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DESCRIPTION OF ONE-ELECTRON THEORIES OF SOLIDS IN TERMS OF PROJECTION OPERATORS*

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ABSTRACT: A unifying review of the different one-electron models for band computations is made using projection operators. The idea is to let the projector select the appropriate behaviour at the cell boundaries. We then find the corresponding equation for the projection component. The APW and KKR methods are dealt with first, using a geometric projector. Expanding the exact effective potential in a perturbation series, the nearly-free electron model is easily derived. Finally, the pseudopotential equation is obtained through a similarity transformation of the original Hamiltonian, following the recent work of Waeber and Stoll.

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1. INTRODUCTION

Band theory has shown itself to be an effective means of explaining the electronic structure of solids, and has yielded a qualitative explanation of many of the properties inherent in solid state systems. It has not been until recently, with the advent of computers, that this qualitative picture has been transformed into a quantitative scheme. Due to the host of complications in solids, many approximations have to be assumed before one can compute numbers. Almost all available computational methods choose a self-consistent procedure to compute the electronic wave functions, which might eventually include some relativistic corrections. In atomic and molecular physics, the Hartree-Fock method has been the most popular tool, due to its many well-known virtues. For a solid, however, the exchange potential, having a non-local character, couples the equations in such a way that one is compelled to replace it by a certain average, thus obtaining a local exchange potential which still corrects the local Coulombic term in part for the fact that an electron does not interact with itself. Although several variations[1] have been proposed as to how to take this average, they can be all traced back to Slater's work[2]. He suggested the use of weighted average of each of the exchange terms, which are different for the different orbitals, preserving still the fact that each electron carries a Fermi hole along with it, hole which would be the same for each electron in this case. Löwdin[3] proved that Slater's way of averaging would yield the best local approximation for the exchange term, minimizing the root mean square deviations. A further simplification is made by taking the local exchange contribution from a free electron gas of the same density as the local density of the electron in the solid, which turns out to be proportional to the third root power of the electron density. A heuristic argument to explain this, due to Slater, is saying that the Fermi hole has a radius proportional to the inverse third root power of the electronic density. The repulsive energy associated with it should then be proportional to the inverse of this radius. The potential constructed in this way localizes the interelectronic repulsion, so that it has a shorter range of interaction than the corresponding Hartree-Fock terms, incorporating an average screening effect for the electrons in the Hamiltonian.

Each electron is thus supposed to feel an average periodic potential built up as a superposition of the one-electron potentials centred at each ion. Near the nucleus, it approaches the isolated atom potential, so it is spherically symmetric, while in the interionic region, close to the Wigner-Seitz cell boundaries, it varies less rapidly and eventually smoothly joins the neighbouring cells averaged contribution. The effects of neighbouring atoms potentials are usually included by using Löwdin's α-expansion[4] in spherical harmonics around the origin of the central ion, resigning oneself to using only the spherically symmetric contribution. Implicit in the potential periodicity is Bloch's theorem, which forces the electron orbitals to be Bloch waves. Since plane waves themselves are Bloch functions, we might think of expanding the one-electron wave function in a series of these, summing over the inverse lattice vectors in order to account for the proper lattice symmetry in the crystal. But due to the large potential depth near the nuclei, this expansion proves in practice to be rather inefficient, since we would expect a more atomic-like behaviour of the orbitals in this region. Slater in 1937[5] introduced the concept of an Augmented Plane Wave in order to correct for this fault. The basis functions should be plane waves near the cell boundaries, but they should be Bloch waves formed from linear combinations of a radial function times a spherical harmonic in the inner regions. To formulate his method, he defined a "muffin-tin" potential, which divides each unit cell into a set of non-overlapping spheres centred on each atom, and the interstitial outer region. The potential is spherically symmetric in the "muffin-tin" spheres, and equal to an average constant in the rest of the cell, the inner potential taking this constant value at the surface of each of the inscribed spheres. Kohn and Rostoker[6] picked up the same type of potential, but formulated the problem in terms of Green functions in what is now known as the KKR method[7].

A different approach was used previously. Bloch sums were found from atomic orbitals centred on each nucleus with the disadvantage that these contain overlap integrals of atomic orbitals centred on different nuclei, integrals which cannot be neglected[8], but only for very special cases. One can instead start with only the core atomic orbitals, which do not overlap appreciably, and take the rest of the functions as plane waves which are forced to be orthogonal to these core functions; this is the essence of the OPW method[9].

In 1959 Phillips and Kleinman[10] suggested a new computational procedure, the "pseudopotential" method, in which they obtained an effective potential for the plane wave expansions starting from the OPW equations. A generalized pseudopotential was later developed by Austin, Heine and Sham[11].

Until very recently[12] all methods used to compute energy bands have utilized a linear expansion of the wave functions as a starting point. By invoking the Rayleigh-Ritz variational principle, a secular equation is attained. This secular equation might not be of the ordinary type, since there might be an implicit dependence upon the energy in the expansion coefficients themselves. This is indeed the case in the APW and KKR methods. Even the original pseudopotential formulations suffer from this "linear disease", because of their starting equations.

We present here an effective Hamiltonian formalism which produces an exact model potential – exact within the prescribed independent particle model – based on the use of projection operators.

The model Hamiltonian which reproduces the APW and the KKR procedures is derived in section 2, by incorporating a boundary condition operator to the effective Hamiltonian. In section 3, the nearly free electron model is trivially obtained by expanding the model Hamiltonian in a power series. The OPW method as well as the problem of narrow bands, as those appearing in transition metals, are briefly touched. Section 4 contains a general review of pseudopotentials using similarity transformations[13].

2. THE MUFFIN TIN POTENTIAL

As explained in the Introduction, the muffin-tin potential is defined dividing each unit cell into two parts by means of a sphere centered on each atom (we are assuming a single atom per unit cell for the sake of simplicity). The spherically symmetric potential in the interior of the spheres is that produced by its corresponding atom plus a correction due to the presence of the other atoms in the crystal, computed self consistently. In the interstitial region between the cell boundaries and the sphere, the potential takes a constant value determined from the continuity of the potential at the sphere boundary.

We now adopt Morse and Korringa's[7] viewpoint, and think of an incident set of plane waves scattered by the "muffin-tin" sphere, to form a stationary Bloch wave. In order to separate the two regions defined by the sphere in each unit cell, we introduce a projection operator $\mathbb{Q}$ which selects out the proper incident wave, namely the one with the correct boundary conditions at the cell boundaries. Thence, with the help of the complement $\mathbb{P} = 1 - \mathbb{Q}$ we can separate the electronic wave equation into a pair of coupled equations. Multiplying the one-electron equation $H\Psi = \mathcal{E}\Psi$ to the left by $\mathbb{Q}$ and $\mathbb{P}$ successively and using the fact that $\mathbb{Q}$ and $\mathbb{P}$ are orthogonal, one gets two coupled equations for $\mathbb{Q}\Psi$ and $\mathbb{P}\Psi$:

$$\begin{aligned} (\mathcal{E} - \mathbb{Q}H\mathbb{Q})\,\mathbb{Q}\Psi &= \mathbb{Q}H\mathbb{P}(\mathbb{P}\Psi) \\ (\mathcal{E} - \mathbb{P}H\mathbb{P})\,\mathbb{P}\Psi &= \mathbb{P}H\mathbb{Q}(\mathbb{Q}\Psi) \end{aligned} \tag{2.1}$$

and substituting into (2.1a), we can write an equation for $\mathbb{Q}\Psi$:

$$[\mathcal{E}-\mathbb{Q}H\mathbb{Q}-\mathbb{Q}H\mathbb{P}(\mathcal{E}-\mathbb{P}H\mathbb{P})^{-1}\mathbb{P}H\mathbb{Q}]\,\mathbb{Q}\Psi=0 \tag{2.3}$$

Upon introducing[14]

$$T=\mathbb{P}(\mathcal{E}-\mathbb{P}H\mathbb{P})^{-1}\mathbb{P} \tag{2.4}$$

an effective Hamiltonian for the component $\mathbb{Q}\Psi$ is defined:

$$H_{\text{eff}}=\mathbb{Q}H\mathbb{Q}+\mathbb{Q}HTH\mathbb{Q} \tag{2.5}$$

Due to the cell division imposed by the "muffin-tin" potential into inner spheres and outer regions in a unit cell, the natural realization for the projection operator in this case would be that which vanishes in the inner spheres, and unity in the outer region. Resolving this into plane waves[15, 16] one has:

$$\mathbb{Q}(r)=\begin{cases} 1=\sum\limits_i |\,k_i\,\rangle\langle\,k_i\,| & \text{in } \Omega_e \\[2ex] 0 & \text{for } 0\leqslant r\leqslant R \end{cases} \tag{2.6}$$

where R is the radius of the muffin-tin sphere and Ω_e is the exterior volume within the unit cell. This projection operator picks up the 'outer part' of the wave function. The i sum is over the reciprocal lattice vectors, so that the projected function will indeed have the expected behaviour.

If the plane waves are normalized to unity in the whole cell volume Ω, they will form an *overcomplete set* in the outer region Ω_e. Defining

$$N_{ij}=\langle\,k_i\,|\,\mathbb{Q}\,|\,k_j\,\rangle \tag{2.7}$$

as the overlap integral, one has in fact:

$$\sum_j N_{ij}\,|\,k_j\,\rangle=|\,k_i\,\rangle \tag{2.8}$$

in Ω_e.

The kinetic energy operator will give rise to unwanted singularities on the sphere boundaries. Slater, in his original formulation[5a], handled this problem by writing the kinetic energy term as $\int \nabla \psi_i^* \nabla \psi_j \, d\tau$. Integrating by parts, it can be shown that this term reduces to the familiar $\int \psi_i^* \nabla^2 \psi_j \, d\tau$ in case there is no contribution from the surface. Since Slater chose functions with a discontinuous slope, the surface integral does not vanish in this case. In the KKR method, there is also a non-vanishing surface integral, this time in terms of the Green function and its normal derivative[6].

Studying a similar type of potential used in nuclear reactions theory[17], Bloch[18a] looked at the problem differently. He showed that the Hamiltonian operator is not Hermitian for this case: Indeed, if $\psi_1(r)$ and $\psi_2(r)$ are any two radial functions,

$$\int_0^R [\psi_1^* H_r \psi_2 - (H_r \psi_1)^* \psi_2] \, r^2 \, dr = -\tfrac{1}{2} \left[r\psi_1^* \frac{d(r\psi_2)}{dr} - \frac{d(r\psi_1)^*}{dr} r\psi_2 \right]_R \tag{2.9}$$

where

$$H_r = -\tfrac{1}{2} \frac{1}{r} \frac{d^2}{dr^2} r + V(r) \tag{2.10}$$

is the radial part of the Hamiltonian for a "muffin-tin" inner sphere of radius R. The right hand side of Eqn. (2.9) will, in general, not vanish.

Instead of imposing boundary conditions at the points $r = R$, we can hermitize the Hamiltonian[18b] by adding a surface term which compensates expression (2.9) when integrated. This is done with the help of the boundary condition operator[15]:

$$B = \delta(r - R)(\mu + \nu \frac{\partial}{\partial n}) \tag{2.11}$$

where μ and ν are arbitrary constants, and $\partial/\partial n$ is the normal derivative at the surface $r = R$.

The projection operator $\mathbb{Q}$ commutes with H except at the boundary surface $r = R$, so that the coupling term between the two equations (2.1), for $\mathbb{Q}\Psi$ and $\mathbb{P}\Psi$, on the right hand side, reduces to $B\mathbb{P}\Psi$ and $B\mathbb{Q}\Psi$ respectively, the equations (2.1) being thus transformed into[15]

$$(\mathcal{E} - \mathbb{Q}H\mathbb{Q} - B)\,\mathbb{Q}\Psi = B\mathbb{P}\Psi \tag{2.12a}$$

$$(\mathcal{E} - \mathbb{P}H\mathbb{P} - B)\,\mathbb{P}\Psi = B\mathbb{Q}\Psi \tag{2.12b}$$

The effective Hamiltonian for the projected function $\mathbb{P}\Psi$ *in* the spheres is:

$$\mathcal{H} = \mathbb{P}H\mathbb{P} + B + B(\mathcal{E} - \mathbb{Q}H\mathbb{Q} - B)^{-1}B \tag{2.13}$$

The homogeneous equation corresponding to (2.12b) is used to obtain the quotient μ/ν:

$$(\mathcal{E} - \mathbb{P}H\mathbb{P} - B)\,\mathbb{P}\Psi = 0 \tag{2.14}$$

The left hand side represents the sum of a continuous function in the interval $(0, R)$ and a Dirac singularity for $r = R$, so it defines[15] the inner eigenfunctions X_λ:

$$(E_\lambda - \mathbb{P}H\mathbb{P})\,X_\lambda = 0 \tag{2.15}$$

for $r < R$, with the appropriate boundary condition:

$$\nu \left.\frac{\partial X_\lambda}{\partial n}\right|_{r=R} = -\left.\mu X_\lambda\right|_{r=R} \tag{2.16}$$

thus fixing μ/ν. The ν is determined from the normalization condition.

On the other hand, the plane waves, solutions to the homogeneous equation associated to (2.12a), are used to expand the reduced Green function in equation (2.13) as:

$$(\mathcal{E} - \mathbb{Q}H\mathbb{Q} - B)^{-1} = \sum_i \frac{|k_i\rangle\langle k_i|}{\mathcal{E} - k_i^2} \tag{2.16}$$

where

$$(k_i^2 - \mathbb{Q}H\mathbb{Q})\,|k_i^2\rangle = 0 \tag{2.17}$$

and the $|k_i>$ are normalized to unity in the *whole* cell volume Ω.

The trial wave function is now chosen to be a linear combination of plane waves outside the sphere. The coefficients are determined simply from the continuity equation. This in turn, follows using the effective Hamiltonian (2.13). Since we are expanding in plane waves, each coefficient in the expansion is actually a Fourier component. This is done in the Appendix.

In the original formulation, Slater selected the inner solutions X_λ to be regular at the origin and joined them smoothly with the l-th component of the plane wave using the well-known expansion in Bessel functions, equation (A.5). In this way we form the APW's, each of which contains a discontinuity of the slope at the sphere boundary.

Once the multipliers μ and ν are found, the coupled homogeneous equations for the coefficients yield a secular equation to obtain the energy $\mathcal{E}$:

$$\left|(k_i^2 - \mathcal{E})\, N_{ij} + \Gamma_{ij}(\mathcal{E})\right| = 0 \tag{2.18}$$

with $\boldsymbol{N}$ and Γ well defined quantities obtained in the Appendix, equations (A.10) and (A.11). The indeces i and j ennumerate the Fourier components. Notice the dependence on the energy $\mathcal{E}$ in the matrix elements Γ. This means that the "secular equation" for $\mathcal{E}$ must be solved iteratively.

The way we deal with the KKR method is briefly mentioned in the Appendix as well. The close relationship between these two methods – APW and KKR – has been extensively discussed elsewhere[16, 19], analyzing the convergence properties of both[16].

3. OTHER MODEL POTENTIALS

Although computations made with OPW and pseudopotential methods, on one hand, and APW and KKR on the other, have been quite successful for many crystals[20], there are cases in which these methods do not yield good results. Such is the case for solids containing transition metal atoms. The APW and pseudopotential formulations do not give a proper account for narrow valence bands, mainly because these arise from 3d atomic orbitals [5d]. The latter extend enough to produce a non-negligible overlap with the neighbouring atoms's orbitals, but they are, nevertheless, bound enough to be considered as "core" orbitals. The APW and KKR methods, on the other hand, using "muffin-tin" potentials, present a similar difficulty: as Ziman, has pointed out[21], the overlapping of deeply bound atomic orbitals lowers the potential barriers, and these bound atomic orbitals merge over the "muffin-tin" zero. In other words, the centrifugal potential in the radial equation becomes dominant near the origin and produces the appearance of virtual levels in the free band. This makes the narrow band calculations strongly dependent on the "muffin-tin" radius, an adjustable parameter with no real physical significance. In order to surmount this difficulty a successful attempt to extend the pseudopotential formulation was made using empirical arguments[22]. The conduction bands have a free-electron behaviour, while the *d* bands are described better from the tight-binding viewpoint, so one can *hybridize* the two sets and obtain very good results with a few semiempirical parameters. Hubbard[12], starting from the KKR formulation, showed that the resonances can be interpreted as a hybridization of nearly-free-electron and tight-binding behaviours. Hubbard adapted Kapur-Peierls'[23] method as used in nuclear theory to obtain his results. This procedure consists of expanding the Green function in eigen-functions of the Hamiltonian with boundary conditions different from the ones prescribed by the problem – one assumes instead that there is no incident wave. Hubbard, however, assumed a "muffin-tin" potential, as in Kapur-Peierls' original formulation.

a) Exact Formulation

An exact model potential can be obtained *without* starting from a "muffin-tin" potential, by choosing an appropriate projection operator $\mathbb{Q}$ in Eqn. (2.3). As one expects a plane wave type of behaviour near the cell boundaries, $\mathbb{Q}$ may be chosen as:

$$\mathbb{Q} = \sum_{\boldsymbol{q}} | \boldsymbol{k} + \boldsymbol{q} \rangle \langle \boldsymbol{k} + \boldsymbol{q} | \qquad (3.1)$$

where $| \boldsymbol{k} + \boldsymbol{q} \rangle$ is a plane wave normalized to unity over a unit cell, and the sum is taken over reciprocal vectors $\boldsymbol{q}$. Should this sum be taken over all reciprocal vectors, the wave function would reduce to a linear combination of plane waves

$$\Psi = \sum_{\boldsymbol{q}} c_{\boldsymbol{q}}(\boldsymbol{k}) | \boldsymbol{k} + \boldsymbol{q} \rangle \qquad (3.2)$$

and the energy bands would come out as solutions of the corresponding infinite secular equation. However, the restriction to a limited number of terms can be corrected by using the whole effective Hamiltonian (2.5), so that the band energies are given by Eqn. (2.3):

$$\sum_q \{ (\mathcal{E}(k) - |k+q|^2)\, \delta_{q'q} < (k+q' | V | k+q> - < k+q' | VT(\mathcal{E}) V | k+q> \} \, c_q = 0 \qquad (3.3)$$

where $c_q = <k+q|\Psi>$. The wave function itself is expressed, with the aid of (2.2), as:

$$\Psi = \sum_q c_q |k+q> + \sum_q c_q (\mathcal{E} - \wp H \wp)^{-1} \wp V |k+q> \qquad (3.4)$$

and the model potential for the plane waves is $V + VT(\mathcal{E})V$, being non-local and energy dependent.

The choice of the potential V is perhaps the crucial point in an energy band calculation. With the projection operator (3.1), one is no longer restricted to the use of a "muffin-tin" potential. The potential V can thus be chosen starting from the free atom Hartree-Fock potential, taking an average exchange term, with the contribution from neighbouring atoms superimposed to it. The main advantage of using an average potential instead of the non-local Hartree-Fock is that computations are highly simplified because the same potential is used for every orbital.

The problem of how to take the average in the exchange term has been extensively discussed. Slater[2] proposed an exchange potential (in a.u.)

$$V_x = -3\,[3\rho(r)/8\pi]^{1/3} \qquad (3.5)$$

where $\rho(r)$ is the electron density, while Kohn and Sham[1], using a variational ansatz, suggested to use 2/3 of this value. Goscinski and the author[24] showed that Slater's way of averaging would overestimate exchange effects, while Kohn and Sham's underestimates them, at least in atomic systems. The criterion used was to compute the deviation from the virial theorem which the calculated orbitals would suffer in both cases. In the same paper, we suggested multiplying the exchange potential (3.5) by a coefficient, in such a way that the virial theorem would be automatically satisfied by the atomic orbitals used to construct the initial potential, hoping that the resultant crystal orbitals would also fulfill it.

Slater has proposed[25] a similar variation of the coefficient α to improve the potential. He uses the functional expansion of the energy in terms of the density[26] and approximates the exchange term by a potential of the form (3.5). He then chooses α such that the total energy coincides with the Hartree-Fock value for the individual atom. When one uses these density expansions to compute the energies, instead of the variational procedure which is usual in the Hartree-Fock method, the virial theorem is automatically fulfilled.[27]. This is the by now well known X_α method, and its virtues have been extensively discussed elsewhere[25].

In this way, we improve the Hartree-Fock potential, simplifying it at the same time, by using an average exchange potential with the appropriate coefficient. We should notice, however, that as long as a self-consistent procedure is used, with single determinantal wave functions, no correlation whatsoever will be included in the wave functions.

Coming back to the wave function, Eqn. (3.4) can be looked upon as a wave function composed of an incident wave plus a scattered portion, T being the reduced Green function Eqn. (2.4). Reduced means essentially the contribution from the orthogonal complement to the incoming wave, in this context.

The operator T can be expanded in terms of the eigenfunctions of $\mathcal{P}H\mathcal{P}$. If

$$\mathcal{P}H\mathcal{P}\,|\chi_s> = \epsilon_s\,|\chi_s> \tag{3.6a}$$

$$\mathcal{P}\,|\chi_s> = |\chi_s> \tag{3.6b}$$

$$T(\mathcal{E}) = \sum_s \frac{|\chi_s><\chi_s|}{\mathcal{E}-\epsilon_s} \tag{3.7}$$

and the last terms in Eqn. (3.3) become

$$\sum_s \frac{1}{\mathcal{E}-\epsilon_s} <k+q'|V|\chi_s><\chi_s|V|k+q> \tag{3.8}$$

Hence, knowing the states χ, one is able to compute the bands $\mathcal{E}(k)$ by an iteration procedure on the "secular" equation (3.3).

The main feature of this effective potential is its explicit resonance form. An extension of the OPW method to include d-orbitals as resonances was discussed in a paper by the author[28]. The argument goes roughly as follows: the eigenvalues of the deep core state can be taken as the appropriate metal bands as we go from the free atoms to the metal, provided we form Bloch waves from these atomic orbitals. The valence states, however, are appreciably changed in metals. In particular, for transition metals, those d-orbitals induce a resonance effect which produces narrow valence bands in the metal[21].

The core state hence can be approximated by the usual secular equation for OPW s, while the d-states should preserve the resonance form, leaving an energy dependent model Hamiltonian. The corresponding secular equation reads as follows:

$$\sum_{\mathbf{q}} \left\{ (\mathcal{E}(\mathbf{k}) - |\mathbf{k}+\mathbf{q}|^2)\,\delta_{\mathbf{q}'\mathbf{q}} - W_{\mathbf{q}'\mathbf{q}} - \frac{\Gamma_{\mathbf{q}'\mathbf{q}}}{\mathcal{E}(\mathbf{k}) - E_\beta} \right\} c_{\mathbf{q}} = 0 \qquad (3.9)$$

which has to be solved iteratively[28]. The $c_{\mathbf{q}}$'s are the coefficients in the expansion in OPW's, and the matrix elements of W and Γ are:

$$W_{\mathbf{q}'\mathbf{q}} = \langle \mathbf{k}+\mathbf{q}' | (V + \sum_{\alpha} (E_{\mathbf{k}+\mathbf{q}} - E_\alpha) | \alpha \rangle\langle \alpha |) | \mathbf{k}+\mathbf{q} \rangle \qquad (3.10)$$

and

$$\Gamma_{\mathbf{q}'\mathbf{q}} = \langle \mathbf{k}+\mathbf{q}' | V\wp | \beta \rangle\langle \beta | \wp V | \mathbf{k}+\mathbf{q} \rangle \qquad (3.11)$$

α denoting the Bloch functions constructed from the core states, and β the one from the d-orbitals. For further details, we refer the reader to Ref. (28), and a paper by Harrison[29].

b) Nearly Free Electron Model

Eqn. (3.3) can be expanded in perturbation series. We take the kinetic energy term as the unperturbed Hamiltonian, and use Löwdin's[14] expansions of T in Rayleigh-Schrödinger or Brillouin-Wigner series respectively:

$$T = R_0 + R_0VR_0 + R_0VR_0VR_0 + \dots \qquad (3.12a)$$

where

$$R_0 = \mathbb{P}(E^{(0)} - H_0)^{-1}\mathbb{P} \tag{3.12b}$$

and $E^{(0)}$ is the diagonal operator of the unperturbed energies in the $\mathbb{Q}$-subspace, and

$$T = T_0 + T_0 V T_0 + T_0 V T_0 V T_0 + \dots . \tag{3.13a}$$

with

$$T_0 = \mathbb{P}(\mathcal{E} - H_0)^{-1}\mathbb{P} \tag{3.13b}$$

The second order to R-S being:

$$\sum_{\boldsymbol{q}} \{(\mathcal{E}(\boldsymbol{k}) - |\boldsymbol{k}+\boldsymbol{q}|^2)\,\delta_{\boldsymbol{q}'\boldsymbol{q}} + \langle \boldsymbol{k}+\boldsymbol{q}'|V + VR_0V|\boldsymbol{k}+\boldsymbol{q}\rangle\}\, c_{\boldsymbol{q}} = 0 \tag{3.14}$$

so the nearly-free-electron model follows immediately.

c) Partial Wave Representation

The momentum space was used throughout, but this is no limitation. We can instead use a "muffin-tin" potential for V, and redefine the projection operator $\mathbb{Q}$ as

$$\mathbb{Q} = \sum_{lm} |L\rangle\langle L| \tag{3.15}$$

in the inner spheres, with $L = j_l(\kappa \boldsymbol{R})\, \mathcal{Y}_{lm}(\boldsymbol{r})$, and $\kappa^2 = \mathcal{E}$, the sum over the lattice harmonics appropriate to the crystal, in order to obtain a partialwave representation *mutatis mutandis*.*

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*See also P t. (12)

4. THE PSEUDOPOTENTIAL

The philosophy behind the pseudopotential theory is quite different. There we seek an equation which has the same eigenvalues as the original one, but whose eigenfunctions are as "smooth" as possible. Smooth in the sense of having removed the rapid atomic-like oscillations near the ions. The corresponding pseudopotential should then be also a smoother function than the usual average potential. It describes a weak interaction between the electrons and the ionic lattice. If this smoothness condition is fulfilled, the *pseudo*functions can be constructed as a linear combination of a few plane waves. The way to choose this pseudopotential is not unique indeed[11]. It actually is somewhat arbitrary, and extensive discussions about which one to use can be found in the literature[11, 30].

The process of going from the original eigenfunctions to the *pseudo* functions can be visualized by means of a similarity transformation[13]. To this end, let us divide the function space into two subspaces, the "core" subspace and the "valence" subspace, defined by the complementary projection operators $\mathbb{C}$ and $\mathbb{V}$ respectively.

$$\mathbb{C} + \mathbb{V} = 1 \tag{4.1}$$

$$\mathbb{C}^2 = \mathbb{C}\,, \quad \mathbb{V}^2 = \mathbb{V} \tag{4.2}$$

A basis in the $\mathbb{C}$-subspace is given by the core states $|\alpha>$ formed as Bloch functions from the free atom or ion lower states:

$$\mathbb{C} = \sum_{\alpha} |\alpha><\alpha| \tag{4.3}$$

$|\alpha>$ being an eigenfunction of the Hamiltonian H, corresponding to the core states

$$H|\alpha> = E_{\alpha}|\alpha> \tag{4.4}$$

Now, to define the *pseudo*wave functions, we split the same space into two different complementary subspaces with the aid of the two orthogonal projectors $\mathbb{Q}$ and $\mathbb{P}$.

The $\mathbb{Q}$ and $\mathbb{P}$-subspaces are chosen to be isomorphous to the $\mathbb{C}$- and

$\mathbb{V}$- ones respectively. In other words, there is a one-to-one correspondence between the core states and the basis functions in the $\mathbb{Q}$-subspace. As a concrete example, we can bear in mind the expression for $\mathbb{Q}$ and $\mathbb{P}$ as in Eqn. (31) since we want the *pseudo*functions to be as smooth as possible. The basis for the $\mathbb{Q}$-subspace in this example contains the lowest plane waves (properly symmetry-adapted):

$$\mathbb{Q} = \sum_{q} \left| k + q \right> \left< k + q \right| \qquad (3.1)$$

where the summation is taken over a limited number of lattice vectors – namely the number of core states. This, of course, is not the only possible choice, but will give rise to the well known OPW pseudopotential, as is shown below.

There is obviously a unitary transformation U which takes us from one basis into the other, i. e., which maps $\mathbb{Q}$ onto $\mathbb{C}$. The explicit expression for this transformation has been found by the author in quite a different context[31]. We first notice that the projector $\mathbb{C}$ commutes with the Hamiltonian H but $\mathbb{Q}$ does not. It is then shown[31] that U is the operator which diagonalizes $\mathbb{Q}$, and can be written as*:

$$U = \exp \left\{ \tfrac{1}{2} \arcsin 2 \left[\mathbb{Q}, \mathbb{C} \right] \right\} \qquad (4.5)$$

The transformation U above is unitary and it maps $\mathbb{Q}$ in $\mathbb{C}$ and $\mathbb{P}$ in $\mathbb{V}$. After Waeber and Stoll[13], we now define a non-singular transformation W in the following way: we want W to map $\mathbb{Q}$ into itself, and simultaneously, to map $\mathbb{P}$ into $\mathbb{V}$. In this way, the "upper" *pseudo*functions have the same energy as the valence states, as it should. In this same paper, they have shown that an explicit form for W is simply

$$W = \mathbb{V} + \mathbb{C}\mathbb{Q} \qquad (4.6)$$

Defining the operator $S = (\mathbb{C} - \mathbb{Q})^2$, the inverse of W can be written as:

$$W^{-1} = 1 + \mathbb{C}\mathbb{P}\,(1 - S)^{-1} \qquad (4.7)$$

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* This is only one possible form for U. Since U diagonalizes $\mathbb{Q}$, and its eigenvalues are infinitely degenerate, U is not uniquely determined.

That this inverse exists follows immediately from the existence of U [13].

The equation for the *pseudo*functions is obtained by making a similarity transformation on the original H:

$$W^{-1}HW|\phi> = \mathcal{E}|\phi> \tag{4.8}$$

The net effect of this transformation is to add a repulsive potential to H which leaves a net weak potential, namely the pseudopotential.

If we are only interested in the valence states, we can concentrate on the $\mathbb{P}$-subspace for the *pseudo*functions, in which case, we can rewrite Eqn. (4.8) as[13]:

$$W^{-1}H\mho|\phi> = \mathcal{E}|\phi> \tag{4.9}$$

for

$$\mathbb{P}|\phi> = |\phi> \tag{4.10}$$

recalling that $\mathbb{Q}|\phi> = 0$ in this case.

Let us now look at the particular choice (3.1). If we multiply the above equation by W to the left, and use (4.6) and (4.3), we obtain the usual OPW pseudopotential equation:

$$\{T + V + \sum_{\alpha}(\mathcal{E} - E_{\alpha})|\alpha><\alpha|\}|\phi> = \mathcal{E}|\phi> \tag{4.11}$$

Since $\mathbb{P}|\phi> = |\phi>$, the functions $|\phi>$ are the *pseudo*functions, and should be formed from a few plane waves. The corresponding pseudopotential

$$V + \sum_{\alpha}(\mathcal{E} - E_{\alpha})|\alpha><\alpha| \tag{4.12}$$

is a weak potential, since it has the effect of orthogonalizing with respect to the core states, responsible for the oscillations of the wave functions near the ions. In fact, $|\phi>$ could be considered as the "plane wave" component of the actual eigenfunctions:

$$|\psi> = |\phi> + \sum_{\alpha} a_{\alpha}|\alpha> \tag{4.13}$$

when expanded in OPW's.

We should note at this point that the transformed Hamiltonian $W^{-1}HW$ is *not* Hermitian, since W is not unitary. Or looking at Eqn. (4.11), we can say equivalently that the Hamiltonian for $|\phi>$ is energy dependent. Despite this fact, the eigenvalues $\mathcal{E}$ are real, and actually coincide with the valence eigenvalues of H. The eigenfunctions $|\phi>$, however, are not orthogonal. This causes no problem, since we can always define a dual basis[15, 32], orthogonal to the original one. For further details, we refer the reader to the original work[13].

5. SUMMARY

To conclude, we would like to remark that the effective Hamiltonian constructed using projection operators has the advantage of yielding a unified viewpoint. The projection operator selects the behaviour far away from the ions, i.e., in the interstitial regions near the cell boundaries. The flexibility to choose its explicit form allows us to interpret the problem either as a scattering problem or from the perturbation point of view; to work in the coordinate space, in the momentum space, or in the partial wave representation. The introduction of a boundary condition operator makes it possible to encompass the "muffin-tin" potential formulations under the same scheme.

The similarity transformation to reduce the pseudopotentials is also written in terms of projectors. In a way, it links the tight-binding method defined by the core functions projector and the free-electron picture described in terms of plane waves. The unitary operator itself cannot be used, because we want the lowest *pseudo*functions to be expressed in terms of a few plane waves as well, since we concentrate only on the valence states, leaving aside the lowest energies which correspond to the core states.

APPENDIX

We start with a trial wave function Ψ, which is expanded in plane waves outside the sphere:

$$\Psi(r) = \sum_j A_j \chi_j(r) \quad \text{in } \Omega_e \tag{A.1}$$

The plane waves in the expansion are defined as $\chi_j = \mathbb{Q}\,|k_j>$ with $\mathbb{Q}$ as in (2.6), while the coefficients A are to be determined. To this end, we write the continuity equation corresponding to the effective Hamiltonian (2.13), analogous to (2.16):

$$\Psi(r)\Big|_{r=R} + \sum_i \frac{|k_i>_R <k_i|B|\Psi>}{\mathcal{E} - k_i^2} = 0 \tag{A.2}$$

This defines the i-th Fourier component for the wave function *outside* the sphere as

$$\frac{<k_i|B|\Psi>}{k_i^2 - \mathcal{E}} \tag{A.3}$$

So, using the expansion (A.1), one gets:

$$\sum_j \frac{<k_j|B|\Psi>}{k_j^2 - \mathcal{E}}\,|k_j> = \sum_j A_j\,|\chi_j> \tag{A.4}$$

Taking Slater's choice, with χ_λ being regular at the origin and joining them smoothly with the plane wave outside the sphere, we can make a partial wave analysis using the decomposition:

$$\exp\,[ik \cdot r] = 4\pi \sum_{lm} i^l j_l(kr)\, \mathcal{Y}^*_{lm}(\hat{k})\, \mathcal{Y}_{lm}(\hat{r}) \tag{A.5}$$

and the boundary condition (2.16):

$$\frac{\mu}{\nu} = - \frac{\mathcal{R}_l'(\mathcal{E}, R)}{\mathcal{R}_l(\mathcal{E}, R)} \tag{A.6}$$

where $\mathcal{R}_l(r)$ is the l-th normalized radial part of the solution of Eqns. (2.15) i.e.,

$$- \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\mathcal{R}_l}{dr} \right) + \left[\frac{l(l+1)}{r^2} + V(r) \right] \mathcal{R}_l = \mathcal{E} \mathcal{R}_l \tag{A.7}$$

the energy $\mathcal{E}$ being chosen to be the same as the characteristic energy[5a] in (2.12). Hence, the integral in (A.4) using expansions (A.1) and (A.5) reduces to:

$$< k_i \,|\, \delta(r-R) \left[- \frac{\mathcal{R}_l'(\mathcal{E}, r)}{\mathcal{R}_l(\mathcal{E}, r)} + \frac{\partial}{\partial n} \right] \nu \,|\, \Psi > =$$

$$= \sum_j A_j \sum_{lm} \frac{(4\pi)^2 R^2}{\Omega} \, j_l(k_i R) \left[- \frac{\mathcal{R}_l'(\mathcal{E}, R)}{\mathcal{R}_l(\mathcal{E}, R)} j_l(k_j R) + j_l'(k_j R) \right] \mathcal{Y}^*_{lm}(\hat{k}_i) \, \mathcal{Y}_{lm}(\hat{k}_j) \tag{A.8}$$

where $\nu = 1 - (\Omega_e / \Omega)$ and the $'$ stands for the derivative with respect to r. Substituting it into (A.4) one is led to a secular equation:

$$\left| (k_i^2 - \mathcal{E}) N_{ij} + \Gamma_{ij}(\mathcal{E}) \right| = 0 \tag{A.9}$$

where

$$\Gamma_{ij} = \frac{4\pi R^2}{\Omega} \sum_l (2l+1) \, P_l(\cos\theta_{ij}) \, j_l(k_i R) \, j_l(k_j R) \left[\frac{\mathcal{R}_l'(\mathcal{E}, R)}{\mathcal{R}_l(\mathcal{E}, R)} - \frac{j_l'(k_j R)}{j_l(k_j R)} \right] \tag{A.10}$$

and[5a]

$$N_{ij} = \delta_{ij} - \frac{4\pi R^2}{\Omega} \frac{j_l(|\mathbf{k}_i - \mathbf{k}_j| R)}{|\mathbf{k}_i - \mathbf{k}_j|} \qquad (A.11)$$

In the KKR method, on the other hand, one starts with the trial wave expansions in the *interior* of the spheres[6]

$$\Psi(r) = \sum_{lm} c_{lm} i^l \mathcal{R}_l(r) \mathcal{Y}_{lm}(\hat{r}) \quad \text{for } r < R$$

instead of Eqn. (A.1). Thus the integral in the continuity Eqn. (A.2) is now given by the expression:

$$<\mathbf{k}_i | B | \Psi> = \frac{4\pi R^2}{\Omega^{\frac{1}{2}}} \sum_{lm} c_{lm} j_l(k_i R) \left[- \mathcal{R}_l'(\mathcal{E}, R) + \frac{j_l'(\kappa R)}{j_l(\kappa R)} \mathcal{R}_l(\mathcal{E}, R) \right] \mathcal{Y}_{lm}(\hat{k}_i) \qquad (A.12)$$

with $\kappa^2 = \mathcal{E}$. The boundary condition equivalent to (A.6) is now

$$\frac{\mu}{\nu} = \frac{j_l'(\kappa R)}{j_l(\kappa R)} \qquad (A.13)$$

The integral (A.12) leads directly to the secular equation derived by Ham and Segall[6b] in an entirely analogous way to that of the APW method seen above.

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RESUMEN

En este artículo se hace una revisión unificada de los modelos monoelectrónicos usados en cálculos de bandas, en términos de operadores de proyección. La idea esencial es seleccionar el comportamiento apropiado en las fronteras de la celda-unidad por medio de proyectores, y acto seguido deducir la ecuación correspondiente para la componente proyectada de la función de onda. Se tratan primero los métodos APW y KKR usando un proyector geométrico. A continuación se deriva el modelo de electrón casi libre expandiendo el potencial efectivo en una serie perturbativa. Por último, se encuentra la ecuación correspondiente a pseudopotenciales usando una transformación de semejanza del operador Hamiltoniano original, siguiendo el trabajo reciente de Waeber y Stoll.