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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

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

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In a recent paper, Badralexe and Freeman purport to provide a "proof" to the effect that the multiple-scattering-theory treatment of waves propagating through a set of potential cells bounded by nonoverlapping spheres, muffin-tin potentials, is valid only in the limit in which the radius of the sphere vanishes (δ-function potentials). In particular, the authors claim that the well-known Korringa-Kohn-Rostoker method for determining the electronic structure of solids leads to a secular equation which is only approximately valid and cannot give the exact energy levels. It is the purpose of this paper to disprove this claim.

The study of electronic structure and related properties of condensed matter is based on methods of solving the Schrödinger equation for a given material, under the proper boundary conditions as imposed by the material's structure. One such method is that of multiple-scattering theory[1] (MST). Within the muffin-tin (MT) approximation to the crystal potential, various MST formalisms for determining the electronic structure of solid materials have been presented by a number of authors,[2–5] all leading to the same secular equation for the band structure. The best known and most widely used formulation is that of Korringa, Kohn, and Rostoker (KKR), which has met with great success in calculating electronic properties of metals[6] and of metallic alloys.[7] At least for the case of MT potentials, the formal validity of MST and of the secular equation of KKR in particular, has been explicitly verified in a number of published works.

(1) In 1965, Morgan[8] showed that the secular equation of KKR for determining the electronic structure obtained within MST is equivalent to that obtained within Slater's method of augmented plane waves[9] (APW).

(2) In 1977, Inglesfield[5] used a real $(\mathbf{r})$ -space matching condition on the Green's function and its derivative to obtain precisely the same secular equation.

(3) In quite a number of recent derivations (of which we cite only a small representative sample),[4,7,10–15] the validity and exactness of the KKR secular equation is either proven directly[4,7,10,11] or is easily established[12–15] if

the considerations given there are specialized to the case of MT potentials.

(4) A great number of experimental results[16] ranging in scope from photoemission studies to the determination of equilibrium lattice constants of metals and many of their alloys have been found in very good agreement with the results of electron-structure calculations based on the KKR secular equation. In contrast to these views, Badralexe and Freeman[17] (BF) have recently claimed that the secular equation of the KKR theory is only an approximation for the case of MT potentials. If the contention of BF were proven to be correct, it would cast doubt on nearly all electronic-structure calculations carried out thus far, not only those based on MST, but also on such formally equivalent[8] theories as the APW, or the more recently developed[18] full-potential linear APW (FLAPW). However, this contention can easily be shown to be wrong, both in terms of general mathematical logic and of specific algebraic manipulations.

First, let us note that while BF do establish the necessity of the familiar KKR secular equation, they question its sufficiency. The fact that this secular equation is necessary implies that it must at least include all solutions of the Schrödinger equation, and thus cannot be approximate, as BF claim. Furthermore, for a given angular momentum value, l, this secular equation yields $(2l+1)^2$ unique eigenvalues, thus precluding the occurrence of nonphysical solutions. This establishes that the KKR secular equation in the converged limit is both sufficient and necessary for determining the solutions of the Schrödinger equation. It follows that any further conditions imposed on the solutions of this secular equation, as done by BF, are either identically satisfied,therefore redundant, or incorrect.

In addition to introducing extraneous conditions, BF also commit algebraic errors in their formal presentations. For example, the sum over L in the second term inside the brackets of their Eq. (28a) is potentially divergent. To see this it suffices to consider a potential that is a finite constant inside a sphere and zero outside, provided that every point inside the sphere satisfies the condition specified in the integral in that equation, and the integrand does not change sign inside the sphere. Given the expansion properties[19] of Bessel and Neumann functions, the divergence follows immediately. Such divergences also appear in subsequent expressions, e.g., Eq. (30), implying that integrals and sums over L cannot be interchanged, and thus rendering any conclusions based on these expressions invalid.

The foregoing discussion disproves the case raised by BF against the validity of MST. In view of previous work, it emerges that in the MT approximation MST provides indeed a proper method for the solution of the Schrödinger equation for complex (multiatom) systems, and the calculation of the electronic structure of such systems.

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