UCRL-100171
PREPRINT

Comment on "Exact Eigenvalue Equation for a Finite and Infinite Collection of Muffin Tin Potentials"

A. Gonis, R. Zeller, P.H. Dederichs,
J.S. Faulkner, B.L. Gyorffy,
D.M. Nicholson, G.M. Stocks,
L. Wille and X.-G.Zhang

This paper was prepared for submittal to
Physical Review B: Solid State

Lawrence Livermore National Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

CIRCULATION COPY
SUBJECT TO RECALL
IN TWO WEEKS

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Comment on "Exact Eigenvalue Equation for a Finite and Infinite Collection of Muffin Tin Potentials"

A. Gonis[1], R. Zeller[2], P. H. Dederichs[2], J. S. Faulkner[3], B. L. Györffy[4], D. M. Nicholson[5], G. M. Stocks[5], L. Wille[3], X.-G. Zhang[6]

[1] Chemistry and materials Science, L-280, Lawrence Livermore National Laboratory, Livermore, CA 94550.

[2] Intitut für Festkörperforschung der Kernforschungsanlage, Postfach 1913, D-5170 Jülich, FRG.

[3] Department of Physics, Florida Atlantic University, Boca Raton, FL 33431-0991.

[4] H. H. Wills Physics Laboratory, University of Bristol, Bristol, UK.

[5] Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[6] Department of Physics and Astronomy, Northwestern University, Evanston, IL 60201.

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, a number of 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, J. G. Morgan [8] showed that the secular equation of KKR for determining the electronic structure obtained within MST is equivalent to that obtained within the method of augmented plane waves [9] (APW).

2. In 1977, J. Inglesfield [5] used a real (**r**-) space matching condition on the Green function 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 electronic 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 all electronic structure calculations carried out thus far, not only those based on MST, but also on such formally equivalent theories as the APW, or the more recently developed [18] full-potential linearized 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 $2l+1$ unique eigenvalues, thus precluding the occurrence of nonphysical solutions. This establishes that the KKR secular equation 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) diverges! To see this it suffices to consider a δ-function like potential, $V(\rho) = V\delta(\rho - \rho_0)$, with ρ_0 satisfying the condition $|\mathbf{r}| > |\mathbf{R} + \rho_0|$ as specified in the integral in that equation. 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), rendering any conclusions based on these expressions invalid.

The foregoing discussion disproves the case against the validity of MST raised by BF. 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 (multi-atom) systems, and the calculation of the electronic structure of such systems.

References

[1] Lord Rayleigh, *Phil. Mag. Str.* 5, 34, 481(1892).

[2] J. Korringa, *Physica* 13, 392(1947).

[3] W. Kohn and N. Rostoker, *Phys. Rev.* 94, 1111(1954).

[4] J. S. Faulkner, *Phys. Rev. B* 19, 6186(1979).

[5] J. E. Inglesfield, *J. Phys. C* 10, 3141(1977).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[7] B. L. Györffy and G. M. Stocks, in: *Electrons in Disordered Metals and Metallic Surfaces*, edited by P. Phariseau, B. L. Györffy, and L. Scheire, NATO ASI series B, Vol. 42 (Plenum, New York, 1979).

[8] J. G. Morgan, *Proc. Phys. Soc.* 89, 365(1966).

[9] J. C. Slater, *Phys. Rev.* 51, 846(1937).

[10] P. Ziesche and G. Lehmann, *Ergebnisse in der Elektronentheorie der Metalle* (Akademie-Verlag, Berlin, 1983).

[11] R. Zeller, *J. Phys. C* 20, 2347(1987).

[12] A. R. Williams and J. van W. Morgan, *J. Phys. C* 7, 37(1974).

[13] C. R. Natoli, M. Benfatto, and S. Doniach, *Phys. Rev. A* 34, 4682(1986).

[14] J. Molenaar, *J. Phys. C* 21, 1455(1988).

[15] R. G. Brown, *J. Phys. B* 21, L309(1988).

[16] Due to lack of space, we cannot attempt even a cursory listing of the great number of relevant works here.

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

[18] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* 24, 864(1981).

[19] M. Danos and L. C. Maximon, *J. Math. Phys.* 6, 766(1965).