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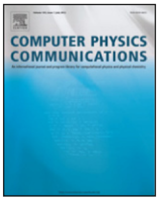

Fully-relativistic full-potential multiple scattering theory: A pathology-free scheme[☆]

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ABSTRACT

The Green function plays an essential role in the Korringa–Kohn–Rostoker (KKR) multiple scattering method. In practice, it is constructed from the regular and irregular solutions of the local Kohn–Sham equation and robust methods exist for spherical potentials. However, when applied to a non-spherical potential, numerical errors from the irregular solutions give rise to pathological behaviors of the charge density at small radius. Here we present a full-potential implementation of the fully-relativistic KKR method to perform *ab initio* self-consistent calculation by directly solving the Dirac differential equations using the generalized variable phase (sine and cosine matrices) formalism Liu et al. (2016). The pathology around the origin is completely eliminated by carrying out the energy integration of the single-site Green function along the real axis. By using an efficient pole-searching technique to identify the zeros of the well-behaved Jost matrices, we demonstrated that this scheme is numerically stable and computationally efficient, with speed comparable to the conventional contour energy integration method, while free of the pathology problem of the charge density. As an application, this method is utilized to investigate the crystal structures of polonium and their bulk properties, which is challenging for a conventional real-energy scheme. The noble metals are also calculated, both as a test of our method and to study the relativistic effects.

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1. Introduction

Multiple scattering theory (MST) underpins a number of widely used methods for solving the electronic structure problem in periodic solids, all of which have their origins in the KKR method originally introduced by Korringa [1] in 1947 and independently re-derived by Kohn and Rostoker [2] in 1953. Two features of MST distinguish it from the conventional Rayleigh–Ritz variational approaches. Firstly, it naturally yields a separation between the single-site potential scattering and structural arrangement (positions) of the individual scatterers. Secondly, in the framework of density functional theory (DFT), it provides an explicit expression for the Green function of the system, which can then be used to calculate the charge and spin densities without explicit calculation of the wavefunctions that are the focus of Rayleigh-Ritz methods. The availability of the Green function makes MST a versatile tool that can be easily combined with other methods to investigate more complex systems than periodic solids. For example, by applying the Dyson's series expansion to the Green function, defects and impurities in an otherwise perfect crystal can be investigated [3]. Another example is the KKR-CPA method, which is based on a combination of MST with the coherent potential approximation (CPA) [4–6] to calculate the configurationally averaged properties of disordered systems, such as random alloys [7,8] and the disordered local moment state of metallic magnets [9]. A more recent development is in the calculation of strongly correlated systems, where the MST Green function can be readily used in conjunction with the GW approximation [10] or the dynamical mean field theory (DMFT) [11]. Moreover, the real space formulation of MST [12] has demonstrated essentially ideal linear scalability on current supercomputing architecture [13], and, as a result, can be employed to study solid state systems with tens of thousands of atoms.

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The originally formulated MST solved the Schrödinger equation within the muffin-tin (MT) potential approximation, where the potential is assumed to be spherically symmetric within the muffin-tin spheres and constant in the interstitial region [1,2]. While the muffin-tin approximation generally works well for systems dominated by metallic bonding, it cannot properly describe a wide range of systems where the asymmetries of the effective potential [14] play an important role, such as surfaces, two-dimensional materials, and systems with directional covalent bonding. In addition, because the Schrödinger equation is nonrelativistic, it cannot properly describe systems where relativistic effects are important. In particular, it does not include spin–orbit coupling (SOC), a subject currently of great interest due to its role in a rich diversity of technologically important phenomena, such as magnetocrystalline anisotropy, Rashba effect, and magnetic skyrmions [15]. To take into account the relativistic effects, a common practice is to treat the relativistic kinematic effects with the scalar-relativistic approximation [16], and include SOC in a perturbative second-variational way. However, this strategy is problematic for heavy-element systems where SOC is not small compared to crystal field splitting. To take into account both relativity and the full shape dependence of the crystal potential on an equal footing, the original MST formulation must be extended to a full-potential, Dirac equation, based theory, and indeed much work has been done in this regard by a number of groups [17–23].

In MST the Green function is constructed from the regular and irregular solutions of the Kohn–Sham equations. In contrast to the MT scheme, a persistent problem in the standard implementation of the full-potential MST is that the numerical errors in the irregular solutions are very difficult to control near the origin [24]. As a result, the charge density calculated from the Green function exhibits pathologies which can extend to a sizable fraction of the muffin-tin radius. The practice employed by Huhne et al. [21] is to drop the non-spherical components of the potential within a cutoff radius r_{ns}. While this is a good approximation for the potential, unfortunately it requires extrapolations of the solutions and charge densities within r_{ns}. Therefore, near the nucleus, the charge density of the valence electrons no longer has the correct undulations, which hinders the accurate determination of the Hellmann–Feynman forces. As an improvement, a sub-interval technique is proposed in Ref. [25] to systematically reduce the numerical error by decreasing the step size when approaching the origin. This method requires significantly more grid points as r_{ns} decreases, and is less effective as l_{max} (angular momentum cutoff of the solutions) increases. In Ref. [26], a modified single-site Green function is proposed to avoid directly using the irregular solutions. However, the volume integral of the irregular solutions is still needed to construct the modified Green function.

In all the above methods, the energy integration of the Green function is carried out in the complex plane. A different strategy to overcome the pathology problem is to split the Green function into the single-site part and the back scattering part, and perform the integration of the single-site Green function along the real axis, while integrating the irregular solution free back scattering part in the complex energy plane. The key observation is that on the real energy axis, the irregular solutions (in the Oak Ridge-Bristol convention of the Green function [27]) make no contribution to the charge and spin densities, therefore can simply be ignored when real energy integration is taken. Although this method completely eliminates the pathology of charge density, it is not popular because the real energy integration is considered to be computationally expensive in the presence of sharp resonance states, and completely fails when shallow bound states exist. However, by making use of an efficient pole-searching algorithm proposed by one of the authors, Y. Wang, we find the real axis energy integration can actually be accomplished reliably and efficiently, with speed similar to the contour integration methods. Furthermore, unlike the unphysical poles due to inverse of the sine matrix [24], the poles obtained in our method directly correspond to the resonance and bound states of the single-atom potential, therefore are physical and numerically stable. Finally, because our method explicitly identifies both bound and virtual bound electron states, it provides an excellent framework for implementing schemes, such as LDA+U [28] and self-interaction correction (SIC) [29,30], aimed at correcting local approximations to the DFT for the effects of strong correlation.

In Section 2 we explain in detail how the poles of the single-site Green function can be used to facilitate the energy integration of the shallow bound states and the resonance states, with efficiency of this scheme demonstrated at the end. Details of our pole-searching technique are presented in Section 3. In Section 4, polonium is used as an example to demonstrate our method. The lattice constants, bulk modulus and crystal structures of Po are calculated from *ab initio* and compared with results from other methods. In Section 5, the density of states and bulk properties of copper, silver, and gold are calculated as a further test of our method and to quantify the increasing impact of relativistic effects.

2. Methods

The two physical quantities of most interest in the present context are the integrated density of states $N(E)$ and the charge density $\rho(\mathbf{r})$. In a typical *ab initio* DFT calculation, these quantities need to be evaluated at each self-consistent loop to determine the new Fermi energy and effective potential. In MST, the charge density is obtained from the energy integral of the retarded Green function $G^{\mathrm{R}}(E, \mathbf{r}, \mathbf{r}')$

$$\rho(\mathbf{r}) = -\frac{1}{\pi}\mathrm{Im}\ \mathrm{Tr}\int_{E_b}^{E_F} G^{\mathrm{R}}(E, \mathbf{r}, \mathbf{r})dE, \tag{1}$$

where E_b is the bottom of the valence band, E_F is the Fermi Energy. The integrated density of states (IDOS) is given by the energy integral of the density of states (DOS) $n(E)$

$$N(E) = \int_{E_b}^{E} n(E')dE', \tag{2}$$

and $n(E)$ is calculated from the volume integral of the retarded Green function

$$n(E) = -\frac{1}{\pi}\mathrm{Im}\ \mathrm{Tr}\int_{\Omega} G^{\mathrm{R}}(E, \mathbf{r}, \mathbf{r})d\mathbf{r}. \tag{3}$$

Since we always work with the retarded Green function, to simplify the notation, in the following, the retarded Green function is simply referred to as the Green function and is denoted by $G(E, \mathbf{r}, \mathbf{r}')$. The Green function is obtained by solving the Dirac–Kohn–Sham equation and the details have been presented in Ref. [17]. Note that to obtain $N(E)$ and $\rho(\mathbf{r})$, the integration along the real energy axis is required. Unfortunately, for bulk materials, the energy integration along the real axis turns out to be infeasible due to the dense set of poles in the multiple scattering Green function. One resolution of this problem is to carry out the integration along a contour in the complex energy plane [31], with the observation that the Green function is holomorphic except for poles at the bound states and a cut on the real axis starting at E_b. Because the DOS becomes increasingly smooth the further the contour is distorted into the complex plane, this method has been found to be very efficient. Indeed, deploying the Gaussian quadrature integration method, only a few dozen energy points are needed to reach a high accuracy. In practice, however, the implementation of the full-potential scheme is hindered by the presence of the irregular solutions in

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