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Efficient solution of the non-linear augmented plane wave secular equation

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Abstract

A new way of solving the *non-linear* secular equation within the augmented plane wave (APW) method is presented. The traditional computation of the APW secular determinant is replaced by a scheme where we follow the eigenvalues of the secular matrix for a number of energies. These eigenvalues, referred to as the meta-eigenvalues of the original APW problem, provide more information about the system for each energy examined than just their product, i.e. the value of the secular determinant. The new scheme for finding the APW eigenvalues can be made considerably more efficient than the traditional one, and is useful in calculations where a linearized approximation to the APW secular matrix is insufficient, such as for optical calculations extending over a wide energy range or for energy dependent effective potentials.

1. Augmented plane wave methods

1.1. The original APW method

The augmented plane-wave (APW) method introduced by Slater in 1937 [1, 2] is optimized to describe wavefunctions in a muffin-tin (MT) potential. In the interstitial region of constant potential, the basis functions consist of plane waves, while inside the MT spheres an eigenstate is better described by the solutions $u_l^\alpha Y_l^m$ of the Schrödinger equation for a spherical potential,

$$\chi(\mathbf{k}_i, E) = \begin{cases} \Omega^{-1/2} e^{i\mathbf{k}_i \cdot \mathbf{r}} & \mathbf{r} \in \text{I} \\ \sum_{L,\alpha} a_L^\alpha(\mathbf{k}_i, E) u_l^\alpha(r_\alpha, E) Y_l^m(\hat{\mathbf{r}}_\alpha) & \mathbf{r} \in \text{MT}. \end{cases} \quad (1)$$

The functions u_l^α satisfy the radial Schrödinger equation for an arbitrary energy E , and Y_l^m are the spherical harmonics. The sum is taken over the condensed angular momentum index $L = \{l, m\}$, and over the MT-sphere index α . Via $\mathbf{k}_i = \mathbf{k} + \mathbf{G}_i$, each basis function is connected to a reciprocal lattice vector \mathbf{G}_i and to a particular k -point. The basis functions are normalized by the square root of the unit cell volume Ω , and the matching constants $a_L^\alpha(\mathbf{k}_i, E)$ ensure that they are continuous everywhere. There is no restriction on the derivatives, thus the APW basis

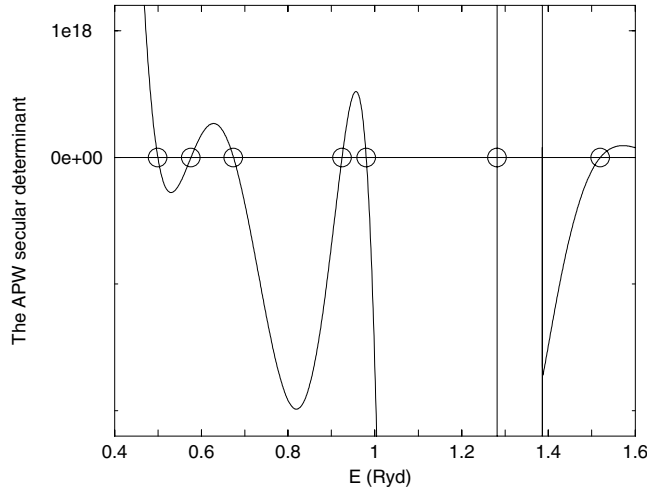


Figure 1. The APW determinant is evaluated for a dense mesh of energies in order to trace the energy eigenvalues. Here, the determinant is evaluated for bcc niobium, at $k = \frac{2\pi}{a}(0.50, 0.25, 0.33)$, with $a = 6.236$ au, $r_{\text{MT}} = 2.65$ au and $r_{\text{MT}}G^{\text{max}} = 9$. The open circles correspond to the exact APW eigenvalues. After reaching a large negative value at 1.25 Ryd, the determinant becomes positive infinite just above 1.38 Ryd. Above this divergence energy the determinant takes a large negative value.

functions may have a kink at the MT-sphere boundary, which demands extra caution as soon as the Laplacian operator is involved, as for the kinetic energy operator [3].

A radial function $u_l^\alpha(r_\alpha, E)$, evaluated at a particular energy E , is only optimal in describing an eigenstate with eigenvalue equal to E . To avoid very large basis set sizes, the APW basis functions must therefore be re-evaluated for each new energy examined. Energy dependent basis functions lead to energy dependent matrix representations, and so the secular equation,

$$\det[\mathcal{H}(E) - E\mathcal{O}(E)] = 0, \quad (2)$$

will be non-linear in energy. Here \mathcal{H} and \mathcal{O} are the Hamiltonian and overlap matrices respectively. The traditional way to find the APW eigenvalues is to evaluate the determinant in equation (2) for a number of energies in order to find its roots, as illustrated in figure 1 for the case of bcc Nb.

1.2. The linearized APW methods

Today, the APW method, along with its earlier improvements, is more or less out-conquered by the computationally more convenient *linearized* forms of the method, such as LAPW [4–6] and the recent APW + lo [3]. In the former, the shape of the augmenting functions in the MT region is changed to become more flexible, while the latter adds complementary basis functions to the original APW basis set. Both linearizations yield a basis set capable of describing eigenfunctions over a larger energy region. This removes the strong energy dependence of the matrices \mathcal{H} and \mathcal{O} , and makes the secular equation, equation (2), *linear* in energy within a certain energy region. All eigenvalues within this energy region can then be found from one diagonalization of the secular matrix.

Although the linearized methods bring many advantages over the APW method, one should remember that their eigenvalues are approximations to the exact APW results. As

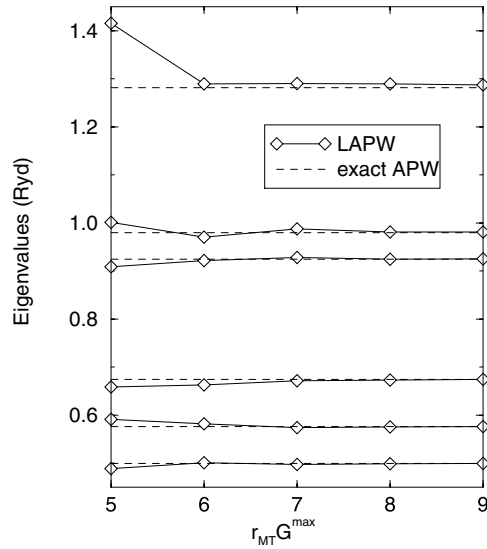


Figure 2. The LAPW eigenvalues of niobium, at $k = \frac{2\pi}{a}(0.50, 0.25, 0.33)$. The linearization energy is set to 0.6 Ryd and the basis set size is varied from 18 plane waves at $r_{MT}G^{max} = 5.0$ to 83 plane waves for $r_{MT}G^{max} = 9.0$.

seen in figure 2, the LAPW eigenvalues are good approximations in an energy region close to the linearization energy, but poorer as this region is enlarged. For a linearization energy of 0.6 Ryd, the five lower eigenstates, which are of mainly *d* character, converge to 1 mRyd within the exact APW result, while the sixth eigenvalue of mainly *s* character differs by almost 6 mRyd. Hence, for calculations over large energy spectra it might be more appropriate to use a non-linearized method, such as the original APW method.

1.3. Other modified APW methods

Before the introduction of the LAPW method there were many suggestions on how to improve upon the original method, especially to avoid the time consuming and cumbersome energy evaluation of the determinant of equation (2). Many of them were efforts in the direction of the LAPW method—to transform the secular problem to an eigenvalue problem by extending the basis set in different ways. Works along this line were e.g. the ones by Schlosser and Marcus [7], Bross [8] and Koelling [9].

An alternative approach had been suggested earlier by Saffren and Slater [10]. Although formulated very differently, it can be viewed as using the fact that the solutions E' to the generalized eigenvalue problem

$$[\mathcal{H}(E) - E'\mathcal{O}(E)]c = 0, \quad (3)$$

are variational with respect to the energy E . In the above equation c is the eigenvector. In a subsequent paper Harmon and Koelling [11] presented schemes to reach the self-consistent solution $E' = E$. The simplest procedure is iterative, and corresponds to using the solutions E' as the evaluation energy E for the matrices in the next step.

The APW method has also continued to be extended after the birth of the LAPW method. For instance, Soler and Williams [12] use an APW method where the eigenstates are found through an iterative process, which then avoids an explicit evaluation of the determinant in equation (2).

In this paper, we present a new and faster way of solving the original energy dependent APW eigenvalue problem, i.e. without modifying the basis set.

2. A short-cut to the APW eigenvalues

It is possible to extract more information from the determinant of equation (2) than just its value at each energy. In this section we present a way to resolve extra information, which results in a new scheme to find the APW eigenvalues.

Let us start by defining the secular matrix,

$$\mathcal{M}(E) \equiv \mathcal{H}(E) - E\mathcal{O}(E). \quad (4)$$

We know that the APW eigenvalues correspond to energies such that $\det[\mathcal{M}] = 0$, and the most straightforward way to find them would be to evaluate this determinant for a number of energies as discussed in section 1.1. However, the secular matrix itself is associated with a set of eigenvalues m_ν , found through the generalized eigenvalue problem,

$$\det[\mathcal{M}(E) - m_\nu\mathcal{O}(E)] = 0 \iff \det[\mathcal{M}'(E) - m_\nu\mathcal{I}] = 0, \quad (5)$$

where \mathcal{I} is the unit matrix and $\mathcal{M}' \equiv \mathcal{O}^{-1/2}\mathcal{M}\mathcal{O}^{-1/2}$.

\mathcal{M}' can always be diagonalized using a unitary matrix \mathcal{U} made up by the eigenvectors of m_ν so that

$$\mathcal{U}^{-1}\mathcal{M}'\mathcal{U} = \begin{pmatrix} m_1 & 0 & 0 & \dots \\ 0 & m_2 & 0 & \dots \\ 0 & 0 & m_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

It is now easy to see that the eigenvalues m_ν , referred to as the meta-eigenvalues of the original APW eigenvalue problem, are connected to the value of $\det[\mathcal{M}]$ through

$$\prod_\nu m_\nu = \det[\mathcal{M}'] = \det[\mathcal{O}^{-1/2}\mathcal{M}\mathcal{O}^{-1/2}] = \frac{\det[\mathcal{M}]}{\det[\mathcal{O}]} \quad (6)$$

Since \mathcal{O} is positive definite $\det[\mathcal{M}] = 0$ corresponds to the fact that at least one meta-eigenvalue $m_\nu = 0$. A double root will coincide with two meta-eigenvalues equal to zero, and so on. We can thereby find the APW eigenvalues ε_μ , for a given k -point in the first Brillouin zone, by searching for the energy roots of the meta-eigenvalues, $m_\nu(E) = 0$. Further, Saffren has shown that the condition $dE'/dE = 0$ is satisfied for each solution E' to the energy dependent eigenvalue problem in equation (3) [10]. In our case E' corresponds to $E + m_\nu$, and hence

$$\left. \frac{dm_\nu}{dE} \right|_{m_\nu=0} = \left. \frac{d(E' - E)}{dE} \right|_{E'=E} = -1. \quad (7)$$

The new task will thus be to retrieve the functions $m_\nu(E)$, using as few diagonalizations of $\mathcal{M}(E)$ as possible. The simplest approach is to diagonalize the secular matrix for a number of energies E_i . Each diagonalization will give a set of meta-eigenvalues $\{m_\nu(E_i)\}_{\nu=1}^N$, where N is the number of basis function. The functional dependence of the meta-eigenvalues on the energy can then be recovered by interpolation. Fortunately, the different meta-eigenvalues do not cross as function of energy, since E is a parameter of the secular matrix, equation (4). The error in the final estimation of an APW eigenvalue depends on the quality of the interpolation. Using for example a bisectioning interpolation scheme, the correct value can be nailed down to an unlimited exactness.

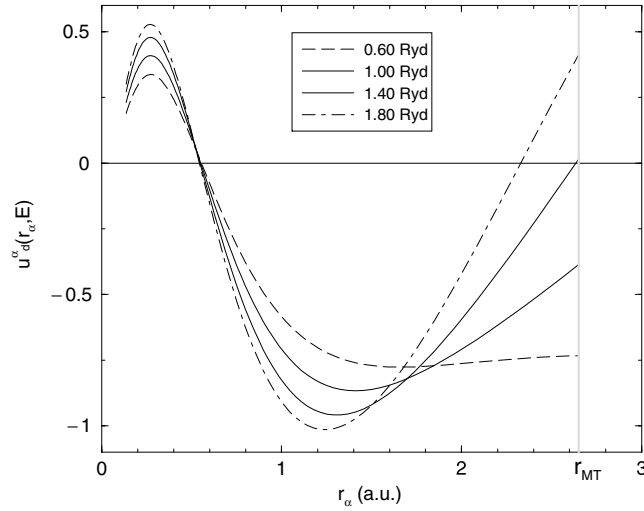


Figure 3. The radial d -function $u_d^\alpha(r_\alpha, E)$ of niobium changes from bonding to anti-bonding state. The matching constants in the APW basis set becomes infinite for energies where the value of u_d^α at $r_\alpha = r_{\text{MT}}$ equals zero.

3. Asymptotic behaviour of APW

There is an asymptotic behaviour hidden in the APW method. In traditional APW the value of the secular determinant diverges for occasional energies, and correspondingly in our scheme, a meta-eigenvalue m_ν can equal zero due to an infinite determinant of the overlap matrix $\mathcal{O}(E)$ instead of indicating an APW eigenvalue. Fortunately, these false indicators of APW eigenvalues are rare, and in the present scheme easily distinguished from the true ones. To start with, however, one must understand why the overlap matrix becomes infinite.

The matching constants $\alpha_L^\alpha(\mathbf{k}_i, E)$ of the basis function augmentation in equation (1) match each term in the MT augmentation to a Bessel function expansion of the plane wave at the sphere boundary $|r_\alpha| = r_{\text{MT}}$,

$$e^{i\mathbf{k}_i \cdot \mathbf{r}} = e^{i\mathbf{k}_i \cdot (\boldsymbol{\tau}_\alpha + \mathbf{r}_\alpha)} = e^{i\mathbf{k}_i \cdot \boldsymbol{\tau}_\alpha} 4\pi \sum_L i^l Y_l^{m*}(\hat{\mathbf{k}}_i) j_l(k_i r_\alpha) Y_l^m(\hat{\mathbf{r}}_\alpha). \quad (8)$$

Here j_l are the Bessel functions and $\boldsymbol{\tau}_\alpha$ is the centre of MT sphere α , with $\mathbf{r} = \boldsymbol{\tau}_\alpha + \mathbf{r}_\alpha$. This yields

$$\alpha_L^\alpha(\mathbf{k}_i, E) = \Omega^{-1/2} e^{i\mathbf{k}_i \cdot \boldsymbol{\tau}_\alpha} 4\pi i^l Y_l^{m*}(\hat{\mathbf{k}}_i) \frac{j_l(k_i r_{\text{MT}})}{u_l^\alpha(r_{\text{MT}}, E)}. \quad (9)$$

Now, since the function u_l^α varies with energy, from bonding to anti-bonding states as seen in figure 3, its value at the sphere boundary will eventually pass through zero for some energy. This happens when the function changes its principal quantum number, adding a new node to u_l^α . The corresponding matching constant will then become infinite, yielding an infinite contribution to the overlap matrix, so that

$$\det[\mathcal{O}(E)] \rightarrow \infty \quad \text{as} \quad u_l^\alpha(r_{\text{MT}}, E) \rightarrow 0. \quad (10)$$

These asymptotic energies can be found by searching for infinite logarithmic derivatives of u_l^α with respect to energy, while in our routine it is sufficient to simply warn the user as soon as $u_l^\alpha(r_{\text{MT}}, E)$ approaches zero or changes sign. One must then be careful not to miss a desired eigenvalue that happens to lie close to such an asymptotic point.

A way around the asymptote problem would be to replace the eigenvalue problem in equation (5) by $\det[\mathcal{M}(E) - n_v \mathcal{I}] = 0$. However, while the introduction of m_v in equation (5) can be regarded as a straightforward generalization of the APW eigenvalues, the new meta-eigenvalues n_v correspond to a transformation of the form $E\mathcal{I} + n_v \mathcal{O}^{-1}$. Thus, although these meta-eigenvalues give us information about the original APW eigenvalue problem exactly at $n_v = 0$, they are found to have a more complicated energy dependence away from these energies.

4. Evaluation of the new scheme

Niobium is a 4d metal which crystallizes in a bcc structure with five valence electrons and so, in a non-spin-polarized calculation, we need to find at least the three lowest lying electron states. This will constitute our trial system for the new APW scheme. All energies are given relative to the so-called MT zero, i.e. the average potential of the interstitial region [6].

We start by examining the meta-eigenvalues in section 4.1 while in section 4.2 we use a simple interpolation routine to find the APW eigenvalues, starting from a converged charge density. In section 4.3 we let the method run self-consistently. All calculations are performed for the full crystal potential, using a scalar relativistic approximation. The density-functional theory [13, 14] is used with the Hedin–Lundqvist [15] version of the local density approximation. The irreducible Brillouin zone is represented by 68 k -points, unless the calculation is performed for a specified k -point. The non-MT part of the potential is taken into account variationally [17].

4.1. The meta-eigenvalues

The efficiency of the present scheme is highly dependent on the choice of interpolation routine. To learn more about the functions $m_v(E)$ that are to be interpolated, we evaluate the eigenvalues of $\mathcal{M}'(E)$ for two different energy grids, one of step-length $\Delta E = 0.1$ Ryd and the other of $\Delta E = 0.01$ Ryd, indicated as (\bullet) and (\cdot) , respectively in figure 4. The meta-eigenvalues $m_v(E)$

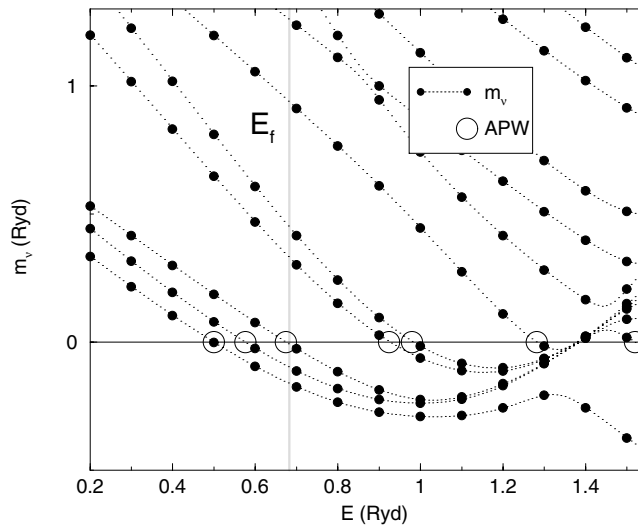


Figure 4. Meta-eigenvalues for niobium, at $k = \frac{2\pi}{a}(0.50, 0.25, 0.33)$. The meta-eigenvalues are evaluated for two different energy steps, $\Delta E = 0.1$ Ryd (\bullet) and $\Delta E = 0.01$ Ryd (\cdot). The basis set size is fixed at $r_{\text{MT}} G^{\text{max}} = 7.0$.

Table 1. Convergence of niobium eigenvalues at $k = \frac{2\pi}{a}(0.50, 0.25, 0.33)$, for increasing degree of the interpolation polynomial (p). The basis set size is fixed by $r_{\text{MT}}G^{\text{max}} = 9.0$. The secular matrix is diagonalized for $p + 1$ energies in the energy interval $E_1 = 0.4$ Ryd to $E_{p+1} = 1.0$ Ryd, starting at E_1 and separated by $\Delta E = (E_{p+1} - E_1)/p$.

Polynomials of degree	APW eigenvalues (Ryd)				
2	0.494 29	0.568 93	0.671 56	0.934 97	0.983 85
3	0.499 51	0.576 31	0.673 27	0.924 66	0.980 38
4	0.499 98	0.576 23	0.674 28	0.924 17	0.980 12
5	0.499 80	0.576 29	0.674 23	0.924 29	0.980 13
∞	0.499 82	0.576 27	0.674 22	0.924 31	0.980 16

are found to be well behaving functions, and can be described by interpolation polynomials $P_v(E)$ of low degrees. The APW eigenvalues will then be found as the real roots of $P_v(E)$, for which the first derivative is negative according to equation (7). m_1 leads to the first eigenvalue of niobium, m_2 to the second eigenvalue and so on. At the asymptote energy at about 1.38 Ryd, the five lowest functions m_v , corresponding to the $l = 2$ states, pass zero due to the infinite overlap matrix. These roots of P_v are however easy to distinguish from the APW eigenvalues, since the polynomials will have positive first derivatives at the asymptote energy.

4.2. From a converged charge density

A main application of the new APW scheme is to find eigenvalues over a wider energy range, starting from an already converged charge density. Since the valence energy region rarely stretches over more than a few Rydbergs, this charge density can be converged using one of the linearized methods discussed in section 1.2.

In table 1 we compare the eigenvalues found from one APW iteration, for different degrees of interpolation polynomials. For an interpolation polynomial of degree p , we use $p + 1$ interpolation energies on a uniform mesh in the energy interval $E_1 = 0.4$ Ryd to $E_{p+1} = 1.0$ Ryd. It is found that the third degree polynomials give a good estimation of the niobium eigenvalues, thus it is sufficient to diagonalize the secular matrix at four different energies to find all eigenvalues.

Here is still a large scope for improvements. Starting from a coarse energy mesh one could for example use a bisection method to track down the APW eigenvalues down to any pre-defined exactness. Instead of full diagonalization, which will give the whole set of N meta-eigenvalues for each energy, an iterative scheme for determining the lowest lying meta-eigenvalues could speed up the computation significantly.

4.3. Self-consistent calculations

One could imagine cases where the secular problem is inherently energy dependent, where the linear energy dependence is broken even for energy independent bases. Such a case would be calculations of quasi-particle spectra involving an energy dependent self-energy, such as e.g. given by the GW approximation [16]. Then a self-consistent scheme could be of great value.

In order to compare the present APW scheme with the two *linearized* methods LAPW [4, 5] and APW + lo [3], we have performed fully self-consistent calculations. To start with, we look at how well the density of states (DoS) of niobium is reproduced by our APW scheme, using a simple interpolation routine of third order polynomials. This requires only four

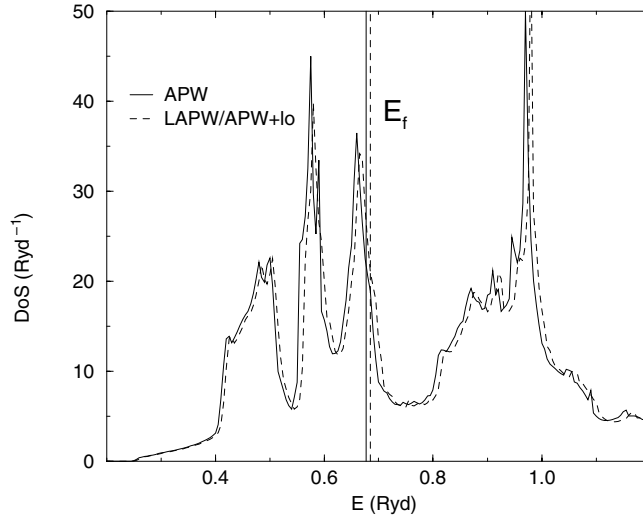


Figure 5. Total DoS for niobium, calculated self-consistently within the LAPW method and the present APW methods. The basis set size is limited by $r_{\text{MT}}G^{\text{max}} = 9.0$, which yields around 80 plane waves at each k -point.

diagonalizations of the secular matrix, where we have chosen a uniform spread of interpolation energies, $E_1 = 0.4$ Ryd, $E_2 = 0.6$ Ryd, $E_3 = 0.8$ Ryd and $E_4 = 1.0$ Ryd. A high plane wave cut-off, corresponding to $r_{\text{MT}}G^{\text{max}} = 9.0$, was used for all three methods. In the two linearized methods, the augmentations of the plane waves together with the complementary spd local orbitals in APW + lo were evaluated at $E = 0.5$ Ryd for $l = s$ and p, while $E = 0.6$ Ryd for higher l quantum numbers. Both these methods used additional s and p local orbitals evaluated at -3.3 and -1.5 Ryd respectively, to treat the 4s and 4p states. The resulting DoS curves are compared in figure 5. While the linearized methods produce identical curves, the one from our self-consistent APW calculation is shifted slightly down in energy. Since we use a crude interpolation routine in the APW scheme, the linearized methods should be considered to give the more exact results in this comparison. However, with a better interpolation routine, the APW scheme will yield an accurate result.

The major problem in the self-consistent APW cycle seems to be a poor convergence of the charge density. Although the total energy converges, there is still a non-vanishing, non-negligible difference in the charge densities of two consecutive iterations. In the present scheme each plane wave coefficient of the eigenfunctions is interpolated using the same interpolation routine as for the eigenvalues, while the augmentation of the basis functions is re-evaluated at each eigenvalue before the charge density is calculated. Thus, the improvement in the charge density must come from the representation of the plane wave coefficients. Either the interpolation should be improved, or, in order to make self-consistent APW calculations, the eigenvectors must be calculated explicitly for each eigenvalue. It should be pointed out that this remains a problem only in our self-consistent calculations.

Earlier [3, 18], we reported on a faster convergence of the APW + lo method with respect to the basis set size, as compared to the LAPW method. In figure 6, we compare the total energies of the present scheme to those of the two linearized methods, for an increasing number of basis functions. The faster convergence of both the energy dependent APW method and the linearized APW + lo method further confirms the advantage of preserving the physical augmenting functions u_l^α inside the MT region.

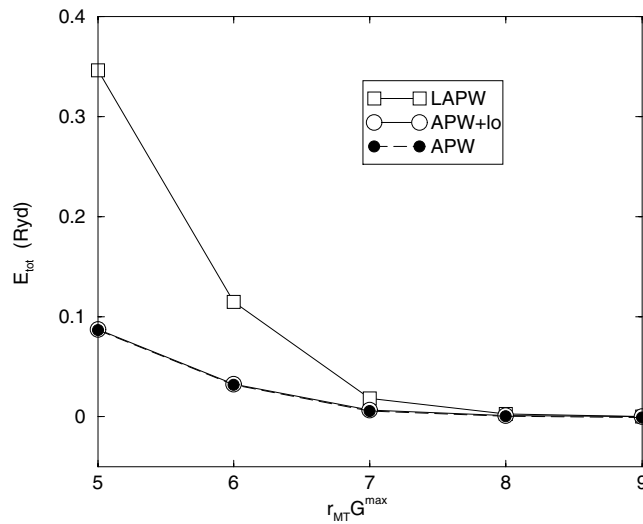


Figure 6. Total energies of niobium versus $r_{MT} G^{max}$ for three different APW schemes, APW, LAPW and APW + lo respectively. The energies are taken relative to the converged APW + lo energy.

5. Conclusion

A new scheme for solving the exact APW eigenvalue problem has been presented. It is shown that, using information from the so-called meta-eigenvalues of the original problem, it is possible to retrieve the APW eigenvalues of our trial system niobium within an error less than 1 mRyd, from only four diagonalizations of the secular matrix. Further, these energies are not chosen with particular care, but spread uniformly over the energy region of interest. This is a significant improvement to the traditional way of solving the APW eigenvalue problem, where the eigenvalues correspond to roots of a complicated function such as that shown in figure 1. This function must be evaluated for a large number of energies in order not to miss any solutions, while our scheme keeps track of the separate eigenvalues by the one to one correspondence with the meta-eigenvalues.

Although the application in this presentation was for one atom per site, this is by no means a limitation. The introduction of the meta-eigenvalues only becomes more powerful for larger dimension of the secular matrix. Still, some care has to be taken with the asymptotic energies.

Compared to linearized versions of the APW method, such as LAPW and APW + lo, the new scheme provides a way to find the eigenvalues over an infinitely large energy region, without the problem of incorrect hybridizations between eigenstates found in different linearization windows. Furthermore, this new scheme could be of use whenever the secular problem is inherently energy dependent, e.g. for calculations of quasi-particle spectra for which the secular matrix includes the real part of the self-energy.

Acknowledgments

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