Response to "Non-muffin-tin band theories of the multiple-scattering type"

R. G. Brown and M. Ciftan
Physics Department, Duke University, Durham, North Carolina 27706
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We respond to the preceding Comment by Faulkner by examining the convergence properties of functions used to represent solutions with Schrödinger's equation in the context of Green's-function band theory. Such evidence as exists on the subject is reviewed. The conclusion drawn is that the data presented in his Comment are sufficient to conclude that "a large fraction of the errors caused by ignoring the non-muffin-tin parts of a potential can be eliminated by the simple expedient of including the nondiagonal parts of the scattering matrix." However, the data presented do not warrant the conclusion that our theory is incorrect through the neglect or incorrect treatment of the "near field" or in any other manner. This is a question that must ultimately be resolved algebraically, but the data so far presented do not seem to be inconsistent with our theory being exact.

The evidence presented by Faulkner in the preceding paper[1] is too weak to warrant the conclusion that our theory[2] is incorrect. At this time we know of no algebraic errors in our derivation, and unless an error in the derivation can be demonstrated unambiguously, we shall continue to stand by our original work. However, it is entirely reasonable to expect our theory, if it is correct, to pass well-constructed numerical tests.

High-precision non-muffin-tin band theory is maturing as a field of investigation, largely due to the cornerstone works of researchers such as Evans and Keller,[3] Ziesche,[4] Williams and van W. Morgan,[5] and Faulkner.[6] It is perhaps time to reinvestigate, in light of the advances made in this field in the last decade or so, what kind of numerical performance we might expect from an exact band theory. It is incorrect to assume that a theory which is exact when expressed in terms of some infinite set of basis functions will necessarily produce better numerical results than the same theory expressed in a good approximation. Both theories become approximate in application because the basis is truncated and because of finite-precision arithmetic in computers.

In this Response we will examine three things. First, we will discuss the representation of solutions to Schrödinger's equation and the question of convergence. Second, we will address several points where we disagree with Faulkner and the reasons for that disagreement. Third, we will present the "nonvariational" derivation of our results in a highly abbreviated form. We omitted this from our original publication[2] in favor of using the Kohn variation[7] to make our derivation resemble, as closely as possible, that of Kohn and Rostoker.[8] As a consequence of this omission some confusion has arisen concerning our derivation for which we apologize. We hope that this derivation makes it clear that, while we prefer the variational approach for reasons detailed in Ref. 2, it is by no means essential to our theory, nor is its use in any way connected with our assertion that our results constitute a generalized solution to the band-structure problem.

When one compares two multiple-scattering solutions of the Schrödinger equation for the infinite crystal, one is at some level comparing how accurately the theories are capable of representing the crystal wave function inside the cell, i.e., one is comparing the basis functions in terms of which the solutions are expressed. (We use the term basis rather loosely throughout to refer to any expansion set that one uses as if it were a basis.) In order to compare the theories numerically, one must then examine the properties of these basis functions. The questions to be answered are the following: Can the basis functions be used to express any exact solution to the differential equation inside the cell (Schrödinger's equation), and can they be used to express any particular solution with given boundary conditions?

These are independent questions. A given set of representation functions (such as that of Williams and van W. Morgan), may be exact solutions to Schrödinger's equation throughout the cell and still be unable to represent correctly some particular solution with given boundary conditions. Alternatively, it is more common in physics to express a problem in terms of a set of functions that manifestly satisfy the boundary conditions for a given problem and then attempt approximately to satisfy Schrödinger's equations in the region of interest.

These questions are further complicated by the observation that a set of representation functions may converge rapidly at first toward the solution of a given boundary-value problem, but can still diverge from the correct solution (by no longer satisfying the differential equation or by departing from the specified boundary conditions), if carried out to a high-enough order. This possibility was commented upon by Ziesche in Ref. 4.

In this respect, at least, our theory is certainly sound. We prove in Ref. 2 that our basis is complete and uniformly convergent; the functions used by Faulkner in Ref. 1 to study our theory [his Eq. (15)], are manifestly so for the empty lattice. Specifically, they satisfy the differential equation, are able to represent an arbitrary (square-integrable) solution in the bounding sphere, and are rapidly convergent.

Faulkner, in Ref. 1, shows by means of examining the rms splitting in empty-lattice calculations that a large fraction of the errors caused by the muffin-tin approximation in a Green's-function band theory can be eliminated by the simple expedient of including the nondiagonal parts of the scattering matrix evaluated in an appropriate basis. While he does not offer any algebraic explanation of why this should be the case, we agree completely with this conclusion.

However, he attributes the rms splitting uniformly present in his cases 1–3 to the neglect of the "near field." Specifi-

cally he claims that "The only approximation . . . in case 1 in Table I is the neglect of the near-field corrections $N(E, \mathbf{k})$." This is not justified in his paper, either algebraically (which would still require a numerical estimate of the near-field correction), or numerically. He does not show us calculations from a theory that contains his near-field correction at all.

Furthermore, there are at least two approximations aside from the near field in his case 1. The scattering matrices required in all these theories are made finite by considering only those elements whose angular-momentum index is ≤ 4. While this is indeed a large number of l values for a Korringa-Kohn-Rostoker (KKR) calculation, this truncation of the basis functions used is certainly an additional approximation and introduces a rms splitting and mean error in the location of the band eigenvalues quite independent of any associated with neglect of a near field. In addition, there is a numerical error associated with the decomposition of the empty lattice potential, the integrations, and the matrix inversion.

Faulkner does not study the l convergence of the theories at all. Instead he uses Williams and van W. Morgan's results as a standard of convergence to justify his use of $l_{\max}=4$ in the scattered wave. He also uses their results, which he closely reproduces in case 1, as a standard of nonconvergence, i.e., as a measure of the near-field error. This seems to be inconsistent. Examining their results we question whether they justify either use.

Williams and van W. Morgan studied the numerical convergence of their technique extensively. They were attempting to gauge the residual errors introduced by truncating the expansion of the sharp "edge" of the empty cellular potential and by truncating their expansion of the scattered wave. They felt that these truncations would be the principal sources of error in their method.

Their results at $l_{\max}=4$ (in the scattered wave), were sufficiently accurate for them to conclude, with considerable numerical justification, that they had derived an exact theory.

Williams and van W. Morgan's results in the convergence study are reproduced in Fig. 1. We have converted their units to rydbergs to make them more easily comparable to Faulkner's dimensionless units. In these results, both the mean-energy error and the rms splitting strongly decrease as $l_{\max}$ in the scattered wave is increased from 0 to 4. There is no reason to assume from this graph that the error in both of these quantities will not continue to get smaller if $l_{\max}$ in the scattered wave is increased beyond 4. Williams and van W. Morgan also held this view: ". . . the inclusion of higher components in the wave function would decrease the errors appreciably."[5] If this were the case then Faulkner would be incorrect in attributing the remaining rms splitting to the near-field error.

This is, as far as we know, the only systematic study of convergence in high-precision band theories of this sort conducted to date. Its implication is clear: Even for the theory of Williams and van W. Morgan where an algebraic near-field error is known to exist, the actual energy error introduced by this near-field error may be much smaller than the truncation error at $l_{\max}=4$.

If this is the case, then our theory would actually be suspect if it did *not* produce approximately the same rms splitting of the eigenenergies as that observed by Williams and van W. Morgan, and later Faulkner. This possibility is

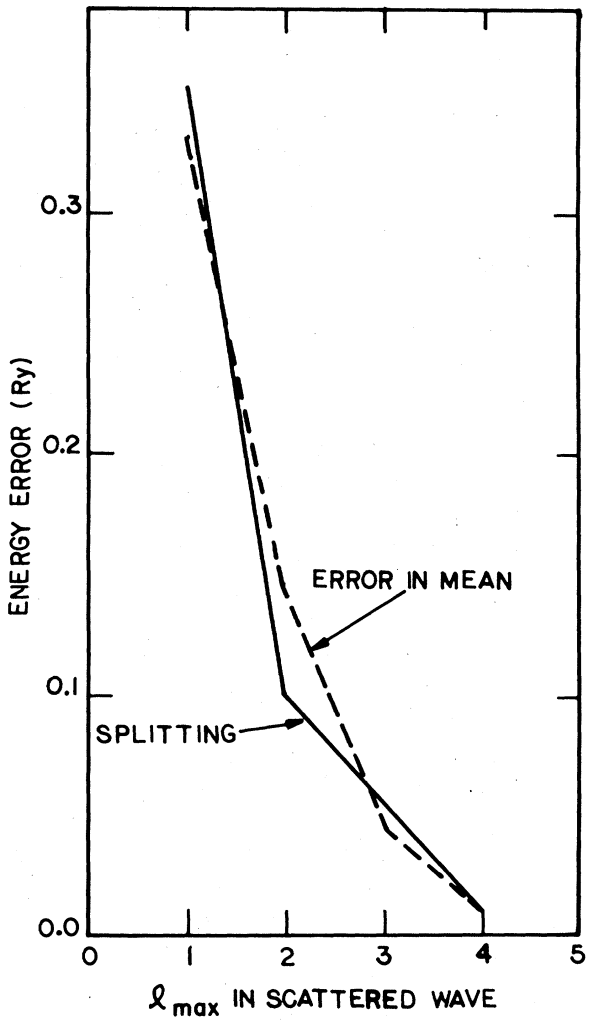

FIG. 1. This is Fig. 3 from Ref. 5. The highest l in the empty-lattice potential is eight, and its depth is 13.6 eV, or 1.0 Ry. The error in the mean and the splitting are still decreasing strongly as $l_{\max}$ is increased from 3 to 4. There is no reason to believe that the error will not continue to decrease as $l_{\max}$ is increased to, say, $l_{\max}=6$.

further supported by the uniformity of the rms splitting reported by Faulkner in his cases 1–3 in spite of very different ways of evaluating the near-field contribution. It is difficult to see how case 2, which is the "worst" approximation on the face of it, could produce the smallest rms splittings at three of the eight points studied if the near-field error were not smaller than the other sources of error uniformly present in all three numerical calculations.

We feel that the study conducted by Faulkner is inadequate to resolve the near-field error, even in those theories where it exists, from the truncation error. Since he did not present for comparison a theory that corrects for the neglect of the near field, his results do not study the near field at all. The sole conclusion that his numerical results seem to justify is that the bulk of the error introduced by the muffin-tin approximation is eliminated by including the off-diagonal elements of the scattering matrix for the cell.

Our derivation is based on our use of the correct basis

functions throughout the bounding sphere. The primary difference between our method (case 3) and the methods Faulkner presents as case 1 and case 2 is that the expansion of the exact solution to the empty-lattice problem, in terms of our basis functions, actually exists. In the other cases the basis functions do not span the space in which the solutions are known to lie (or if they do it has yet to be demonstrated); therefore it is unsurprising that they may require some correction factor.

On the other hand, the expansion functions used in case 1 and case 2 are able to represent the actual solution quite closely throughout most of the volume of interest (in fact all three basis sets are identical everywhere inside the muffin-tin sphere), and it is also not surprising that they get very good results. However, until the expansions used in all cases are sufficiently converged that the truncation and numerical error are strictly less than any method error, one will not be able to tell numerically just how large the correction factor required will be.

Faulkner makes, in his discussion, the statement, "The variational step that they [we] use . . . plays a different role from the one in Ref. 6 [Kohn and Rostoker]." This is incorrect. We use it in precisely the same manner that Kohn and Rostoker[8] used it when deriving the secular determinant of KKR band theory. Because some confusion has arisen as to whether the derivation of a Green's-function (or multiple-scattering) band theory can include a variational step as a means of extracting a secular determinant, we would like to note that our actual result is Eq. (3.21) on page 4573 (of Ref. 2), which is derived directly from the Lippmann-Schwinger equation for the infinite lattice.

Any method one prefers, including a straightforward projection against spherical harmonics such as that used by Kohn and Rostoker in their Appendix 1, can be used to obtain the same secular determinant [Eq. (3.27) on page 4573]. In fact, Faulkner himself notes that "it is not surprising that the results are identical with the ones that arise from the multiple-scattering equations" when discussing the Kohn variation on page 6189 of Ref. 6.

To elucidate this point we present the "nonvariational" derivation below. We follow precisely the same step (projection against a spherical harmonic), going from Eq. (3.21) [which is equivalent to Kohn and Rostoker's (A1.3)] to an equation equivalent to their (A1.4) from which (3.27) directly follows. This projection is allowed because our basis functions, and hence our solutions, are defined throughout the bounding sphere.

We begin with Eq. (3.21) from Ref. 2 [$L \equiv (l,m)$],

$$\sum_L \sum_{L'} J_{L'}(\mathbf{r}) \left[C^{\Omega}_{LL'}(\infty) + \frac{1}{\kappa} \sum_{L'} B_{L'L''} S^{\Omega}_{LL''}(\infty) \right] a_L = 0 .$$

We multiply through by a spherical harmonic and integrate over the sphere $r = r_{bs} - \epsilon$ where r_{bs} is the radius of the bounding sphere and let $\epsilon \to 0$. We obtain then a set of equations (indexed by L'),

$$\sum_L \kappa^{l'} j_{l'}(\kappa r_{bs}) \left[C^{\Omega}_{LL'}(\infty) + \frac{1}{\kappa} \sum_{L''} B_{L'L''} S^{\Omega}_{LL''}(\infty) \right] a_L = 0 .$$

Finally, we divide out the $\kappa^{l'} j_{l'}(\kappa r_{bs})$ from each equation to obtain our secular Eq. (3.27) below from which the secular determinant trivially follows.

$$\sum_L \left[C^{\Omega}_{LL'}(\infty) + \frac{1}{\kappa} \sum_{L''} B_{L'L''} S^{\Omega}_{LL''}(\infty) \right] a_L = 0 .$$

In order for this last step to be valid, $j_{l'}(\kappa r_{bs})$ must obviously be unequal to zero for each l'. This is the projective analog to the condition (3.25) derived in Ref. 2.

Williams and van W. Morgan's multiple-scattering derivation used precisely this method to obtain their secular determinant, but in their case it was not valid. Their basis functions are defined to be zero outside of the (central) cell; hence their Eqs. (2.10) and (2.11) are defined only for r restricted to the cell. At the step in their derivation where they obtain their secular equation by multiplying Eqs. (2.10) and (2.11) by a spherical harmonic and integrating over angles, the region of integration extends outside of the cell for r greater than the muffin-tin radius. The orthogonality relation for spherical harmonics cannot, therefore, be used at this point. However, a variational derivation like Kohn and Rostoker's can always be used, and yields (unsurprisingly), the same secular determinant as that previously obtained by Williams and van W. Morgan, with an associated consistency condition analogous to (3.25). It is for this reason that we prefer it.

On the other hand, Faulkner is quite correct in his statement that the introduction of a variational step will not help the convergence of a Green's-function or multiple-scattering theory of this kind. That is determined by the completeness and convergence properties of the functions used as a basis alone. Variation can give one information on the rate of convergence and it can ensure that one optimize one's use of a truncated basis, but it will not improve it. Variation cannot make a poor representation into a good one, in band theory or anywhere else. This point has been made before by Faulkner (in Ref. 6), and we agree with it wholeheartedly.

The phase-functional basis we use is demonstrably a complete and convergent basis within the bounding sphere (manifestly so in the case of the empty lattice). It is, in fact, a way of solving Schrödinger's equation for very general local potentials that is perhaps underexploited in physics today. It can be used to obtain bound-state energies, wave functions, and scattering states all within the same theory with orthogonality built in. It is the strength of this approach that we feel adds credence to our algebraic conclusion that our theory is exact.

In conclusion we would like to summarize our position. We do not feel that Faulkner's results study the near-field correction at all, and hence we cannot accept any of his conclusions concerning it. In particular we do not think that he has shown our work to be in error, either algebraically or numerically.

The issue here is not whether or not a near-field correction will improve the convergence of the theory; the question is whether or not a theory without a near-field correction will converge at all to the correct result. Clearly all of the methods studied by Faulkner as cases 1–3 are converging strongly to the correct result and there is no reason to assume from the results obtained to date that they would not continue to do so if l_{max} were increased.

To give Faulkner his due, we must admit that neither do his calculations support our contention that our method is exact. We agree that at some point, in some problem, our

method should be demonstrably better than the other methods. We do not feel that that point should necessarily have been reached in this calculation.

The conclusion that we feel his results best justify is his original one. The calculations (together with those of Williams and van W. Morgan), demonstrate that "a large fraction of the errors caused by ignoring the non-muffin-tin parts of the potential can be eliminated by the simple expedient of including the nondiagonal parts of the scattering matrix." Such a conclusion can only encourage further study into this fascinating problem, both in application to physically interesting cases and as a means to a deeper understanding.

Note added in proof. We have just completed an exhaustive numerical study of the empty lattice problem that compares our method to that of Williams and van W. Morgan. In particular, we study the convergence properties of the two high-precision theories at $l-\max$ in the scattered wave up to 6. Our results, summarized, show the following: First, the mean error term behaves quadratically in the depth of the potential, with small higher-order terms. Second, Faulkner's results can all be understood in terms of quadratic functions with approximately the same second derivatives that intersect at one point. If one draws two parabolas with this property one can easily see that one will be larger than the other on exactly half the real number line. Third, when the calculation is extended to $l-\max=6$, the rms errors resulting from the application of our method lie uniformly and consistently below those resulting from the method of Williams and van W. Morgan at the same two points in the band studied by Faulkner. This is because the second derivative of our error curve is smaller than theirs, hence our curve is flatter. Furthermore, the overall error, especially in the eigenenergies corresponding to low angular momenta, dramatically decreases as the higher-order scattering terms are included in both theories, indicating that they are both still strongly converging. From this we must conclude that the observed error in both theories, even at $l-\max=6$, still comes primarily from the truncation of the potential and/or the scattering matrix, not from the "near-field" error. We will present the numbers and graphs resulting from this study, as well as discuss the issue in greater detail, in a paper we are preparing for publication.

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