Boundary conditions for augmented plane wave methods

Christian Brouder

Institut de minéralogie et de physique des milieux condensés, UMR CNRS 7590, Université Pierre et Marie Curie, case 115, 4 place Jussieu, F-75252 Paris Cedex 05, France

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The augmented plane wave method uses the Rayleigh-Ritz principle for basis functions that are continuous but with discontinuous derivatives and the kinetic energy is written as a pair of gradients rather than as a Laplacian. It is shown here that this procedure is fully justified from the mathematical point of view. The domain of the self-adjoint Hamiltonian, which does not contain functions with discontinuous derivatives, is extended to its form domain, which contains them, and this modifies the form of the kinetic energy. Moreover, it is argued that discontinuous basis functions should be avoided.

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I. INTRODUCTION

The augmented plane wave (APW) method and its by-products are among the most powerful electronic structure calculation schemes. The augmented plane wave method was invented by Slater in 1937. Its basic idea is to partition the crystal into two types of regions: (i) non-overlapping spheres $S_a$ centered around all constituent atomic sites and (ii) the remaining interstitial region. The solutions $\psi(r)$ of the Schrödinger equation are expanded over basis wavefunctions $\phi_i(r)$ which are plane waves in the interstitial region and spherical waves inside each sphere. The coefficients of this expansion are obtained through the Rayleigh-Ritz principle by finding the extrema of the Rayleigh quotient

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (1)$$

A subtle point of the APW method is the boundary conditions for the basis functions $\phi_i$ at the surface of the spheres $S_a$. Various choices can be found in the literature. In the linearized APW method, the basis functions and their derivatives are continuous at the spheres. In the original APW method, as well as in the recent linearized APW method with local orbitals, the basis functions are only continuous at the spheres. Moreover, many authors proposed to use basis functions that are discontinuous at the spheres.

The boundary conditions are important to define the basis functions but also to define the Rayleigh quotient itself. If the functions and their derivatives are continuous, an integration by parts (or Green’s first identity) shows that the kinetic energy term of the Hamiltonian can be written in two equivalent forms:

$$- \int \phi_i^*(r) \Delta \phi_j(r) \, dr = \int (\nabla \phi_i(r))^* \cdot \nabla \phi_j(r) \, dr. \quad (2)$$

If the derivatives of the basis functions are not continuous, then the left-hand side (i.e. the Laplacian form) and the right-hand side (the gradient form) of equation (2) are generally different and the question is: which one (if any) is correct? Slater’s answer is “the second, more fundamental form is the correct one, as it is the one which directly enters the variation principle from which Schrödinger’s equation is derived”. Obviously, this is not a very convincing argument because the variational principle can be written with the kinetic energy in the Laplacian form as well as in the gradient form. Still, this argument (and practical success) has been up to now the only one to justify the use of the gradient form. If the basis functions are not continuous, additional terms are introduced but the method looses many of the attractive features of the standard APW approach.

The purpose of this paper is to show that the question of the boundary conditions in the APW method is not a matter of physical principles, but a well defined mathematical question with a precise answer which is: basis functions with discontinuous derivatives are valid if the gradient form is used and discontinuous basis functions should be employed with much caution because they do not allow for a correct variational principle.

To obtain this answer, we make a short trip in the mathematical theory of Hamiltonian operators. We first consider the fact that realistic Hamiltonians $H$ are defined on a subspace $D(H)$ of the Hilbert space called the domain of $H$. The Rayleigh-Ritz principle holds for basis functions in the domain of $H$. However, the domain of $H$ does not contain functions with discontinuous derivatives. To extend the possible basis functions, we use the form domain $Q(H)$ of $H$. We show that the Rayleigh-Ritz principle is still valid on $Q(H)$ if the gradient form of the kinetic energy is used. These results fully confirm Slater’s intuitions. Finally, we show that the Rayleigh-Ritz principle is not valid if the basis functions are not continuous. This implies a number of unpleasant consequences which show that discontinuous basis functions should be used with great care.
II. THE HAMILTONIAN AND ITS DOMAIN

It is sometimes thought that a Hamiltonian is a Hermitian operator $H$ defined on a Hilbert space $\mathcal{H}$ in the sense that for any $\phi, \psi$ in $\mathcal{H}$ we have $\langle H\phi | \psi \rangle = \langle \phi | H\psi \rangle$. This not true for realistic Hamiltonians. The Helling-Toeplitz theorem (ref. 12, p.25) tells us that an operator $H$ can satisfy $\langle H\phi | \psi \rangle = \langle \phi | H\psi \rangle$ for all $\phi, \psi$ in $\mathcal{H}$ if and only if the eigenenergies of $H$ are between a minimum and a maximum finite energy. Realistic Hamiltonians have a minimum energy (that of the ground state) but they have no maximum energy. From the physical point of view, a system represented by a Hamiltonian with a maximum energy would completely reflect photons or electrons above that energy. Experiment tells us that very high energy photons and electrons go through matter so such Hamiltonian is not realistic. From the mathematical point of view, the Hamiltonians made of a kinetic energy term plus a potential energy term that is periodic or go to zero at infinity (plus some regularity assumptions) has no maximum energy.

As a consequence, a realistic Hamiltonian $H$ is not defined on a Hilbert space $\mathcal{H}$ but on a subspace $D(H)$ of $\mathcal{H}$, called the domain of $H$, such that $H(\phi) \in \mathcal{H}$ for any $\phi \in D(H)$. We shall see that the question of the boundary conditions turns out to be a question concerning the domain of $H$.

A. Self-adjoint Hamiltonian

Since the difference between the Laplacian and the gradient forms comes from the kinetic energy, we shall take the example of $H = -\Delta$ in the Hilbert space of square integrable functions $L^2(\mathbb{R}^3)$. What is the domain of $H$? In fact, many domains are possible. Let us be very conservative and take the domain $D_{\text{min}}$ to be the set of infinitely differentiable functions with compact support (i.e. which are zero outside a bounded domain of $\mathbb{R}^3$). It is clear that $D_{\text{min}}$ is included in $L^2(\mathbb{R}^3)$ and that $H$ is well defined on $D_{\text{min}}$. However this is not the domain that we want because the domain of the adjoint of $H$ is not $D_{\text{min}}$.

The Hamiltonian $H$ with domain $D_{\text{min}}$ has the adjoint $H^\dagger$ with domain $D(H^\dagger)$ defined as follows (ref. 12 p.252). For any $\psi \in D(H^\dagger)$ and $\phi \in D_{\text{min}}$, $\int \phi^*(r)(H^\dagger \psi(r))dr = -\int (\Delta \phi(r))^* \psi(r)dr$. The function $\phi$ is smooth and with compact support, so the previous relation shows that $H^\dagger \psi(r) = -\Delta \psi(r)$ in the sense of distributions. As such, $\psi$ does not need to be continuous for $\Delta \psi(r)$ to have a meaning in the sense of distributions. But $H^\dagger$ is an operator from $\mathcal{H}$ to $\mathcal{H}$, therefore $\Delta \psi(r)$ must belong to $\mathcal{H}$. To summarize, the adjoint of $H$ with domain $D_{\text{min}}$ is the operator $-\Delta$ acting in the sense of distributions, and its domain is the set of square integrable functions $\psi$ such that $\Delta \psi$ is square integrable.

It can be shown that the domain of $H^\dagger$ is the second Sobolev space $W_2^2$ (ref. 13, p.55).

From this example, it is clear that the domain of $H$ and of $H^\dagger$ can be different. An operator is called self-adjoint when $H = H^\dagger$ and the domain of $H$ is equal to the domain of $H^\dagger$. We want self-adjoint operators because many properties that we take for granted in quantum physics (Rayleigh-Ritz principle, expansion over eigenstates, unitarity of $\exp(itH)$, etc.) are valid only for self-adjoint operators (ref. 12, p.256).

Is there a domain over which $H = -\Delta$ is self-adjoint? Yes, and this domain is unique, it is $W_2$ (ref. 12, p.54). This unicity is not general. For example, the radial Schrödinger operator

$$h = -\frac{d^2}{dr^2} - \frac{2}{r} \frac{d}{dr} + \frac{\ell(\ell + 1)}{r^2},$$

(3)

has only one self-adjoint domain when $\ell \neq 0$, but has a family of self-adjoint domains when $\ell = 0$ (technically, this is because the Laplacian is not essentially self-adjoint in a space of dimension $n < 4$, see e.g. p.129).

B. Rayleigh-Ritz principle

The importance of the self-adjoint domain $D(H)$ of $H$ for the APW method comes from the fact that, if $H$ is self-adjoint and bounded from below (i.e. has a ground state), then for any $n$-dimensional subspace $V$ of $D(H)$ with orthonormal basis $\phi_i$, the $k$-th eigenvalue $\lambda_k$ of the matrix $\langle \phi_i | H | \phi_j \rangle$ is larger than the $k$-th eigenvalue $E_k$ of $H$. Moreover, for realistic Hamiltonians, it can be shown that $\lambda_0$ converges to the ground state energy $E_0$ of $H$ as the dimension $n$ of $V$ increases (ref. 17 p.82). In favorable cases all the eigenvalues $\lambda_k$ converge to $E_k$. This happens in particular when the eigenvalues are discrete, which is the case of the Bloch energies $E_n(k)$ for a given Brillouin zone vector $k$.

In other words, if the basis functions $\phi_i$ belong to $D(H)$, the Rayleigh-Ritz principle gives an approximate ground state with an energy greater than the true ground state, and the approximate ground state converges to the true ground state by increasing the number of basis functions. This is exactly the properties we assume when using the Rayleigh-Ritz principle. It seems that the question of the boundary conditions is solved by determining which basis functions belong to $D(H)$. However, if the derivative of a basis function $\phi$ is not continuous at the sphere boundary, then the second derivative involved in the condition $\Delta \phi \in L^2(\mathbb{R}^3)$ brings a Dirac $\delta$ function at the sphere radius, and the square of the $\delta$ function is not defined, so $\Delta \phi$ does not belong to $L^2(\mathbb{R}^3)$. Therefore, for a basis function to be in $D(H)$, it must be continuous with continuous derivatives at the sphere boundary.

III. RELAXING THE BOUNDARY CONDITION

The previous result is disappointing because the condition of a continuous derivative at the boundary seems
much too strong. Many successful calculations of solid-state properties were carried out with basis functions that are only continuous at the sphere boundary. There should be a way to enlarge the domain of the basis function. This way exists, it is called the theory of quadratic forms (ref. [12] p.276).

A. Quadratic forms

We consider only the quadratic form associated with a self-adjoint operator $H$, and more precisely with $H = -\Delta$. This quadratic form is defined by

\[ Q(\phi, \psi) = \langle \phi | H | \psi \rangle = - \int \phi^*(r) \Delta \psi(r), \]  

(4)

for any $\phi$ and $\psi$ in $D(H)$. In general, $Q$ can be extended to a domain $Q(H)$ larger than $D(H)$. To increase the domain of $Q$ we rewrite the quadratic form as

\[ Q(\phi, \psi) = \int \nabla \phi^*(r) \cdot \nabla \psi(r). \]

(5)

The transformation from (4) to (5) is valid if $\phi$ and $\psi$ are in $D(H)$. Now the form (5) has a larger domain $Q(H)$ defined as the set of $\phi(r) \in L^2(\mathbb{R}^3)$ such that $\nabla \phi(r) \in L^2(\mathbb{R}^3)$. This is a Hilbert space called the first Sobolev space $W_1$ (ref. [14] p.50). This way of enlarging the domain of $Q$ is mathematically unambiguous: equation (5) defines a closable quadratic form on $D(H)$ and its (unique) closure is the quadratic form $Q$ given by equation (6) with domain $Q(H) = W_1$ (ref. [14] p.177).

B. Rayleigh-Ritz principle for quadratic forms

This extension of the domain of $H$ is interesting only if we can use the Rayleigh-Ritz principle. It is not difficult to show that this is the case. For any $n$-dimensional subspace $V$ of $Q(H)$ with orthonormal basis $\phi_i$, the $k$-th eigenvalue $\lambda_k$ of the matrix $\langle \phi_i | H | \phi_j \rangle$ is larger than the $k$-th eigenvalue $E_k$ of $H$. In favorable cases, $\lambda_k$ converge to $E_k$ by increasing the dimension of $V$.

We can now determine the regularity of the basis functions. If they are continuous at the sphere boundary, the derivative along the sphere radius has a step, which is a square integrable function. Therefore, the APW basis functions are in $Q(H)$ if they are continuous. We can even prove that they have to be continuous. This is done with Sobolev’s lemma (ref. [14] p.52). However, we must not consider the Sobolev space $W_1(\mathbb{R}^3)$ but the Sobolev space $W_1(\mathbb{R})$ because the use of radial wave functions transforms the three-dimensional gradient into a one-dimensional gradient. Inside sphere $S_\alpha$, the radial function is $f_{\text{Bessel}}(r\alpha)$ (see note [3]), outside this sphere an expansion of the plane wave over spherical harmonics shows that the radial function is proportional to the Bessel function $j_\ell(kr\alpha)$. We want the gradient of this radial function to be square integrable, so the radial function is in $W_1(\mathbb{R})$. Sobolev’s lemma tells us now that all functions of $W_1(\mathbb{R})$ are continuous, so the radial functions are continuous in $Q(H)$.

C. Realistic Hamiltonians

In the foregoing sections, we dealt only with the operator $-\Delta$, whereas interesting Hamiltonians have the form $H = -\Delta + V$, where $V$ is a real potential, which is smooth except for Coulomb singularities at the nuclei. In an atom or a molecule, $V$ goes to zero at infinity, in a crystal $V$ is periodic. It turns out that the addition of a potential does not modify our conclusions.

For an atom or a molecule, the potential $V$ is the sum of a finite number of Coulomb potentials plus a bounded and square integrable potential (e.g. the exchange and correlation potentials in the local density approximation to the density functional theory). For these potentials, $H$ is self-adjoint on the same domain as $-\Delta$ (ref. [14] p. 165). Thus, the Coulomb singularities do not change the domain. Moreover, the form domain is the same as that of $-\Delta$ (this is essentially because the difference between $D(H)$ and $Q(H)$ comes from the fact that the first one uses $\Delta \phi$ whereas the second one uses $\nabla \phi$, and this does not depend on $V$ if the singularities of $V$ are not stronger than the Coulomb potential). Therefore, the whole discussion is still valid for realistic Hamiltonians representing an atom or a molecule.

For a solid, similar results are available. If $\Omega$ is a primitive cell of the crystal, the Hilbert space $\mathcal{H}_k$ for the Brillouin zone vector $k$ is the set of functions $f(r)$ that are square integrable on $\Omega$ and satisfy the Bloch conditions $f(r + R) = \exp(i k \cdot R) f(r)$ and $\nabla f(r + R) = \exp(i k \cdot R) \nabla f(r)$, for any point $r$ on the surface of $\Omega$ and any lattice vector $R$ such that $r + R$ is also on the surface of $\Omega$ (ref. [14] p. 303). If $H(k)$ is the Hamiltonian $-\Delta + V$ acting on $\mathcal{H}_k$ and if the periodic potential $V$ is smooth except for a finite number of Coulombic singularities, the domain of $H(k)$ is the Sobolev space $W_2(\Omega)$, i.e. the set of functions $\phi$ of $\mathcal{H}_k$ such that $\Delta \phi$ is square integrable on $\Omega$. The Bloch conditions ensure that the quadratic form associated with $H(k)$ is

\[ Q(\phi, \psi) = - \int_\Omega \phi^*(r) \Delta \psi(r) + \int_\Omega \phi^*(r) V(r) \psi(r) \]

\[ = \int_\Omega \nabla \phi^*(r) \cdot \nabla \psi(r) + \int_\Omega \phi^*(r) V(r) \psi(r). \]

for any $\phi$ and $\psi$ in $D(H(k))$. Again the second expression for $Q$ can be extended to the form domain $Q(H(k)) = W_1(\Omega)$. Therefore, the whole discussion remains valid in the presence of a periodic potential and the basis functions must be continuous at the sphere boundary.
D. Discontinuous functions

We can try to further relax the boundary conditions and to take basis functions which are not continuous at the sphere boundary. This was proposed by a number of authors.10,11,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39

Among practitioners of APW methods, the prevailing opinion is that discontinuous boundary conditions are legitimate. For example, Shaughnessy and coll.40 state that “There is no a priori reason why the different forms of the basis functions, inside and outside the spheres, should match in either value or slope at the sphere surface”.

We saw that there is a good reason for using continuous basis functions. This ensures the validity of the Rayleigh-Ritz principle, from which we can deduce that to each state of the eigenvalue problem on the reduced vector space V corresponds a state of H, that the eigenvalues of the reduced problem are larger than the corresponding eigenvalue of H, and that convergence to the eigenvalues of H can be achieved by increasing the dimension of V.

One could be optimistic and hope that the Rayleigh-Ritz principle is still valid for discontinuous functions. However, such a hope is generally not fulfilled. This was shown by Brownstein,13 who investigated simple Hamiltonians H with discontinuous basis functions. He showed that discontinuity can lead to rather unpleasant consequences: (i) spurious states appear, for example states with energies smaller than the ground state of H, (ii) increasing the dimension of the reduced vector space V does not always improve the agreement with the true eigenvalues, (iii) the degeneracy of the states can be wrong. Moreover, when complex wavefunctions are used (this is necessary in band-structure calculations), some formulations give an energy which is a complex number.39 These phenomena are obviously quite dangerous when one tries to calculate (or predict) properties of matter and it seems reasonable that discontinuous basis functions are not used in practical implementations of the APW method. Of course, as shown by Brownstein, calculations using discontinuous basis functions can yield correct results in favorable cases. But no general principle ensures that the results of the computation are the correct energies and eigenstates of H.

IV. CONCLUSION

The results of this paper are clear-cut: for the Rayleigh-Ritz principle to be valid the basis functions have to be continuous at the sphere boundary and the gradient form of the kinetic energy operator has to be used.

However, the practical implementation of this condition looks suspect because the basis functions are expanded over spherical harmonics inside the spheres, up to a maximum angular momentum ℓmax. No finite expansion over spherical harmonics can match continuously plane waves outside the spheres. Therefore, the basis functions seem to be discontinuous. This is precisely what motivated Leigh14 to investigate the APW method with discontinuous basis functions.

In practice, the APW computer codes do not calculate the additional terms derived by Leigh to take the discontinuity into account, they use the equations for continuous basis functions and they truncate the basis. In mathematical terms, the basis functions are continuous but the Hamiltonian quadratic form Q is replaced by Qℓ which strips off from Q all spherical harmonics larger than ℓ inside the atomic spheres. In most applications we are only interested in a fixed number of lowest eigenvalues, and it is observed that the eigenvalues converge with ℓ. The standard physical argument for this is the fact that the kinetic energy term ℓ(ℓ + 1)/r2 becomes very large and hides the influence of the potential or of the energy.40 However, as far as I know, further mathematical work is required to rigorously confirm this.

Finally, we would like to come back to Slater’s intuition. We saw that the form domain is the correct set in which basis functions can be chosen. So we might reformulate Slater’s statement as “quadratic forms are more fundamental than self-adjoint operators”. This is confirmed by another property. We saw that a Hamiltonian H can have several domains over which it is self-adjoint. Only one of these domains is included in the form domain of the quadratic form corresponding to H (ref. 14 p. 177). Different domains correspond to different boundary conditions and therefore to different predictions of physical properties. It turns out that experimental results are given by the domain selected by the quadratic form.41 So it seems that, after all, Slater was right and that quadratic forms are indeed more fundamental.

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21 This can be understood by the following qualitative argument. If a function $\phi(r) = r^\alpha$ is such that $\Delta \phi(r)$ is square integrable, then $\alpha > 1/2$. Now $\phi(r)$ multiplied by a Coulomb potential has a singularity in $r^{\alpha-1}$ which is square integrable. Thus the Coulomb singularity does not restrict the domain of $H$.

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