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ABSTRACT

The generalization of the Augmented Plane Wave Method, made by Ferreira et al, is retaken, and its consequences fully explored. We show that, among the possible values for λ, the parameter of the generalized method, $\lambda = 0$ which corresponds to the standand APW, is usually the best choice. Further, it is shown that the results for $\lambda = \infty$, when compared with those of $\lambda = 0$ (standand APW), can be used to estimate the quality of the calculation and the degree of convergence.

1. Introduction

In a recent paper, here refered to as I, Ferreira et al (1974) took the lead of Leigh (1956) and of Schlosser and Marcus (1963) to study the possible implications of the full variational expression for the energy, when the basis functions are descontinuous. They showed that the following variational expression

$$\varepsilon = \{ \int_{\Omega_o} d\Omega \; (\nabla\psi_o^* \cdot \nabla\psi_o + \psi_o^* V \psi_o) + \int_{\Omega_i} d\Omega \; \psi_i^* H \psi_i$$

$$+ \int dS \; \psi_o^* \partial_n \psi_i + \int dS \; (\psi_o - \psi_i)\partial_n \psi_i^* - \lambda R^2 \int dS \; (\partial_n \psi_o^* - \partial_n \psi_i^*)(\partial_n \psi_o - \partial_n \psi_i) \; \}$$

$$/ \; \{ \int_{\Omega_i} d\Omega \; \psi_i^* \psi_i + \int_{\Omega_o} d\Omega \; \psi_o^* \psi_o \; \} \qquad (1)$$

where λ is an arbitrary parameter, when used with the expansions

$$\psi_o = \sum C_{\underset{\sim}{k}} \exp(i\underset{\sim}{k}.\underset{\sim}{r}) \qquad (2)$$

in the Ω_o region, and

$$\psi_i = \sum C_{\ell m} Y_{\ell m}(r) \; u_{\ell \varepsilon_o}(r) \; / \; u_{\ell \varepsilon_o}(R) \qquad (3)$$

in the Ω_i region, lead to a generalization of the Augmented Plane Wave method, in which

$$\psi_o + \lambda R^2 \partial_n \psi_o$$

is continuous to

$$\psi_i + \lambda R^2 \partial_n \psi_i$$

at the surface separating the regions Ω_o and Ω_i. This result can be most easily seen if one makes independent variations $\delta\psi_o$ and $\delta\psi_i$ of the trial functions in the two regions. A variation on ψ_i^* leads to the following equation

$$\int_{\Omega_i} d\Omega\ \delta\psi_i^* \left[H - \varepsilon\right] \psi_i + \int dS\ \partial_n \delta\psi_i^* \left(\psi_o + \lambda R^2 \partial_n \psi_o - \psi_i - \lambda R^2 \partial_n \psi_i\right) = 0 \tag{4}$$

which is satisfied if ψ_i is a solution of Schroedinger's equation and if $\psi + \lambda R^2 \partial_n \psi$ is continuous, while a variation on ψ_o^* leads to

$$\int_{\Omega_o} d\Omega\ \delta\psi_o^* \left[H - \varepsilon\right] \psi_o + \int dS\ \delta\psi_o^* \left(\partial_n \psi_i - \partial_n \psi_o\right) + \lambda R^2 \int dS\ \partial_n \delta\psi_o^* \left(\partial_n \psi_i - \partial_n \psi_o\right) = 0 \tag{5}$$

from which follows the secular equation

$$\sum_{\underset{\sim}{k}} D_{\underset{\sim}{k}'\underset{\sim}{k}}\ C_{\underset{\sim}{k}} = 0 \tag{6}$$

where

$$\begin{aligned} D_{\underset{\sim}{k}'\underset{\sim}{k}} = {} & \Omega \left(\underset{\sim}{k}.\underset{\sim}{k}'\ O_{\underset{\sim}{k}-\underset{\sim}{k}'} - \varepsilon\ O_{\underset{\sim}{k}-\underset{\sim}{k}'} + V_{\underset{\sim}{k}-\underset{\sim}{k}'}\right) \\ & + 4\pi \exp\left[\, i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{r}_o\right] \sum (2\ell+1)\ P_\ell(\underset{\sim}{k}.\underset{\sim}{k}')\ j_\ell(kR)\ j_\ell(k'R) \\ & \times \frac{L_\ell(\varepsilon) + \lambda \left[L_\ell(\varepsilon)\left(D_\ell(k) + D_\ell(k')\right) - D_\ell(k)\ D_\ell(k')\right]}{1 + \lambda\ L_\ell(\varepsilon)} \end{aligned} \tag{7}$$

For an infinite secular matrix, the eigenvalue should not depend on λ, but for a finite matrix it was shown in I that

$$\frac{d\varepsilon}{d\lambda} < 0 \tag{8}$$

Thus, it was proposed in I to study the degree of convergence of the calculated eigenvalues by means of a study of the dependence of ε on λ. We have made this numerical study in a one-dimensional Kronig -

Penney model, and in the three-dimensional solid Argon and face-centered cubic Iron. A typical result is shown in Fig. 1 where one sees that, aside from a small region of positive values of λ, the eigenvalue is not strongly dependent on λ. The paper by Ferreira et al was a bit pessimistic because their conjectures were based on a preliminary study of the region $\lambda > 0$. They concluded that the APW method could only be used when the divergencies such as that of Fig.1 in the $\lambda > 0$ region were absent. As it will be seen shortly, these divergencies are unavoidable, on the other hand, the proper region to study is the $\lambda < 0$ semi-axis.

It will be the purpose of the present paper to show further properties of the generalized APW method as well as show some of its results in several calculations.

Insert Fig. 1

2. New properties of the generalized method

The first point not to be missed is that in (1) the term containing λ is negative definite. Thus, even for a very small positive value of λ, the expression for ϵ has no bounded spectrum of eigenvalues. By choosing a special form of ψ_o, which is significantly non zero just at the surface of separation of the two regions, we can make ϵ as negatively large as we wish. On the other hand, for $\lambda < 0$, (1) has a proper spectrum bounded from below by the ground state.

Secondly, the secular equation obtained by equating the determinant of the matrix (7) to zero can be considered as an equation for λ at any given value of ϵ. As it will be seen shortly, the number of solutions of this equation is a constant which does not depend on the value of ϵ. Thus the branches in Fig.1 never disappear and must extend to $\epsilon = -\infty$. These branches cross the ϵ axis at the APW solution ($\lambda = 0$) and must appear as diverging towards $\epsilon = -\infty$ at certain positive values of λ. On the other hand, for $\lambda < 0$, because of their monotonic behaviour, the branches must diverge at $\lambda = -\infty$ for certain values of ϵ, to reappear at $\lambda = +\infty$. In these terms, the general behaviour of the solutions presented in Fig.1 can be understood. It may be said in passing that the divergence at some positive values of λ is in no way associated with the vanishing of the denominators

$$1 + \lambda L_\ell(\epsilon_o)$$

of (7), as it was conjectured in I. The values of λ at which these divergencies are observed bear no relation to the values of the

logarithmic derivatives and depend on the size of the secular matrix.

The denominators

$$1 + \lambda\, L_\ell(\varepsilon_o)$$

lead to an apparent difficulty in the "good" region $\lambda < 0$. For high values of ℓ ,

$$L_\ell(\varepsilon_o) \simeq \ell\, R > 0$$

and when scanning λ one finds a succession of poles whose values are

$$\lambda_\ell = -1/L_\ell \simeq -\frac{1}{\ell R}$$

The secular determinant thus appears as a very singular function of λ in the region $\lambda < 0$. To solve this difficulty we begin by making a small generalization in Eq. (1). The term in λ is now written as

$$-\sum_{\ell m} \lambda_\ell \int dS\, Y^*_{\ell m}(\partial_n \psi_o - \partial_n \psi_i) \int dS\, Y_{\ell m}(\partial_n \psi^*_o - \partial_n \psi^*_i)$$

with a different λ - value for each angular momentum. Then we return to the original secular determinant made out of the matrix H with components $H_{kk'}$, $H_{k\ell m}$ and $H_{\ell m, \ell' m'}$ as in Eqs. (22), (23) and (24) of I. In that form it is apparent that the secular determinant H is a polynomial function of λ_ℓ . Then proceeding with the Gauss elimination of the (ℓm) degrees of freedom, and letting D be the determinant of (7), we obtain

$$H = D \prod_\ell \left[-L_\ell(\varepsilon_o) - \lambda_\ell\, L_\ell(\varepsilon_o)^2 \right]^{2\ell+1}$$

Passing to the limit of $\lambda_\ell \to \infty$, and since D tends to a finite value, one sees that the determinant H is a polynomial of degree $2\ell+1$ in λ_ℓ . Thus, though D has poles at $-1/L_\ell$, these

singularities can be eliminated by multiplying the determinant by $\left[1 + \lambda_\ell \, L_\ell(\varepsilon_o) \right]^{2\ell+1}$. The net product has the regular behaviour of a polynomial function of λ_ℓ . At this point it must be remarked that the case is different when one uses symmetrized combinations of spherical harmonics. For example, if in the composition of the state being calculated there enters just one combination of the harmonics $Y_{\ell m}$, then H is a polynomial function of λ_ℓ of degree one.

The polynomial λ-dependence of the secular determinant can be also seen in a different way. Let us make the following transformation

$$\chi_\ell = \frac{\lambda_\ell}{1 + \lambda_\ell \, L_\ell(\varepsilon_o)}$$

Then the matrix element becomes

$$D_{\underset{\sim}{k}'\underset{\sim}{k}} = \Omega \, (\underset{\sim}{k}.\underset{\sim}{k}' \, O_{\underset{\sim}{k}-\underset{\sim}{k}'} - \varepsilon \, O_{\underset{\sim}{k}-\underset{\sim}{k}'} + V_{\underset{\sim}{k}-\underset{\sim}{k}'})$$

$$+ 4\pi \exp\left[i(\underset{\sim}{k}-\underset{\sim}{k}').\underset{\sim}{r}_o \right] \sum (2\ell+1) \, P_\ell(\underset{\sim}{k}.\underset{\sim}{k}') \, j_\ell(kR) \, j_\ell(k'R)$$

$$X \, \{ \, L_\ell(\varepsilon_o) - \chi_\ell \left[L_\ell(\varepsilon_o) - D_\ell(k) \right] \left[L_\ell(\varepsilon_o) - D_\ell(k') \right] \}$$

where it is clear that the determinant D is a polynomial function in χ_ℓ . On the other hand, we can write the term in χ_ℓ as

$$- \chi_\ell \sum_m \{ \, 4\pi \exp(i\underset{\sim}{k}.\underset{\sim}{r}_o) \, Y_{\ell m}(\underset{\sim}{k}) \, j_\ell(kR) \left[L_\ell(\varepsilon_o) - D_\ell(k) \right] \}$$

$$X \, \{ \, 4\pi \exp(-i\underset{\sim}{k}'.\underset{\sim}{r}_o) \, Y_{\ell m}(\underset{\sim}{k}')^* \, j_\ell(k'R) \left[L_\ell(\varepsilon_o) - D_\ell(k') \right] \}$$

which shows that this term is a sum of dyadics made out of vectors whose components are

$$4\pi \exp(i\underset{\sim}{k}.\underset{\sim}{r}_o)\, Y_{\ell m}(\underset{\sim}{k})\, j_\ell(kR) \left[L_\ell(\varepsilon_o) - D_\ell(k) \right]$$

There are $(2\ell+1)$ dyadics being summed, and each one has just one non-zero eigenvalue. Also, this single eigenvalue is positive. Thus the matrix being multiplied by χ_ℓ is a singular matrix with just $2\ell+1$ eigenvalues and it is non-negative definite. Thus we arrive at the conclusion that the equation

$$D = 0$$

is a polynomial one, and because of the non-negative definiteness of the matrix multiplying χ_ℓ, all its roots are real, for whatever value of the energy ε. We thus prove the assertion made earlier about the number of branches, in a figure such as Fig. 1, being a constant for any value of the energy ε.

3. Numerical calculations and conclusions

The energies determined at $\lambda = 0$ (conventional APW) and $\lambda = \infty$ (basis functions with a continuous normal derivative) are upper bounds to the true eigenvalue. This fact can be concluded from the positive definiteness of the operator in (1) for negative values of λ. If one wants a better approximant to the true energy eigenvalue, one would try to establish a criterion for a choice of an optimum value of λ. In our calculations, three criteria were tried:

1 - minimum variance of the k-distribution

If convergence has been attained in a calculation, and assuming

$$\sum C_k^* C_k = 1$$

the variance

$$\sigma = \sum k^2 C_k^* C_k$$

should be small, since the coefficients corresponding to the large wave vectors are negligible. Thus, for any given trial energy, the secular equation was solved for λ and the coefficients C_k were determined, from which the variance was calculated. The energy and value of λ were chosen so that the variance was minimum.

2 - minimum entropy of the k-distribution

The entropy is defined by

$$S = - \sum C_k^* C_k \ln C_k^* C_k$$

Again, near convergence this quantity should be small. This criterion is based on the same ideas as the former, so it yields analogous results.

3 - obedience to the Schroedinger's equation in the region Ω_o

The basis functions satisfy Schroedinger's equation in the region Ω_i but not in the region Ω_o . Thus the following quantity

$$\Delta = \frac{\int_{\Omega_o} (H - \epsilon)\, \psi_o^* \,(H - \epsilon)\, \psi_o \, d\Omega}{\int_{\Omega_o} \psi_o^* \, \psi_o \, d\Omega}$$

reflects, in a simple way, how well the solution satisfies Schroedinger's equation in Ω_o . The value of λ and ϵ are chosen so that this quantity Δ is minimum.

Insert Tables

Our main results are shown in Table 1, for a one-dimensional Kronig-Penney model, Table 2 for a face-centered cubic Iron, and Table 3 for solid Argon. The chosen Iron states were d-type and thus we made $\lambda_\ell = 0$ except for $\ell = 2$. The chosen Argon state was s and we made λ_o non null, the other λ_ℓ being set equal to zero. It is quite remarkable that, for a given secular matrix size, the conventional APW method $(\lambda = 0)$ is usually the best choice. Only exceptionally, one can improve on the APW result by choosing λ according to one of the three criteria. In those cases, the amount of added work in choosing λ according to one of the criteria is not compensating.

The tables also show that, when one nears convergence, by increasing the size of the secular determinant, the energies calculated according to the different schemes all tend to the true eigenvalue. The calculation with $\lambda = \infty$ is as simple as the one with

$\lambda = 0$ (APW) and can be made in paralel therewith. In all our results, the difference between the true eigenvalue and the APW result is much smaller than the difference between the APW result and the result with $\lambda = \infty$. Thus this latter difference can be used as a limit to the error being made in the APW calculation. We found no other practical use for the generalization of the augmented plane wave method.

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TABLE 1. Energy levels of the 2nd band of a Kronig-Penney model, calculated according to different schemes.

$k = 0$, Exact value = -3.872					
Dimension of Matrix*	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda = \infty$
3	-3.271	-	-	-	-
4	-3.742	-4.725	-4.925	-4.550	-3.300
5	-3.850	-4.100	-4.200	-4.050	-3.800
7	-3.872	-3.884	-3.888	-3.880	-3.868
* Symmetrized combinations of plane waves were used					
$k = \pi/2a$, Exact value = -4.757					
Dimension of Matrix	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda = \infty$
5	-2.768	-	-	-	-
7	-4.233	-4.150	-5.450	-5.100	-
9	-4.643	-4.850	-4.900	-4.850	-4.250
$k = \pi/a$, Exact value = -5.435					
Dimension of Matrix	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda = \infty$
5	-3.617	-	-	-	-
7	-4.949	-5.500	-	-5.525	-1.110
9	-5.329	-5.500	-5.550	-5.475	-4.950

TABLE 2. Energy levels for FCC Iron. Symmetrized combinations of basis functions were used.

Γ'_{25} - d band					
Dimension of Matrix	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda_2 = \infty$
1	-0.9886	-	-	-	-
2	-0.9964	-	-	-0.9927	-0.9734
3	-0.9970	-1.0006	-1.0008	-0.9910	-0.9905
4	-0.9970	-1.0006	-1.0008	-0.9910	-0.9905
5	-0.9980	-0.9988	-0.9988	-0.9979	-0.9977
6	-0.9980	-0.9986	-0.9985	-0.9978	-0.9978
7	-0.9980	-0.9985	-0.9985	-0.9980	-0.9979
8	-0.9980	-0.9982	-0.9983	-0.9980	-0.9980

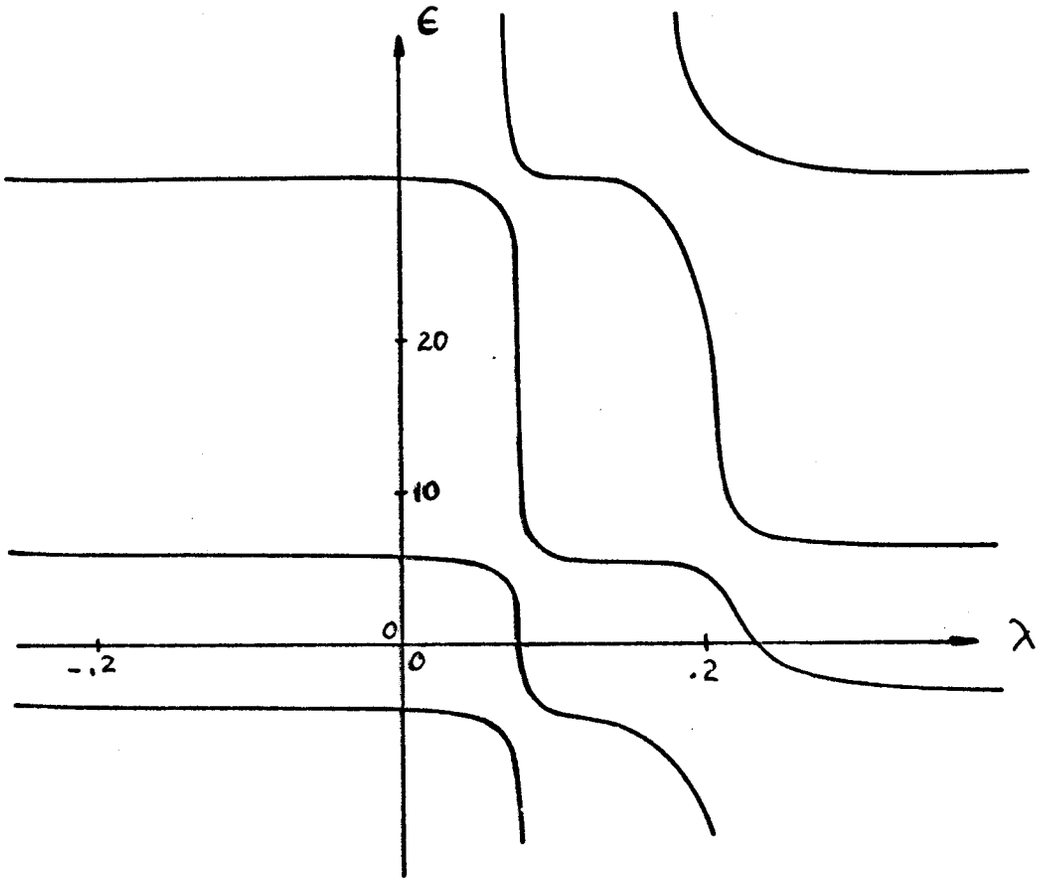
Γ_{12} - d band					
Dimension of Matrix	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda_2 = \infty$
1	-0.8991	-	-	-	-
2	-0.9030	-	-	-0.9016	-0.8763
3	-0.9055	-0.9076	-0.9077	-0.9048	-0.9043
4	-0.9057	-0.9066	-0.9066	-0.9056	-0.9053
5	-0.9057	-0.9066	-0.9066	-0.9056	-0.9053
6	-0.9057	-0.9062	-0.9063	-0.9056	-0.9053
7	-0.9057	-0.9058	-0.9058	-0.9057	-0.9055
8	-0.9057	-0.9057	-0.9058	-0.9057	-0.9055

TABLE 3. Energy levels for solid Argon. Symmetrized combinations of basis were used.

Γ_1 - s band					
Dimension of Matrix	APW	Variance Criterion	Entropy Criterion	Schroedinger Criterion	$\lambda_o = \infty$
1	-0.2100	-	-	-	-
2	-0.2108	-0.2134	-0.2134	-0.2092	-0.2034
3	-0.2111	-0.2116	-0.2116	-0.2110	-0.2105
4	-0.2111	-0.2111	-0.2111	-0.2111	-0.2109
5	-0.2111	-0.2111	-0.2111	-0.2111	-0.2109

FIGURE CAPTION

Figure 1. ϵ vs λ for a Kronig-Penney model. Observe that in the region $\lambda < 0$ the eigenvalue is almost independent of λ .


ϵ
20
10
0
λ
-.2
0
.2