II.6 INTERPOLATION AND INTEGRATION IN RECIPROCAL SPACE

II.6a. Theory

This section presents a technique for approximating integrals of **k**-dependent quantities over the BZ, as needed for determining the Fermi energy ϵ_F of conductors, for reconstructing the P matrix in direct space during the self-consistent procedure, for calculating total and projected densities of states (DOS) (see section I.3e and appendix B). It is based on two simple concepts: the expansion of **k** dependent functions (eigenvalues, eigenvectors) in a Fourier series, and the expansion of energy dependent quantities (DOSs) into Legendre polynomials. In this section each band is identified by superscript (j), so $\epsilon^{(j)}(\mathbf{k})$ is the j-th eigenvalue at point **k**.

The general DOS $\rho(\epsilon)$ is a function of energy which can be expressed as follows for a periodic system:

$$\rho(\epsilon) = \sum_{j=1}^{p} \rho^{(j)}(\epsilon) \qquad \text{II.6.1}$$

$$\rho^{(j)}(\epsilon) = \frac{1}{V_B} \int_{BZ} R^{(j)}(\mathbf{k})\ \delta[\epsilon-\epsilon^{(j)}(\mathbf{k})]\ d\mathbf{k} \qquad \text{II.6.2}$$

The overall DOS is the sum of contributions $\rho^{(j)}(\epsilon)$ from individual energy bands. In the present scheme the number of bands, p, equals the number of AOs associated with each crystal cell and is therefore finite; each band spans a limited energy interval $A^{(j)} \leq \epsilon^{(j)}(\mathbf{k}) \leq B^{(j)}$. The weighting function $R^{(j)}(\mathbf{k})$ characterizes the specific DOS. Three types of $R^{(j)}(\mathbf{k})$ functions are here considered:

$$R_o^{(j)}(\mathbf{k}) = 2 \qquad \text{II.6.3a}$$

$$R_{\mu\nu g}^{(j)}(\mathbf{k}) = 2\ a_{\mu j}^{*}(\mathbf{k})\ a_{\nu j}(\mathbf{k})\ e^{i\mathbf{k}\cdot\mathbf{g}} \qquad \text{II.6.3b}$$

$$R_{\lambda}^{(j)}(\mathbf{k}) = 2\ \Sigma_{\mu\epsilon\lambda}\ \Sigma_{\nu}\ a_{\mu j}^{*}(\mathbf{k})\ a_{\nu j}(\mathbf{k})\ S_{\mu\nu}(\mathbf{k}) \qquad \text{II.6.3c}$$

The density $\rho_o{}^{(j)}(\epsilon)$ associated with the trivial weighting function $R_o{}^{(j)}$ is obviously the total DOS for the j-th band. It can be used to determine the Fermi energy of the system, ϵ_F, through the condition:

$$q = \Sigma_j \int_{-\infty}^{\epsilon_F} d\epsilon\ \rho_o^{(j)}(\epsilon) \qquad \text{II.6.4}$$

where q is the number of electrons per unit cell. The weighting function $R_{\mu\nu g}{}^{(j)}(\mathbf{k})$ of equation II.6.3b defines the projected DOS associated with the AOs $[\mu 0]$ and $[\nu g]$, and gives $P^{g}{}_{\mu\nu}$ after summation over the band index j and integration up to ϵ_F. Finally, equation II.6.3c defines the total DOS projected onto a given set of AOs (a shell or an atom) according to a Mulliken population analysis. Due to the trace operation $(\Sigma_{\mu\epsilon\lambda}\ \Sigma_{\nu})$, $R_{\lambda}{}^{(j)}(\mathbf{k})$ is a totally symmetric function of **k**. This is generally not true for the expression II.6.3b; however, symmetric functions $R_{\mu\nu gS}{}^{(j)}(\mathbf{k})$ can be obtained from

$R_{\mu\nu g}^{(j)}(\mathbf{k})$ by averaging over all the points $\mathbf{k}^V$ of the "star of $\mathbf{k}$" generated from $\mathbf{k}$ by application of the h operators V of the point group (see section II.7):

$$R_{\mu\nu gS}^{(j)}(\mathbf{k}) = [\ \Sigma_{V=1}^{h}\ R_{\mu\nu g}^{(j)}(\mathbf{k}^V)\ ]/h \qquad \text{II.6.5}$$

Obviously, $R_{\mu\nu gS}^{(j)}(\mathbf{k})$ gives the same result as $R_{\mu\nu g}^{(j)}(\mathbf{k})$ when the integral II.6.2 is performed, since $\epsilon(\mathbf{k})$ and the integration region are also totally symmetric with respect to point group operators.

In the following, we shall first consider the contribution from an individual band, and drop accordingly the band index j; the general multiband case will finally be discussed. Only the 3-dimensional case is treated since nothing is changed when passing to systems of lower dimensionality.

The integrals II.6.2 must be evaluated starting from the knowledge of $R(\mathbf{k})$ and $\epsilon(\mathbf{k})$ at a certain number of sampling points where the one-electron equations have been solved. The set K of sampling points comprises here $S=s_1 \cdot s_2 \cdot s_3$ points $\mathbf{k}_i$ belonging to a regular net (see equation I.3.15):

$$\mathbf{k}_i = (i_1/s_1)\ \mathbf{B}_1 + (i_2/s_2)\ \mathbf{B}_2 + (i_3/s_3)\ \mathbf{B}_3 \qquad [\ 0 \leq i_j < s_j] \qquad \text{II.6.6}$$

The shrinking factors s_1, s_2, s_3 are chosen in such a way so that all high multiplicity (special) points in the BZ belong to K; band extremes are then likely to occur at one of the sampling points. If symmetrical functions $R_S(\mathbf{k})$ are considered, one can restrict oneself to the subset K' comprising S' sampling points that belong to the irreducible part of the BZ (IBZ). Each $\mathbf{k}_i \in K'$ point has a geometrical weight w_i attached, which is proportional to the number of non equivalent $\mathbf{k}$ vectors in its star, and satisfies $\Sigma_i\ w_i = 1$.

An interpolation scheme of the kind discussed in section I.3e is now used for obtaining the approximate analytic expression $\tilde{R}(\mathbf{k})$ and $\tilde{\epsilon}(\mathbf{k})$ of $R(\mathbf{k})$ and $\epsilon(\mathbf{k})$ in the form of a truncated Fourier expansion (see equation I.3.13). Here we choose as follows the expansion set G of lattice vectors. Consider a superlattice characterized by "supertranslation vectors" $\underline{\mathbf{a}}_1 = s_1\mathbf{a}_1$, $\underline{\mathbf{a}}_2 = s_2\mathbf{a}_2$, $\underline{\mathbf{a}}_3 = s_3\mathbf{a}_3$, and take the corresponding "super-Wigner-Seitz cell". The set G now comprises all lattice vectors $\mathbf{g}$ which are inside or at the surface of this supercell. Each vector $\mathbf{g} \in G$ is assigned a weight $W_g = 1/p_g$; for vectors inside the supercell, $p_g = 1$; for those at its surface p_g is the number of vectors of the star of $\mathbf{g}$, which are equivalent to each other through a superlattice vector $\underline{\mathbf{h}}$. The following orthonormality conditions are easily seen to hold for all $\mathbf{g},\mathbf{g}' \in G$, $\mathbf{k},\mathbf{k}' \in K$ (note that the $\mathbf{k}_i$'s are reciprocal lattice vectors of the superlattice):

$$\frac{1}{S}\ \Sigma_{\mathbf{k}_i \in K}\ \exp[i\ \mathbf{k}_i \cdot (\mathbf{g}-\mathbf{g}')] = \delta_{\mathbf{g}(\mathbf{g}'+\underline{\mathbf{h}})} \qquad \text{II.6.7}$$

$$\frac{1}{S}\ \Sigma_{\mathbf{g} \in G}\ W_g\ \exp[i\ (\mathbf{k}_i - \mathbf{k}_{i'}) \cdot \mathbf{g}] = \delta_{ii'} \qquad \text{II.6.8}$$

We can now define an approximate analytic expression $\tilde{f}(\mathbf{k})$ which coincides with the original one $f(\mathbf{k})$ at all sampling points, and satisfies the periodicity condition $\tilde{f}(\mathbf{k}) = \tilde{f}(\mathbf{k}+\mathbf{K})$:

$$\underset{\sim}{f}(\mathbf{k}) = \Sigma_{\mathbf{h}\epsilon G}\, W_h\, \underset{\sim}{f}_h \quad \exp(i\,\mathbf{k}\cdot\mathbf{h}) \qquad \text{II.6.9}$$

$$\underset{\sim}{f}_h = \frac{1}{S}\, \Sigma_{\mathbf{k}_i\epsilon K}\, f(\mathbf{k}_i)\, \exp(-i\,\mathbf{k}_i\cdot\mathbf{h}) \qquad \text{II.6.10}$$

If totally symmetric functions are considered, all Fourier coefficients are equal when referring to $\mathbf{g}\epsilon G$ vectors that belong to the same "star" S_m of symmetry related lattice vectors. Following Monkhorst and Pack (1976) we can then use real symmetrized plane waves (SPW) $A_m(\mathbf{k})$ as an expansion set:

$$A_m(\mathbf{k}) = N_m^{-1/2}\, \Sigma_{\mathbf{g}\epsilon S_m}\, \exp(i\,\mathbf{k}\cdot\mathbf{g}) \qquad \text{II.6.11}$$

$$\frac{1}{V_B} \int_{BZ} d\mathbf{k}\, A_m(\mathbf{k})\, A_n(\mathbf{k}) = \delta_{mn} \qquad \text{II.6.12}$$

Here N_m is the number of vectors of the m-th star, and m is comprised between 0 and M, corresponding to the star of the largest $\mathbf{g}\epsilon G$ vectors. When using SPWs as an expansion set, we must associate to each of them a weight $W_m = 1/p_m$, where p_m is the number of partners (in the sense specified above) of the vectors of that star: so, $W_m = 1$ for internal stars, and $W_m < 1$ for stars at the surface of the super-Wigner-Seitz cell. We can thus write, for instance:

$$\underset{\sim}{\epsilon}(\mathbf{k}) = \Sigma_{m=o}^{M}\, W_m\, \underset{\sim}{\epsilon}_m\, A_m(\mathbf{k}) \qquad \text{II.6.13}$$

$$\underset{\sim}{\epsilon}_m = \Sigma_{\mathbf{k}_i\epsilon K'}\, w_i\, A_m(\mathbf{k}_i)\, \epsilon(\mathbf{k}_i) \qquad \text{II.6.14}$$

For expanding the $R_{\mu\nu g}(\mathbf{k})$ function defined by equation II.6.3b we could directly use equation II.6.9 and 10 (Angonoa et al 1984b) with the substitution $f \to R_{\mu\nu g}$. However, it is convenient first to obtain approximate expressions for the eigenvector coefficient products $\alpha_{\mu\nu}(\mathbf{k}) = 2a_\mu^*(\mathbf{k})a_\nu(\mathbf{k})$ of the chosen band according to those equations, and then use them for expressing $\underset{\sim}{R}_{\mu\nu g}(\mathbf{k})$:

$$\underset{\sim}{R}_{\mu\nu g}(\mathbf{k}) = \Sigma_{\mathbf{h}\epsilon G}\, W_h\, \underset{\sim}{\alpha}_{\mu\nu h}\, \exp[i\,\mathbf{k}\cdot(\mathbf{g}+\mathbf{h})] \qquad \text{II.6.15}$$

$$\underset{\sim}{\alpha}_{\mu\nu h} = \frac{2}{S}\, \Sigma_{\mathbf{k}_i\epsilon K}\, a_\mu^*(\mathbf{k}_i)\, a_\nu(\mathbf{k}_i)\, \exp(-i\,\mathbf{k}_i\cdot\mathbf{h}) \qquad \text{II.6.16}$$

With this procedure, one takes into account the presence of the oscillating $\exp(i\mathbf{k}\cdot\mathbf{g})$ factor from the start, so that the approximate expression becomes exact in the limit when $\mathbf{a}^{(j)}(\mathbf{k})$ is $\mathbf{k}$-independent, or more generally, when $\underset{\sim}{\alpha}_{\mu\nu}(\mathbf{k})$ is a good approximation of the eigenvector product. The corresponding symmetrized expression of $\underset{\sim}{R}(\mathbf{k})$ is:

$$\underset{\sim}{R}_{\mu\nu gS}(\mathbf{k}) = \Sigma_{m=o}^{M}\, \underset{\sim}{R}_{\mu\nu gm}\, A_m(\mathbf{k}) =$$

$$= \Sigma_m\, N_m^{-1/2} \left[\Sigma_{\mathbf{h}\epsilon G}^{(m,h,g)}\, W_h\, \underset{\sim}{\alpha}_{\mu\nu h} \right] A_m(\mathbf{k}) \qquad \text{II.6.17}$$

where the sum $\Sigma^{(m,h,g)}$ is extended to those $\mathbf{h}\epsilon G$ vectors such that $\mathbf{g}+\mathbf{h}$ belongs to the m-th star. When evaluating this expression, use can be made of the symmetry properties of the $\underset{\sim}{\alpha}_{\mu\nu h}$ coefficients (equation II.7.26).

We can now use the approximate expressions $\tilde{\epsilon}(\mathbf{k})$ and $\tilde{R}(\mathbf{k})$ (equations II.6.13 and 15) instead of the exact ones in equation II.6.2. For evaluating the integral over the BZ, we consider a technique (Pisani 1982; Angonoa et al 1984b) based on the formal expansion of the DOS in a truncated series of Legendre polynomials

$$\Phi_\ell(x) = \Sigma_{i=0}^{\ell} c_i^{(\ell)} x^i \qquad [\ -1 \leq x \leq 1\ ] \qquad \text{II.6.18}$$

for which the well-known properties hold true (Abramowitz and Stegun 1965):

$$\left.\begin{aligned} c_i^{(\ell)} &= \frac{(-1)^{(\ell-i)/2}\ (\ell+i)!}{2^\ell\ [(\ell-i)/2]!\ [(\ell+i)/2]!\ i!} \qquad [\ \text{even}\ \ \ell-i\ ] \\ c_i^{(\ell)} &= 0 \qquad\qquad\qquad\qquad\qquad\qquad [\ \text{odd}\ \ \ell-i\ ] \end{aligned}\right\} \qquad \text{II.6.19}$$

$$\int_{-1}^{1} dx\ \Phi_\ell(x)\ \Phi_{\ell'}(x) = h_\ell\ \delta_{\ell\ell'} \quad ; \quad h_\ell = 2/(2\ell+1) \qquad \text{II.6.20}$$

$$\int_{-1}^{1} dx\ \Phi_\ell(x) = 2\ \delta_{\ell 0} \qquad \text{II.6.21}$$

It is expedient to introduce, for each band, a new variable x, linearly related to ϵ as follows (A and B are the lower and upper extreme of the band considered):

$$x(\epsilon) = q\ \epsilon - r \quad ; \quad q = 2/(B-A) \quad ; \quad r = (B+A)/(B-A) \qquad \text{II.6.22}$$

We will also define:

$$X(\mathbf{k}) \equiv x[\underset{\sim}{\epsilon}(\mathbf{k})] \qquad \text{II.6.23}$$

Since by definition: $A \leq \tilde{\epsilon}(\mathbf{k}) \leq B$, we have $-1 \leq X(\mathbf{k}) \leq 1$. With respect to the new variable, the associated DOS $\rho'(x)$ can then differ from zero only in the interval $-1 \leq x \leq 1$, and the expansion can be considered:

$$\rho'(x) = \frac{1}{V_B} \int_{BZ} d\mathbf{k}\ \tilde{R}(\mathbf{k})\ \delta[x - X(\mathbf{k})] = \Sigma_\ell\ \underset{\sim}{f}_\ell\ \Phi_\ell(x) \qquad \text{II.6.24}$$

Multiplying this equation by $\Phi_\ell(x)$ and integrating over x yields:

$$h_\ell\ \underset{\sim}{f}_\ell = \frac{1}{V_B} \int_{BZ} d\mathbf{k}\ \tilde{R}(\mathbf{k})\ \Phi_\ell[X(\mathbf{k})] \qquad \text{II.6.25}$$

On the other hand, from equations II.6.13, II.6.22 and II.6.23:

$$X(\mathbf{k}) = \Sigma_{m=0}^{M} \underset{\sim}{x}_m\ A_m(\mathbf{k}) \qquad , \text{ with} \qquad \text{II.6.26}$$

$$\underset{\sim}{x}_0 = q\ \underset{\sim}{\epsilon}_0 - r \quad ; \quad \underset{\sim}{x}_{m>0} = q\ \underset{\sim}{\epsilon}_m \qquad , \text{ whence} \qquad \text{II.6.27}$$

$$\Phi_\ell[X(\mathbf{k})] = \Sigma_{n=0}^{N_\ell} \underset{\sim}{F}_{n\ell}\ A_n(\mathbf{k}) \qquad \text{II.6.28}$$

because products of SPWs are a linear combination of such functions:

$$A_m(\mathbf{k})\ A_{m'}(\mathbf{k}) = \Sigma_{n=1}^{P}\ g^n_{mm'}\ A_n(\mathbf{k}) \qquad \text{II.6.29}$$

The $\underset{\sim}{F}_{n\ell}$ "Fourier-Legendre" coefficients play a key role in the theory. They are obtained starting from

$$\underset{\sim}{F}_{no} = \underset{\sim}{\delta}_{no} \quad ; \quad \underset{\sim}{F}_{n1} = \underset{\sim}{x}_n \qquad \text{II.6.30}$$

and using the recursion relation

$$\underset{\sim}{F}_{n\ell+1} = \frac{2\ell+1}{\ell+1}\ \Sigma_{mm'}\ \underset{\sim}{F}_{m\ell}\ g^n_{mm'}\ \underset{\sim}{x}_{m'} - \frac{\ell}{\ell+1}\ \underset{\sim}{F}_{n\ell-1} \qquad \text{II.6.31}$$

By substituting II.6.17 and II.6.28 into II.6.25 and using the orthonormality of SPWs (II.6.12), we obtain the important result:

$$\underset{\sim}{f}_{\mu\nu g\ell} = \frac{1}{h_\ell}\ \Sigma_{m=o}^{M}\ \underset{\sim}{R}_{\mu\nu gm}\ \underset{\sim}{F}_{m\ell} \qquad \text{II.6.32}$$

which permits the reconstruction of the projected DOS $\rho'(x)$ according to equation II.6.24. In the case of total DOSs, because of equation II.6.3a, we simply have:

$$\underset{\sim}{f}_{o\ell} = \frac{2}{h_\ell}\ \underset{\sim}{F}_{o\ell} \qquad \text{II.6.33}$$

The results II.6.32, 33 are exact if the Fourier expansion of $\rho'(x)$ as defined in equation II.6.24 is convergent. This is obviously not always the case. Critical situations, such as occur for instance in model cubic metallic systems, have been discussed by Pisani (1982). In practice, the expansion is truncated to some maximum ℓ_{max} value, and the approximate expression is a good approximation of the real DOS except near critical energy points. If an accurate description of the DOS in these critical regions is required, use can be made for instance of the analytic-quadratic version of the tetrahedron scheme (Boon et al 1986).

The multiband DOS can be expressed as a sum of the individual band contributions:

$$\underset{\sim}{\rho}(\epsilon) = \Sigma_j\ q^{(j)}\underset{\sim}{\rho}'^{(j)}(q^{(j)}\epsilon - r^{(j)}) \qquad \text{II.6.34}$$

and is therefore a patchwise continuous function of ϵ, the discontinuities occurring at band extremes. In each continuity region $\rho(\epsilon)$ is a polynomial of degree $\ell_{max}+1$ so that integrated quantities are very easily obtained.

In particular, when determining the Fermi energy, we need to calculate for arbitrary E the number N(E) of states (per unit cell) with energy less than E. By indicating with $n_<$ the number of bands whose upper extreme $B^{(j)}$ is less than E, and with Σ'_j a sum extended to those bands for which $A^{(j)} < E < B^{(j)}$, we have:

$$N(E) = \Sigma_j \int_{-\infty}^{E} d\epsilon\ \rho_o^{(j)}(\epsilon) =$$

$$= 2\ n_{\angle} + 2\ \Sigma_j' \sum_{\ell=o}^{\ell_{max}} \{\underset{\sim}{F}_{o\ell}^{(j)}/h_\ell\}\ \Phi_\ell[x^{(j)}(E)] \qquad \text{II.6.35}$$

$$\Phi_\ell(x) = \int_{-i}^{x} dt\ \Phi_\ell(t) = C_o^{(\ell)} + \sum_{i=1}^{\ell+1} C_i^{(\ell)}\ x^i \qquad \text{II.6.36}$$

$$C_o^{(\ell)} = \sum_{i=0}^{\ell} \frac{(-1)^{i+1}}{i+1}\ c_i^{(\ell)}\ ;\quad C_{i+1}^{(\ell)} = c_i^{(\ell)}/(i+1) \qquad [0 \leq i \leq \ell] \qquad \text{II.6.37}$$

The Fermi energy ϵ_F is then easily determined by numerically solving equation II.6.4, that is: $q = N(\epsilon_F)$.

When reconstructing the P matrix, one must distinguish the contribution from fully occupied bands and from partially occupied bands (such as are present in the case of conductors):

$$P_{\mu\nu g}^{(j)} = \underset{\sim}{R}_{\mu\nu go}^{(j)} = W_g\ \underset{\sim}{\alpha}_{\mu\nu(-g)}^{(j)} \qquad [\text{fully occupied band, } g \in G] \qquad \text{II.6.38}$$

$$P_{\mu\nu g}^{(j)} = \underset{\sim}{R}_{\mu\nu go}^{(j)} = 0 \qquad [\text{fully occupied band, } g \notin G] \qquad \text{II.6.39}$$

$$P_{\mu\nu g}^{(j)} = \Sigma_\ell\ \underset{\sim}{f}_{\mu\nu g\ell}^{(j)}\ \Phi_\ell[x^{(j)}(\epsilon_F)] \qquad [\text{partially occupied band}] \qquad \text{II.6.40}$$

with $\Phi_\ell(x)$ defined as in equation II.6.36.

Figure II.6.1 clarifies the sequence of operations to be performed in the application of the scheme described in this section. In spite of its apparent complexity, the algorithm is extremely fast because in its essence it reduces to a few matrix multiplications.

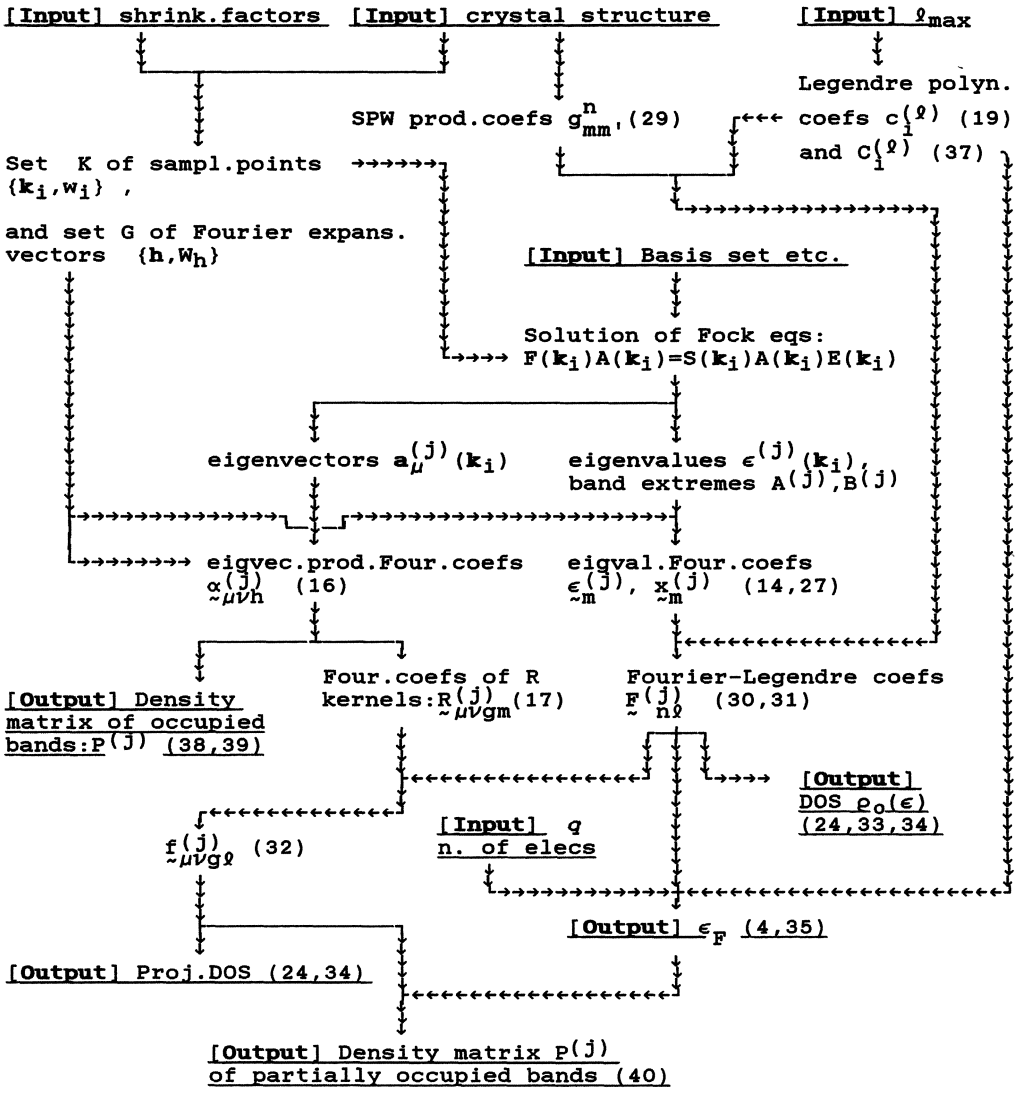

Figure II.6.1. Interpolation and integration scheme described in this section. Numbers in parentheses (xx,yy,...) refer to the corresponding equations II.6.xx, II.6.yy, etc.