Reply to "Comment on 'Exact eigenvalue equation for a finite and infinite collection of muffin-tin potentials'"

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The assertions of the preceding Comment are shown to be without foundation and incorrect. Their conclusions are shown to rely on a misinterpretation of the literature including our work [Phys. Rev. B 37, 10 469 (1988)].

The authors of the preceding Comment[1] question the conclusion of our paper[2] that the common multiple-scattering treatment of the Schrödinger equation for muffin-tin (MT) potentials is not an exact result but an approximation. They do so on the grounds of (i) an appeal to authority and experimental data, (ii) what they call "general mathematical logic," and (iii) an attempt to locate algebraic errors in our derivation.

Before showing that all these arguments are unfounded, we briefly recall the issue in question, in particular the meaning of an "exact result." According to the postulates of quantum mechanics, a solution is exact if it (a) satisfies the Schrödinger equation, $(-\Delta+V)\Psi=E\Psi$, for the given potential, and if it (b) belongs to a certain Hilbert space. As is well known, the presence of the second derivative in condition (a) not only requires the continuity of the function Ψ everywhere but also that of its first derivative (otherwise the Hamiltonian would no longer be self-adjoint). For the case of a periodic potential the condition (b) requires square integrability over the unit cell and

$$\Psi(\boldsymbol{\rho}+\mathbf{R})=e^{i\mathbf{k}\cdot\mathbf{R}}\Psi(\boldsymbol{\rho}) , \tag{2a}$$

$$\nabla\Psi(\boldsymbol{\rho}+\mathbf{R})=e^{i\mathbf{k}\cdot\mathbf{R}}\nabla\Psi(\boldsymbol{\rho}) , \tag{2b}$$

on the boundary of the unit cell.

In our paper,[2] we found that the wave function obtained by the Korringa-Kohn-Rostoker (KKR) method—given as a multipole expansion around the center of a unit cell—can be matched continuously to the multipole expansion around the center of an adjacent cell, but at certain points (e.g., on the surface of the muffin-tin sphere) the derivatives do not match (cf., points C and F in Fig. 2 of Ref. 2). Therefore the KKR wave function fails to satisfy condition (a) identically everywhere, and we concluded that the KKR method is not exact in the sense of the definition above. We further showed that the equivalence can be restored if the KKR equation is supplemented with certain additional conditions, namely Eqs. (32) or (43) in our paper.[2]

In view of this definition of exactness, the suggestion[1] that the experimental results support the exactness of KKR is rather bizarre. Apart from the fact that MT potentials do not occur in nature, photoemission experiments can hardly answer questions about the continuity of the derivatives. In physics, one cannot live without approximations, and many of the most important and fruitful physical concepts have the word "approximation" in their very names: local-density approximation (LDA), coherent-potential approximation (CPA), random-phase approximation (RPA), and many others. Multiple-scattering theory (MST) and KKR are—as was repeatedly emphasized in our papers—extremely useful, important and reliable tools in solid-state physics, and their lack of exactness does not, in anyway, cast doubt on all band-structure calculations performed with use of the KKR method, augmented-plane-wave (APW) method, full-potential linear (APW) (FLAPW) method, and other methods known to provide excellent approximations to the exact solutions. (That these methods are approximate was demonstrated in the references[3–7] cited in the preceding Comment.) It does cast doubt on certain theories based on an imperfect treatment of MST and purporting to be generalizations thereof. Some of the "recent developments," whereof the Comment[1] cites a "representative sample" to support the exactness of MST, are devoted to such theories. The fact that these theories heavily contradict each other (for example, as regards the existence and nature of the so-called "near-field corrections") is rather a point against the exactness of MST.[8,9]

Similarly, the authorities to whom the preceding Comment[1] appeals, present the formal side of proofs which, as far as they go, are undoubtedly correct. They do indeed derive the (infinite set of) KKR equations from the original (integral or differential) eigenvalue equation but they do not show the converse, namely that the eigenvalue equation can be derived from the KKR equations. (That this cannot be done is the main point of our paper.) The question of sufficiency of the KKR equations and the question of the continuity of the derivative are not addressed in these papers, and there are no reasons why a necessary condition should automatically be sufficient, or why the continuity of a function should guarantee the continuity of the derivative.

The fallacy of the argument[1] that $2l+1$ equations in $2l+1$ unknowns have a unique solution that cannot satisfy further conditions is also apparent; these equations are not the KKR equations. They are an approximation to the infinite system of equations that constitute the KKR equation. Thus, the arguments in the preceding Comment called "general mathematical logic" (for which no proof is given) starts by misrepresenting (or misunder-

standing) our discussion about necessary versus sufficient conditions. As stated several times in our paper,[2] the KKR equation represents but a necessary condition that the (infinite number of) A_L coefficients must satisfy—not a necessary condition for solution of the Schrödinger equation. We demonstrated there that the KKR equations are not sufficient for finding the A_L coefficients; to do so requires specific boundary conditions. They are clearly not "extraneous." Clearly, the preceding Comment disregards the fact that we deal here with an infinite system of equations with an infinite number of unknowns, A_L. To see the difference in views, let the number of these coefficients be truncated at, say, n. Then our paper[2] maintains that the "n" equations ($n \to \infty$) determining these coefficients must consist in, say, n_1 equations expressing KKR conditions and, say, n_2 equations expressing the continuity of the derivative, with $n = n_1 + n_2$. In this language, the difference between the KKR approach and our approach is clear, while KKR always chooses $n_2 = 0$ and $n_1 = n$ (thus disregarding the matching of the derivative and keeping only the matching of the functions), we introduce $n_2 \neq 0$ (thus matching both the function and the derivative).

The preceding Comment asserts (again without proof) that they found algebraic mistakes in our paper. To support this broad charge, they claim as their only example that ". . . the second term in brackets in our Eq. 28(a) is potentially divergent . . . "[10] and illustrate this by introducing a simple potential that is a finite constant inside a sphere and zero outside. They then totally ignore or misunderstand the physics and mathematics of the variable-phase method (VPM) and all we said both before and after Eq. 28(a). They then proceed, contrary to our paper, to expand the Neumann function and interchange the order of integration and L summation—a procedure that produces a well-known divergence: from the properties of Bessel and Neumann functions, $\sum_L j_L(\mathbf{r}) n_L(\mathbf{r}')$ is finite if and only if $r < r'$. Now, the variable-phase-method[11] expression

$$\Phi_L(\mathbf{r}) = \sum_{L'} j_{L'}(\mathbf{r}) \left[\delta_{LL'} - \int_{r' \leq r} n_{L'}(\mathbf{r}') V(\mathbf{r}') \Phi_L(\mathbf{r}') \right] + \sum_{L'} n_{L'}(\mathbf{r}) \left[\int_{r' \leq r} j_{L'}(\mathbf{r}') V(\mathbf{r}') \Phi_L(\mathbf{r}') \right] ,$$

which always has $r' \leq r$, is still valid provided that the integration is carried out first—as is always done in our work. Thus there are no divergencies in Eq. (30) or otherwise in our paper because the phase—represented by the terms involving these integrals and denoted by $\Gamma^0_{LL'}$ and $\Sigma^0_{LL'}$ in our Eq. (31)—is always calculated first. The convergence of this procedure was established in detail long ago.[11]

Finally, one may question whether in their eagerness to prove us wrong, the authors of the preceding Comment have really read our paper. For example, they claim in their abstract that we provide a proof that MST "is valid in the limit in which the radius of the sphere vanishes (δ-function potential)." As any reader may verify, the only mention of a δ function in our paper occurs in Ref. 11 that defers this issue to the literature.

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[1] A. Gonis *et al.*, preceding Comment, Phys. Rev. B **41**, 10224 (1990).

[2] E. Badralexe and A. J. Freeman, Phys. Rev. B **37**, 10469 (1988).

[3] J. C. Slater, Ref. 9 in the preceding Comment (Ref. 1); T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967); J. M. Ziman, in *Solid State Physics,* edited by H. Ehrenreich *et al.* (Academic, New York, 1971), Vol. 26.

[4] J. C. Slater, Phys. Rev. **145**, 599 (1966).

[5] F. S. Ham and B. Segall, Phys. Rev. **124**, 1786 (1961).

[6] J. C. Slater, Phys. Rev. **92**, 603 (1953); H. Bross and H. Stohr, Phys. Lett. **8**, 25 (1964); H. Bross and K. H. Anthony, Phys. Status Solidi **22**, 667 (1967).

[7] Thus, in attempting to show that KKR and APW are equivalent, Morgan and also Ziman (Ref. 3) implicitly acknowledged that KKR is not an exact method since APW is known to contain an approximation. This was explicitly mentioned in Slater's original paper (Ref. 3) and also discussed in the well-known book of Loucks (Ref. 3). Basically, this approximation is manifested by a discontinuity of the derivative of the wave function across the MT sphere. Conversely, as emphasized by Slater (Ref. 4), such a discontinuity is also encountered in the KKR. This problem with the derivative was treated computationally long ago (Ref. 5): if the KKR wave function is matched at different radii (in the interstitial region) with a superposition of plane waves, then the results obtained are different. Moreover, various schemes to smooth the derivative in both APW and KKR have been devised (Ref. 6) but with a resulting large increase in computational complexity.

[8] R. Zeller, Phys. Rev. B **38**, 5993 (1988).

[9] Note that none of these theories managed to obtain support by giving a soluble case, or, as one of the authors of the preceding Comment (Ref. 1) put it in a recent paper (Ref. 8): "Only Badralexe and Freeman [in Phys. Rev. B **36**, 1376 (1987); **37**, 1067 (1988)] are able to prove analytically that their equations exactly reproduce the eigenvalue given by (1) (i.e., the case of constant periodic potential). For all other types of multiple-scattering equations, . . . only numerical investigations were possible."

[10] Whatever "potentially divergent" means, it is outside the range of mathematics, since a series is either divergent or convergent (on a certain domain).

[11] F. Calogero, *Variable Phase Approach to Potential Scattering* (Academic, New York, 1967); F. Calogero, Nuovo Cim. [Serie 9] **28**, 66 (1963); F. Calogero and J. M. Charap, *ibid.* **32**, 1665 (1964).