we can alter the form factor and solve for Equation 17 and subsequently Equation 11 as many times as necessary until good agreement is found between the experimental and calculated response functions. Techniques such as machine learning (i.e. genetic algorithms and neural networks) can also be implemented to automate the process of comparing the response functions to experiments and modifying the form function. This fitting method to obtain accurate pseudopotentials is at the heart of EPM.

With the pseudopontential form factor, we can now calculate the different energy levels needed to build the band structure of semiconductors such as GaAs. An outline of the entire process used to derive the band structure from the EPM is summarized in Figure 2.

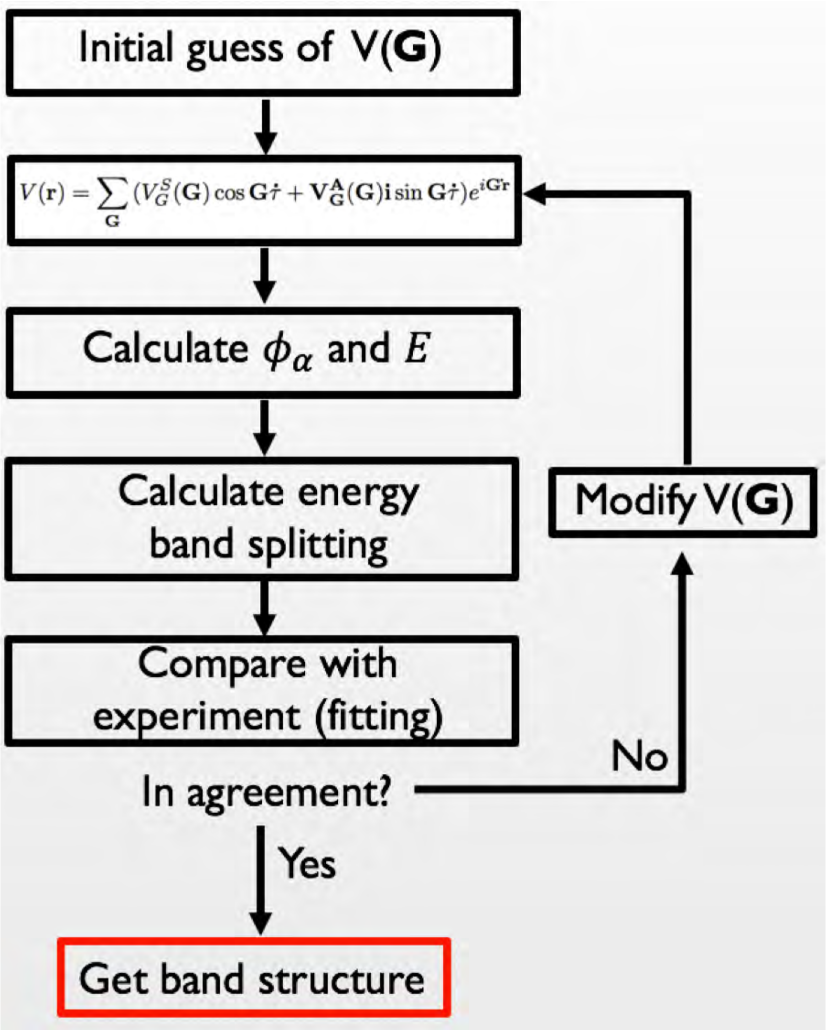


Figure 2: Work flow for obtaining the band structure from the empirical pseudopotential.

5 Deriving other forms of the pseudopotential with EPM

The EPM derived in the previous section can also be used to derive other forms of the pseudopotential, in particular, the self-consistent ab-initio pseudopotential.

For EPM, we assumed $V(G)$ represents the total one-electron potential for a valence electron when it should be self-consistent, that is a new valence electron potential should be calculated by the wavefunction from an electronic structure which is in turn calculated by a previous valence electron potential. This process is repeated until there is no change in the wavefunction or the valence electron potential. This is particularly useful in surface and interface calculations where the electronic charge of the atoms in the surface or interface region will relax quite a lot. Similar to the feedback loop used to derive the EPM in Figure 2, the self-consistent pseudopotential will take in an empirical pseudopotential and solve Schrodinger's equation to obtain the wave function and charge density and repeats this process until the wavefunction and charge density no longer vary.

The EPM can also be used to obtain another form of the pseudopotential, the ab-initio pseudopotential. This particular pseudopotential is useful for total energy calculations and calculating the structure of solids. This form is in part based on the self-consistent pseudopotential whereby the pseudowavefunction is normalized in such a way that there is no change when going from the pseudowavefunction to the all-electron wavefunction. An energy cutoff is used to determine how much the normalized pseudowavefunction deviates from the all-electron wavefunction.

6 Implications of Cohen's contributions

As mentioned before, Cohen's work on the EPM provided us with more information on the semiconductor class of materials than ever before and it is thanks to his work that we now know so much about semiconductors and the optical response function of solids. Perhaps just as important, the EPM paved the way for deriving more advanced forms of the pseudopotential such as the self-consistent and ab-initio pseudopotential. The latter in particular allows for structural relaxation and total energy calculations which can provide a host of information depending on the structure being modeled such as the lattice volume, bulk modulus and various thermodynamic quantities such as cohesive energy, formation energy and interfacial properties. The efforts of Cohen and his predecessors now allow us to not only study molecules, but a broad class of solids, molecules, clusters, and even quantum confined materials such as nanotubes. The development of the ab-initio pseudopotential also paved the way for Density function theory as a more viable tool in computational chemistry. More recently, thanks to the development of the EPM, new materials with exotic properties such as superconductivity can even be predicted [10]. His accomplishments and perhaps just as important, the implications, earns Marvin Cohen his place in history as the recipient of the 1979 Buckley Prize.

References

[1] Enrico Fermi. Sopra lo Spostamento per Pressione delle Righe Elevate delle Serie Spettrali. *Nuovo Cimento*, 11(145):157–166, 1934. ISSN 00296341. doi: 10.1007/BF02959829.

[2] H. Hellmann. A New Approximation Method in the Problem of Many Electrons. *The Journal of Chemical Physics*, 3(1):61–61, 1935. ISSN 0021-9606. doi: 10.1063/1.1749559. URL `http://aip.scitation.org/doi/10.1063/1.1749559`.

[3] Conyers Herring. A new method for calculating wave functions in crystals. *Physical Review*, 57(12):1169–1177, 1940. ISSN 0031899X. doi: 10.1103/PhysRev.57.1169.

[4] James C. Phillips and Leonard Kleinman. New method for calculating wave functions in crystals and molecules. *Physical Review*, 116(2):287–294, 1959. ISSN 0031899X. doi: 10.1103/PhysRev.116.287.

[5] Morrel H. Cohen and V. Heine. Cancellation of kinetic and potential energy in atoms, molecules, and solids. *Physical Review*, 122(6):1821–1826, 1961. ISSN 0031899X. doi: 10.1103/PhysRev.122.1821.

[6] D. Brust, M. L. COHEN, and J. C. Phillips. Reflectance and Photoemission from Si. *Physical Review Letters*, 9(9):389–392, 1962.

[7] M. L. Cohen and J. C. Phillips. Spectral analysis of photoemissive yields in Si, Ge, GaAs, GaSb, InAs, and InSb. *Physical Review*, 139(3A), 1965. ISSN 0031899X. doi: 10.1103/PhysRev.139.A912.

[8] Marvin L. Cohen and T. K. Bergstresser. Band structures and pseudopotential form factors for fourteen semiconductors of the diamond and zinc-blende structures. 16(1965), 1966.

[9] James R. Chelikowsky and Marvin L. Cohen. Nonlocal pseudopotential calculations for the electronic structure of eleven diamond and zinc-blende semiconductors. *Physical Review B*, 14(2):556–582, 1976. ISSN 01631829. doi: 10.1103/PhysRevB.14.556.

[10] M L Cohen. Predicting new solids and superconductors. *Science (New York, N.Y.)*, 234(4776):549–53, 1986. ISSN 0036-8075. doi: 10.1126/science.234.4776.549. URL `http://www.ncbi.nlm.nih.gov/pubmed/17835563`.