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Citation: Chin. Phys. B . 2019, 28(8): 087101. **doi:** 10.1088/1674-1056/28/8/087101
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Electronic structure from equivalent differential equations of Hartree–Fock equations

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(Received 21 January 2019; revised manuscript received 29 April 2019; published online 9 July 2019)

A strict universal method of calculating the electronic structure of condensed matter from the Hartree–Fock equation is proposed. It is based on a partial differential equation (PDE) strictly equivalent to the Hartree–Fock equation, which is an integral–differential equation of fermion single-body wavefunctions. Although the maximum order of the differential operator in the Hartree–Fock equation is 2, the mathematical property of its integral kernel function can warrant the equation to be strictly equivalent to a 4th-order nonlinear partial differential equation of fermion single-body wavefunctions. This allows the electronic structure calculation to eliminate empirical and random choices of the starting trial wavefunction (which is inevitable for achieving rapid convergence with respect to iterative times, in the iterative method of studying integral–differential equations), and strictly relates the electronic structure to the space boundary conditions of the single-body wavefunction.

Keywords: Hartree–Fock equation, many-electron system, electronic structure

PACS: 71.10.–w, 71.15.–m **DOI:** 10.1088/1674-1056/28/8/087101

1. Introduction

Exactly solving the wavefunction of a quantum many-body system is the kernel task of several main branches of modern physics, such as that of nuclear structures in nuclear physics,[1,2] and that of the electronic structures of multi-electron atoms, molecules[3] and solids[4] in condensed matter physics. The difficulty in solving true/exact wavefunctions has promoted the progress of various approximation methods.[5–37] The Hartree–Fock (HF) equation is among the most widely used of these methods. Its kernel approximation is that the wavefunction of a many-fermion system can be expressed by the Slater determinant of the single-fermion wavefunction[5–7] as well as its various linear combinations.[8,9] Consequently, solving a multi-body wavefunction is simplified into solving the single-body wavefunction in a self-consistent field.

As an integral–differential equation, the HF equation is naturally attacked by the iterative method, the most popular method of solving integral–differential equations. Although this is a universal method, its efficiency is limited because achieving fast convergence of trial solutions with respect to the iterative times requires empirically and skillfully choosing the starting trial solution. If the convergence requirement is expressed as $\lim_{i\to\infty}|\psi_{i+1}(\psi_0)-\psi_i(\psi_0)|=0$ for any x, where ψ_0 is the initial trial function of variable x and ψ_i represents the derived function after the i-th iteration, one can find this requirement to be the uniform convergence requirement which is the most severe in various convergence requirements. Clearly, whether convergence can be reached is closely related to the starting trial solution ψ_0 which needs to be chosen empirically and randomly in order to rapidly converge with respect to the iterative times.

This difficulty promotes solution of the integral–differential equation through its corresponding partial differential equation (PDE). The merit of doing so is to avoid having to empirically and randomly choose the starting trial solution and instead relate a strict solution to the conditions for determining a solution. But such a corresponding PDE is often based on approximations. For example, in density functional theory (DFT),[10–16] the kernel approximation is to assume the integral term in the HF equation equals a summation of the products of single-body wavefunctions in finite number and hence transforms an integral–differential equation into a PDE with the same order (still a 2nd-order PDE). As shown below, if the single-body wavefunction is described with a PDE, the PDE should be at least 3rd-order, rather than 2nd-order.

Compared with the iterative method, the stricter method of solving the integral–differential equation solves its strictly equivalent PDE. For an integral–differential equation whose partial differential operator's maximum order is N, it should be mathematically equivalent to at least an $(N+1)$-th-order PDE. Therefore, the HF equation, the maximum order of whose differential operator is 2, should be mathematically equivalent to at least a 3rd-order PDE of the single-body wavefunction. In the following section, a strict theory indicates that the HF equation is equivalent to a 4th-order PDE.

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2. Theory and method

2.1. Main idea

The single-electron wavefunction in solids is identified by wavevector k. The HF equation of $\psi_k = |\psi_k| \exp(\mathrm{i}kr - \mathrm{i}E_k t)$ reads as

$$\begin{aligned} 0 = {} & \mathrm{i}\hbar\partial_t \ln\psi_k + \frac{\hbar^2}{2m_e}\left[\nabla^2 \ln\psi_k + (\nabla \ln\psi_k)^2\right] \\ & + \frac{e^2}{4\pi\varepsilon_0}\left[U_\mathrm{L} + U_\mathrm{c} + \frac{UX_k}{\psi_k}\right], \end{aligned} \tag{1}$$

where the two real-valued functions U_L and U_c satisfy the Poisson equations (Q_l and R_l are the charge and the position of the l-th ion) and the complex-valued function UX_k reads as

$$\begin{aligned} & \nabla^2 U_\mathrm{L} = \sum_l Q_l \delta(r - R_l), \\ & \nabla^2 U_\mathrm{c} = -\sum_k |\psi_k|^2, \\ & U_\mathrm{c}\psi_k + UX_k = -\int \frac{\psi_k(r')\, w^*(r')}{|r - r'|}\mathrm{d}^3 r' * w(r), \end{aligned} \tag{2}$$

where w is defined as $\sum_q \psi^*_{k+q}(r')\,\psi_{k+q}(r) = w^*(r')\,w(r)$. Here, because the summations over q and over $k+q$ are different expressions of the same object, w is k-independent. Besides the HF equation, each ψ_k also satisfies

$$\frac{\Omega}{4\pi^3} = \int_\Omega |\psi_k|^2 \mathrm{d}^3 r, \tag{3}$$

where $\Omega = a^3$ is the volume of a cell, a is the lattice constant, V_FS is the volume of the Fermi sphere, and $Ze * Qc$ is the total ionic charge per cell. Moreover, the $|\psi_k|$ are orthogonal to each other.

In DFT,[10–16] the exchange–correlation energy UX_k is assumed to be in a simple functional of n and ∇n, where n is the total electronic density and then each HF equation, which is an integral–differential equation of ψ_k, is approximated to be a differential one with the same order, *i.e.*, a 2nd-order PDE. As previously mentioned, if the single-body wavefunction is described with a PDE, the PDE should be at least 3rd-order, rather than 2nd-order.

Actually, it is unnecessary to depend on those assumptions for UX_k. There exists a strict and straightforward method of solving the HF equations. By denoting $|\psi_k|$ as $|\psi_k| = s_k * w$, we can re-write each HF as

$$\begin{aligned} 0 = {} & \frac{1}{2}\left[\frac{\nabla^2 s_k}{s_k} + 2\frac{\nabla s_k}{s_k}\cdot\frac{\nabla w}{w} + \frac{\nabla^2 w}{w}\right] \\ & - \frac{k^2}{2} + \mathrm{i}\frac{k\cdot\nabla[s_k w]}{s_k w} \\ & + \lambda\left[U_\mathrm{L} + \int \frac{s_k w^2 \mathrm{e}^{\mathrm{i}kr}}{|r - r'|}\mathrm{d}^3 r' \frac{1}{s_k \mathrm{e}^{\mathrm{i}kr}}\right] + E_k, \end{aligned} \tag{4}$$

where E_k is space-independent and also time-independent. All terms in this form belong to one of two classes: one is k-dependent and the other k-independent. The condition for an equation in such a form having solutions at any k-value is that all k-independent terms in Eq. (4) form a closed relation and the k-dependent terms are governed by a few k-independent terms, *i.e.*

$$0 = \frac{1}{2}\frac{\nabla^2 w}{w} + \lambda U_\mathrm{L} + E_0 + \beta r; \tag{5}$$

$$\begin{aligned} 0 = {} & \frac{1}{2}\left[\frac{\nabla^2 s_k}{s_k} + 2\frac{\nabla s_k}{s_k}\cdot\frac{\nabla w}{w}\right] - \frac{k^2}{2} + \mathrm{i}\frac{k\cdot\nabla[s_k w]}{s_k w} \\ & + \lambda\int \frac{s_k w^2 \mathrm{e}^{\mathrm{i}kr}}{|r - r'|}\mathrm{d}^3 r' \frac{1}{s_k \mathrm{e}^{\mathrm{i}kr}} + E_k - E_0 - \beta r, \end{aligned} \tag{6}$$

where E_0 is the corresponding atomic level of those extended-states and β is a constant $\neq 0$. Equation (5) is a 2nd-order linear PDE of w, and its solution is determined by a physical boundary condition $w|_{r=R_i} = 0$ which means the density of valence electrons at the cation position is 0. Moreover, the linearity of Eq. (5) can warrant $\int_\Omega w^2 \mathrm{d}^3 r = Qc$ to be satisfied easily by multiplying the solution of Eq. (5) by a constant.

Due to the $(1/r)$-dependent part of the operator $\partial_{rr} + (2/r)\partial_r$ in Eq. (5), $0 = \partial_r w|_{r=0} = w_1$ exists if $\beta = 0$. But the mathematical property of the isotropic part of U_L, or the fact that $1/\sqrt{1+\alpha r^2}$ is a power series of r^2, determines the expansion coefficients w_i of $w = \sum_{i\geq 0} w_i r^i$ as 0 for all odd i in the case of $\beta = 0$. This might be unable to warrant the physical boundary condition $w|_{r=R_i} = 0$ to be fulfilled when $\beta = 0$. In contrast, if $\beta \neq 0$, it is possible for $w_{2k+1\geq 3} \neq 0$ to appear, which is favorable for the fulfillment of the physical boundary condition.

After knowing the profile of the total particle density w^2 from Eq. (5), each $|\psi_k|$, or each "relative probability amplitude" $s_k = |\psi_k|/w$, can be solved from Eq. (6). The real part and the imaginary part of Eq. (6) yield

$$VC_k \sin(kr) - VS_k \cos(kr) = k\cdot\left[\frac{\nabla s_k}{s_k} + \frac{\nabla w}{w}\right] s_k, \tag{7}$$

$$VC_k \cos(kr) + VS_k \sin(kr) = -\left[M_k + \Delta E_k - \beta r\right] s_k, \tag{8}$$

where

$$\nabla^2 VC_k = \lambda s_k w^2 \cos(kr), \tag{9}$$

$$\nabla^2 VS_k = \lambda s_k w^2 \sin(kr), \tag{10}$$

$$M_k = \frac{1}{2}\frac{\nabla^2 s_k + 2\nabla s_k \cdot \nabla \ln w}{s_k}, \tag{11}$$

$$\Delta E_k = E_k - E_0 - \frac{k^2}{2}, \tag{12}$$

$$\lambda = \frac{\mathrm{e}^2 m_e\,[pm]}{4\pi\varepsilon_0\hbar^2} = \frac{0.0014}{0.076}. \tag{13}$$

Having obtained the expressions of VS and VC in terms of s_k and ΔE_k from Eqs. (7) and (8), we can substitute them into Eqs. (9) and (10) and have

$$\nabla^2\{-M_k s_k\cos(kr)+\sin(kr)(s_k k\cdot\nabla\ln[s_k w])\}-\lambda s_k w^2\cos(kr)=-k^2[\Delta E_k s_k-\beta r s_k]\cos(kr)$$
$$+\left[\Delta E_k\nabla^2 s_k-\beta\nabla^2(rs_k)\right]\cos(kr)-2[\Delta E_k k\cdot\nabla s_k-\beta k\cdot\nabla(rs_k)]\sin(kr)-\frac{2k}{r}[\Delta E_k s_k-\beta r s_k]\sin(kr), \quad (14)$$
$$\nabla^2\{-M_k s_k\sin(kr)-\cos(kr)(s_k k\cdot\nabla\ln[s_k w])\}-\lambda s_k w^2\sin(kr)=-k^2[\Delta E_k s_k-\beta r s_k]\sin(kr)$$
$$+\left[\Delta E_k\nabla^2 s_k-\beta\nabla^2(rs_k)\right]\sin(kr)+2[\Delta E_k k\cdot\nabla s_k-\beta k\cdot\nabla(rs_k)]\cos(kr)+\frac{2k}{r}[\Delta E_k s_k-\beta r s_k]\cos(kr). \quad (15)$$

Comparing the $\sin(kr)$-dependent terms, as well as the $\cos(kr)$-dependent terms, in Eqs. (14) and (15), we obtain 4 equations respectively for their $\sin(kr)$-dependent terms and $\cos(kr)$-dependent terms. The four equations are in fact 2 pairs and in each pair the two equations are the same because one is merely the other multiplied by a constant. Thus, we obtain two equations:

$$0=\nabla^2[-M_k s_k]+k^2[M_k s_k]+\frac{2k}{r}[s_k k\cdot\nabla\ln(s_k w)]+2k\cdot\nabla[s_k k\cdot\nabla\ln(s_k w)]-\lambda s_k w^2+\Delta E_k\left[k^2 s_k-\nabla^2 s_k\right]$$
$$-k^2\beta r s_k+\beta\nabla^2(rs_k), \quad (16)$$
$$0=2k\cdot\nabla[M_k s_k]+\frac{2k}{r}[M_k s_k]+2\Delta E_k k\cdot\nabla s_k+\frac{2k}{r}\Delta E_k s_k-k^2[s_k k\cdot\nabla\ln(s_k w)]+\nabla^2[s_k k\cdot\nabla\ln(s_k w)]$$
$$-2\beta k\cdot\nabla(rs_k)-\frac{2k}{r}\beta r s_k. \quad (17)$$

Here, we utilize the formulas

$$\nabla^2\sin(kr)=\left[-k^2\sin(kr)+\frac{2k}{r}\cos(kr)\right], \quad (18)$$
$$\nabla^2\cos(kr)=\left[-k^2\cos(kr)-\frac{2k}{r}\sin(kr)\right]. \quad (19)$$

Note that equations (16) and (17) are a 4th-order linear PDE set of s_k. Therefore, equation (3) can be easily satisfied by multiplying the solution of Eqs. (16) and (17) by a constant.

Equations (16) and (17) are of the same general form: $0=J0_{16}+J1_{16}\Delta E_k$ and $0=J0_{17}+J1_{17}\Delta E_k$, where $J0_{16,17}$ and $J1_{16,17}$ are space–time functions and ΔE_k is a space–time-independent constant satisfying $\nabla\Delta E_k=0$. In principle, equations (16) and (17) and $\nabla\Delta E_k=0$ can finally lead to a self-consistent higher-order PDE of s_k, whose solution can lead to a self-consistent value of ΔE_k. In the following subsection, we explain in detail how to derive self-consistently an electron structure from Eqs. (16) and (17) and $\nabla\Delta E_k=0$.

2.2. Detailed mathematics

Solutions of Eqs. (16) and (17) are determined by the boundary conditions $\{\nabla^{0\sim3}s_k|_{r=0}\}$. For the simplicity of symbols, we first present a detailed formula for the isotropic case where all quantities are (θ,ϕ)-independent. By introducing the power series expressions $s_k=\sum_{i\geq0}s_{k,i}r^i$ and $w=\sum_{i\geq0}w_i r^i$ and comparing terms proportional to r^i in Eqs. (16) and (17) order-by-order, we can find that equations (16) and (17) lead to a recurrence formula of $s_{k,i}$ (see later Eqs. (30) and (44)). Because the isotropic parts of ∇^4 and of $\nabla\nabla^2$ read as

$$\left[\partial_{rr}+\frac{2}{r}\partial_r\right]\left[\partial_{rr}+\frac{2}{r}\partial_r\right]=\partial_{rrrr}+\frac{4}{r}\partial_{rrr}, \quad (20)$$
$$\partial_r\left[\partial_{rr}+\frac{2}{r}\partial_r\right]=\partial_{rrr}+\frac{2}{r}\partial_{rr}-\frac{2}{r^2}\partial_r, \quad (21)$$

Equations (16) and (17) are of the same general form $0=H_2/r^2+H_1/r+H_0$, where $H_{2,1,0}$ are analytic functions of r. Note that equation (16) $0=HA_2/r^2+HA_1/r+HA_0$ does not contain any terms that are proportional to r^{-2} and hence $HA_2\equiv0$ exists. In contrast, the term $2k\cdot\nabla[M_k s_k]=k\nabla\nabla^2 s_k+2k\nabla[\nabla s_k\cdot\nabla\ln w]$ in Eq. (17) will have a contribution proportional to r^{-2}, *i.e.*, through $-k\cdot(2/r^2)\partial_r s_k$ in $k\nabla\nabla^2 s_k$. But another term $(2k/r)[M_k s_k]=(2k/r)\left[(1/2)\nabla^2 s_k+\nabla s_k\cdot\nabla\ln w\right]$ has an opposite contribution proportional to r^{-2}, through $(k/r)\cdot(2/r)\partial_r s_k$ in $(2k/r)\cdot(1/2)\nabla^2 s_k$. Therefore, equation (17) yields

$$\frac{HB_2}{r^2}\equiv-\frac{k}{2}\frac{2}{r^2}\partial_r s_k+\frac{k}{r}\frac{1}{r}\partial_r s_k=0. \quad (22)$$

Because of Eqs. (20) and (21), there exist

$$\frac{HB_1}{r}\equiv\frac{k}{r}\partial_{rr}s_k+\frac{k}{r}\frac{1}{2}\partial_{rr}s_k+\frac{k}{r}\Delta E_k s_k$$
$$+\frac{k}{r}\partial_r s_k\partial_r\ln w+\frac{k}{r}\partial_{rr}s_k+\frac{k}{r}\partial_r[s_k\partial_r\ln w]$$
$$\equiv\frac{5}{2}\frac{k}{r}\partial_{rr}s_k+2\frac{k}{r}\partial_r s_k\partial_r\ln w$$
$$+\frac{k}{r}\Delta E_k s_k+\frac{k}{r}s_k\partial_{rr}\ln w, \quad (23)$$
$$\frac{HA_1}{r}\equiv-\frac{1}{2}\frac{4}{r}\partial_{rrr}s_k-\frac{2}{r}\partial_r[\partial_r s_k\partial_r\ln w]$$
$$+\frac{k^2}{r}\partial_r s_k+\frac{2k^2}{r}[\partial_r s_k+s_k\partial_r\ln w]$$
$$-\Delta E_k\frac{2}{r}\partial_r s_k+\beta\frac{2}{r}s_k$$
$$\equiv-\frac{2}{r}\partial_{rrr}s_k-\frac{2\partial_{rr}s_k}{r}\partial_r\ln w$$
$$-\frac{2\partial_r s_k}{r}\left[\partial_{rr}\ln w-\frac{3}{2}k^2+\Delta E_k\right]$$
$$+\frac{2s_k}{r}\left[k^2\partial_r\ln w+\beta\right], \quad (24)$$

and

$$\begin{aligned}HB_0 \equiv & \frac{k}{2}\left[\partial_{rrr}s_k+2\partial_{rr}s_k\partial_r\ln w+2\partial_r s_k\partial_{rr}\ln w\right]+k\Delta E_k\partial_r s_k\\ & -k\frac{k^2}{2}\left[\partial_r s_k+s_k\partial_r\ln w\right]\\ & +k\frac{1}{2}\left[\partial_{rrr}s_k+\partial_{rr}\left(s_k\partial_r\ln w\right)\right]-2k\beta s_k-k\beta r\partial_r s_k\\ \equiv & k\{\partial_{rrr}s_k+\frac{3}{2}\partial_r\ln w\partial_{rr}s_k\\ & +\left[2\partial_{rr}\ln w+\Delta E_k-\frac{k^2}{2}-\beta r\right]\partial_r s_k\\ & +\left[\frac{1}{2}\partial_{rrr}\ln w-\frac{k^2}{2}\partial_r\ln w-2\beta\right]s_k\}, \end{aligned}\tag{25}$$

$$\begin{aligned}HA_0 \equiv & -\frac{1}{2}\partial_{rrrr}s_k-\partial_{rr}\left[\partial_r s_k\partial_r\ln w\right]\\ & +k^2\left[\frac{1}{2}\partial_{rr}s_k+\partial_r s_k\partial_r\ln w\right]\\ & +2k^2\left[\partial_{rr}s_k+s_k\partial_{rr}\ln w+\partial_r s_k\partial_r\ln w\right]-\lambda s_k w^2\\ & +\Delta E_k\left[k^2 s_k-\partial_{rr}s_k\right]+\beta r\left[\partial_{rr}s_k-k^2 s_k\right]+4\beta\partial_r s_k\\ \equiv & -\frac{1}{2}\partial_{rrrr}s_k-\partial_r\ln w*\partial_{rrr}s_k\\ & +\left[-2\partial_{rr}\ln w+\frac{5}{2}k^2-\Delta E_k+\beta r\right]*\partial_{rr}s_k\\ & +\left[-\partial_{rrr}\ln w+3k^2\partial_{rr}\ln w+4\beta\right]*\partial_r s_k\\ & +\left[2k^2\partial_{rr}\ln w-\lambda w^2+k^2\Delta E_k-\beta k^2 r\right]*s_k. \end{aligned}\tag{26}$$

Using the power series of $HA_1=\sum_i HA_{1,i}r^i$, HA_0, HB_1, and HB_0, we find that equations (16) and (17) lead to $0=HA_1|_{r=0}=HB_1|_{r=0}$, or $0=HA_{1,0}=HB_{1,0}$. Likewise, the fact that all terms that are proportional to r^0 in Eqs. (16) and (17) should be 0, leads to $0=HA_{1,1}+HA_{0,0}$ and $0=HB_{1,1}+HB_{0,0}$.

$0=HB_{1,0}$ and $0=HA_{1,0}$ read as

$$\begin{aligned}0 = & k\{5s_{k,2}+2s_{k,1}\partial_r\ln w|_{r=0}\\ & +\left[\Delta E_k+\partial_{rr}\ln w|_{r=0}\right]s_{k,0}\}, \end{aligned}\tag{27}$$

$$\begin{aligned}0 = & 6s_{k,3}+2\partial_r\ln w|_{r=0}s_{k,2}+\left[\partial_{rr}\ln w|_{r=0}-\frac{3}{2}k^2+\Delta E_k\right]s_{k,1}\\ & -\left[k^2\partial_r\ln w|_{r=0}+\beta\right]s_{k,0}, \end{aligned}\tag{28}$$

and $0=HA_{1,1}+HA_{0,0}$ and $0=HB_{1,1}+HB_{0,0}$ read as

$$\begin{aligned}0 = & \{6s_{k,3}+3\partial_r\ln w|_{r=0}s_{k,2}+\left[2\partial_{rr}\ln w|_{r=0}+\Delta E_k-\frac{1}{2}k^2\right]s_{k,1}\\ & +\left[\frac{1}{2}\partial_{rrr}\ln w|_{r=0}-\frac{1}{2}k^2\partial_r\ln w|_{r=0}-2\beta\right]s_{k,0}\}\\ & +\left\{\frac{5}{2}6s_{k,3}+4\partial_r\ln w|_{r=0}s_{k,2}\right.\\ & \left.+\left[3\partial_r\ln w|_{r=0}+\Delta E_k\right]s_{k,1}+\partial_{rrr}\ln w|_{r=0}s_{k,0}\right\}\\ = & 21s_{k,3}+7\partial_r\ln w|_{r=0}s_{k,2}\\ & +\left[2\partial_{rr}\ln w|_{r=0}+3\partial_r\ln w|_{r=0}+2\Delta E_k-\frac{1}{2}k^2\right]s_{k,1}\\ & +\left[\frac{3}{2}\partial_{rrr}\ln w|_{r=0}-\frac{1}{2}k^2\partial_r\ln w|_{r=0}-2\beta\right]s_{k,0}, \end{aligned}\tag{29}$$

$$\begin{aligned}0 = & \{-12s_{k,4}-6\partial_r\ln w|_{r=0}s_{k,3}\\ & -\left[4\partial_{rr}\ln w|_{r=0}+5k^2-2\Delta E_k\right]s_{k,2}\\ & +\left[3k^2\partial_r\ln w|_{r=0}-\partial_{rrr}\ln w|_{r=0}+4\beta\right]s_{k,1}\\ & +\left[2k^2\partial_{rr}\ln w|_{r=0}-\lambda w_0^2+\Delta E_k k^2\right]s_{k,0}\}\\ & +\{-48s_{k,4}-12\partial_r\ln w|_{r=0}s_{k,3}\\ & +\left[-8\partial_{rr}\ln w|_{r=0}+3k^2-\Delta E_k\right]*s_{k,2}\\ & +\left[-2\partial_{rrr}\ln w|_{r=0}+2k^2\partial_r\ln w|_{r=0}+2\beta\right]*s_{k,1}\\ & +2k^2\partial_{rr}\ln w|_{r=0}*s_{k,0}\}\\ = & \{-60s_{k,4}-18\partial_r\ln w|_{r=0}s_{k,3}\\ & +\left[-12\partial_{rr}\ln w|_{r=0}-2k^2+\Delta E_k\right]s_{k,2}\\ & +\left[5k^2\partial_r\ln w|_{r=0}-3\partial_{rrr}\ln w|_{r=0}+6\beta\right]s_{k,1}\\ & +\left[4k^2\partial_{rr}\ln w|_{r=0}-\lambda w_0^2+\Delta E_k k^2\right]s_{k,0}\}. \end{aligned}\tag{30}$$

Moreover, from Eq. (17), we can express ΔE_k as

$$\Delta E_k = -\frac{\left[C_0+C_1/r\right]}{\left[\partial_r s_k+s_k/r\right]}=-\frac{\left[rC_0+C_1\right]}{r\partial_r s_k+s_k},\tag{31}$$

where analytic functions C_0 and C_1 are defined as

$$C_0=\frac{HB_0}{k}-\Delta E_k*\partial_r s_k=\partial_{rrr}s_k+\frac{3}{2}\partial_r\ln w\partial_{rr}s_k+\left[2\partial_{rr}\ln w-\frac{k^2}{2}-\beta r\right]\partial_r s_k+\left[\frac{1}{2}\partial_{rrr}\ln w-\frac{k^2}{2}\partial_r\ln w-2\beta\right]s_k,\tag{32}$$

$$C_1=\frac{HB_1}{k}-\Delta E_k*s_k=\frac{5}{2}\partial_{rr}s_k+2\partial_r s_k\partial_r\ln w+s_k\partial_{rr}\ln w.\tag{33}$$

Thus, $\nabla\Delta E_k=0$ can be written as

$$0=-\frac{1}{2}\frac{\left[C_0+r\partial_r C_0+\partial_r C_1\right]*\left[r\partial_r s_k+s_k\right]-\left[rC_0+C_1\right]*\left[2\partial_r s_k+r\partial_{rr}s_k\right]}{\left[r\partial_r s_k+s_k\right]^2}\tag{34}$$

or

$$0=r^2\left[\partial_r C_0\partial_r s_k-C_0\partial_{rr}s_k\right]+r\left[\left(C_0+\partial_r C_1\right)*\partial_r s_k+\partial_r C_0*s_k-2C_0\partial_r s_k-C_1\partial_{rr}s_k\right]+\left[\left(C_0+\partial_r C_1\right)*s_k-2C_1\partial_r s_k\right].\tag{35}$$

Equation (35) requires its r^0-related part to equal 0:

$$0=\left[\left(C_0+\partial_r C_1\right)*s_k-2C_1\partial_r s_k\right]|_{r=0}=\left\{\left[\frac{7\partial_{rrr}s_k}{2}+\frac{7\partial_r\ln w}{2}\partial_{rr}s_k+\left(5\partial_{rr}\ln w-\frac{k^2}{2}-\beta r\right)*\partial_r s_k\right]*s_k\right\}_{r=0}$$

$$
\begin{aligned}
&+\left\{\left[\left(\frac{3\partial_{rrr}\ln w}{2}-\frac{k^2}{2}\partial_r\ln w-2\beta\right)*s_k\right]*s_k\right\}_{r=0}\{-[5\partial_{rr}s_k+4\partial_r\ln w\partial_r s_k+2\partial_{rr}\ln w*s_k]*\partial_r s_k\}|_{r=0}\\
&=\left\{\left[\frac{7}{2}\partial_{rrr}s_k+\frac{7}{2}\partial_r\ln w*\partial_{rr}s_k+\left(3\partial_{rr}\ln w-\frac{k^2}{2}\right)*\partial_r s_k\right]*s_k\right\}_{r=0}\\
&+\left\{\left[\left(\frac{3}{2}\partial_{rrr}\ln w-\frac{k^2}{2}\partial_r\ln w-2\beta\right)*s_k\right]*s_k*s_k\right\}_{r=0}\{-[5\partial_{rr}s_k+4\partial_r\ln w\partial_r s_k]*\partial_r s_k\}|_{r=0}. \qquad (36)
\end{aligned}
$$

This requirement leads to

$$
\begin{aligned}
0=&\,42s_{k,3}+7\partial_r\ln w|_{r=0}*s_{k,2}+\left[3\partial_{rr}\ln w|_{r=0}-\frac{1}{2}k^2\right]s_{k,1}-\left[\frac{3}{2}\partial_{rrr}\ln w|_{r=0}-\frac{1}{2}k^2\partial_r\ln w|_{r=0}-2\beta\right]s_{k,0}\\
&-10\frac{s_{k,1}}{s_{k,0}}s_{k,2}-4\frac{s_{k,1}}{s_{k,0}}s_{k,1}\partial_r\ln w|_{r=0}. \qquad (37)
\end{aligned}
$$

2.3. Main theoretical results

Equations (27)–(29) and (37) can lead to a close relation to ΔE_k and the boundary conditions

$$\{s_k|_{r=0},\partial_r s_k|_{r=0},\partial_{rr}s_k|_{r=0},\partial_{rrr}s_k|_{r=0}\}=\{s_{k,0},s_{k,1},2s_{k,2},6s_{k,3}\}.$$

Because of the formulas

$$h_1\equiv\partial_r\ln w|_{r=0}=\left.\frac{\partial_r w}{w}\right|_{r=0}=\frac{w_1}{w_0}, \qquad (38)$$

$$h_2\equiv\partial_{rr}\ln w|_{r=0}=\left.\frac{\partial_{rr}w}{w}\right|_{r=0}-\left.\left[\frac{\partial_r w}{w}\right]^2\right|_{r=0}=\frac{2w_2}{w_0}-\left[\frac{w_1}{w_0}\right]^2, \qquad (39)$$

$$h_3\equiv\partial_{rrr}\ln w|_{r=0}=\left.\frac{\partial_{rrr}w}{w}\right|_{r=0}-3\left.\frac{\partial_{rr}w\partial_r w}{w^2}\right|_{r=0}+2\left.\left[\frac{\partial_r w}{w}\right]^3\right|_{r=0}=6\frac{w_3}{w_0}-6\frac{w_2w_1}{w_0^2}+2\left[\frac{w_1}{w_0}\right]^3, \qquad (40)$$

we finally obtain a quadratic equation of ΔE_k as follows:

$$0=[\Delta E_k]^2+a_1*[\Delta E_k]+a_0, \qquad (41)$$

where

$$a_1=\frac{133-234h_1}{21h_1-42}k^2+\frac{42h_2+84h_1-(325/2)\beta-42h_1^2-5h_3}{21h_1-42}, \qquad (42)$$

$$
\begin{aligned}
a_0=&\,\frac{\frac{45}{4}h_1}{21h_1-42}k^4+\frac{14h_1h_2+225h_1^2-84h_1^3-(885/4)h_3+(555/2)\beta}{21h_1-42}k^2\\
&+\left\{\frac{-21h_1h_2^2+42h_1^2h_2-45h_1h_3+270\beta h_1-42h_1^2h_3-42\beta h_1^2}{21h_1-42}+\frac{+(105/2)h_2h_3-105\beta h_2}{21h_1-42}\right\}. \qquad (43)
\end{aligned}
$$

Equation (30) is the lowest-order version, or the $i=0$ version, of the recurrence formula

$$s_{k,i+4}=F\left(s_{k,i+3},s_{k,i+2},s_{k,i+1},s_{k,i},\Delta E_k,k^2,\beta\right). \qquad (44)$$

2.4. Feasibility of extension to more realistic anisotropic case

The same procedure can be extended to more realistic anisotropic cases. $U_{\rm L}$ is (θ,ϕ)-dependent,

$$U_{\rm L}=\sum_{m>=0}\sum_i\frac{Q_i}{\sqrt{r^2+R_i^2}}\left(\frac{2rR_i}{r^2+R_i^2}\right)^{2m}\kappa_i^{2m}, \qquad (45)$$

where

$$\kappa_i=\sin\theta\sin\theta_i\cos(\phi-\phi_i)+\cos\theta\cos\theta_i, \qquad (46)$$

$$\left[\frac{\cos\theta}{\sin\theta}\partial_\theta+\partial_{\theta\theta}+\frac{1}{\sin^2\theta}\partial_{\phi\phi}\right]\kappa_i=-2\kappa_i, \qquad (47)$$

$$\kappa_i^2+(\partial_\theta\kappa_i)^2+\left(\frac{1}{\sin\theta}\partial_\phi\kappa_i\right)^2=1, \qquad (48)$$

with w^2 being dependent on κ. Note that κ and the spherical harmonic function $\mathrm{Y}_1^{m=-1,0,1}$ satisfy a common equation

$$\left[\frac{\cos\theta}{\sin\theta}\partial_\theta+\partial_{\theta\theta}+\frac{1}{\sin^2\theta}\partial_{\phi\phi}\right]X=-2X.$$

Therefore, corresponding to the expression in Eq. (45), w and s_k have similar expressions $F=\sum_m FR_m(r)\,\kappa^m$. Namely,

when $U_{\rm L}$ is (θ,ϕ)-dependent, equation (4) will correspond to a set of equations, each of which is for all terms associated with κ^m. The radial coefficient function $s_{k,m}$ in each $s_k = \sum_m s_{k,m}(r)\,\kappa^m$ can be solved from this set, where $s_{k,m}(r) = \sum_i s_{k,m,i} r^i$. Note that those $\kappa^{m\geq 1}$-components should warrant

$$\int_\Omega s_{k,m}^2 \kappa^{2m>0}\,{\rm d}^3 r = 0.$$

Thus, for (θ,ϕ)-dependent $U_{\rm L} = \sum_m U_{{\rm L},m}(r)\,\kappa^{2m}$, we can solve, in a procedure similar to that presented previously, $s_{k,m,i}$ and $w_{m,i}$ from the κ^m-related terms of Eqs. (5) and (6).

3. Numerical results and discussion

Because an HF equation is a differential–integral equation, its Green function (GF) will contain infinite terms related to the unperturbed GF which is associated with a differential equation. Although many terms are small enough to be negligible, their number is so large that their summation is not negligible. Therefore, the GF of an HF equation is difficult to exactly solve. If the HF equation is approximated as a differential equation by making assumptions for UX_k, such as DFT,[10–21] it will be a troublesome task to verify the self-consistency of these assumptions because of a fundamental discrepancy: the differential equation that the single-body wavefunction satisfies should be at least 3rd-order, rather than the 2nd-order that the approximation assumes.

In contrast, our method does not require any assumption for UX_k. It is based on the inherent mathematical properties of the coupled HF equations under the same constraint condition and hence self-consistency can be warranted fully.

We use this method to calculate the 3d-band of a transition metal, *i.e.*, the dimensionless parameter is chosen to be $E_0 = -13.6/9 \times 76000$. Two elements of the body-centered cubic (bcc) crystal type and two elements of the face-centered cubic (fcc) type are chosen, and their lattice constants can be found in some typical textbooks.[38,39] Their 3d-bands all contain multiple electrons and hence ought to be studied by many-body methods. For the bcc type, the origin of the space coordinate frame is chosen to be located at the center of a face of the cell. For the fcc type, the origin is chosen to be located at the center of the cell. Obviously, applying LCAO to the 3d-band cannot warrant the HF equation to be satisfied, because the Hamiltonian of the molecule/solid is not a linear combination of the atomic Hamiltonian.

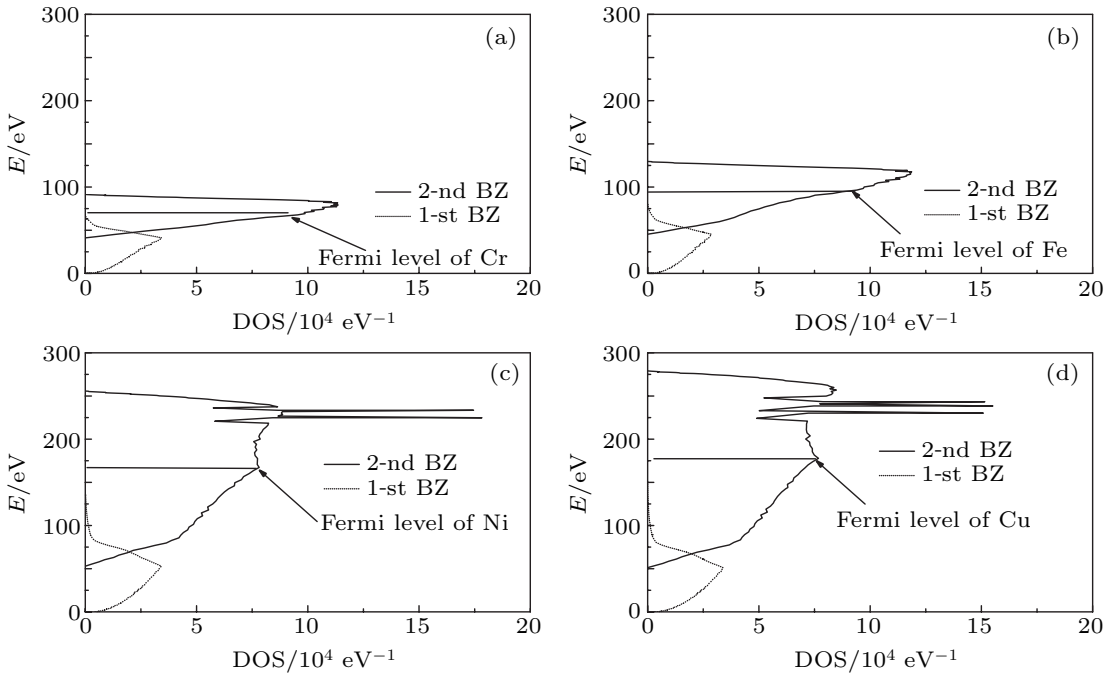


Fig. 1. DOS curves.

According to the solutions of Eqs. (41)–(43) in the case of $h_1 = 0$, ΔE_k is $\sim G + D/[(133/42)k^2 + G]$, where G and $D < 0$ are both constant. The curves of the density of states (DOS) are plotted in Fig. 1 and the Fermi level $E_{\rm F}$ is shown in Fig. 2. Because what is calculated in the present research is for approximate cases where $U_{\rm L}$ is taken as isotropic and non-magnetic, it is unrealistic to expect the calculated results to accord complet ely with experimental measurements. But figure 2 indicates that the density of states at the Fermi surface is nearly inversely proportional to the number of the 3d-valence. The DOS $(E_k = E_{\rm F})$ when the 3d-shell is half-filled is higher than the density of states when the 3d-shell is nearly completely filled. This is a qualitatively reasonable result for a non-magnetic Hamiltonian.

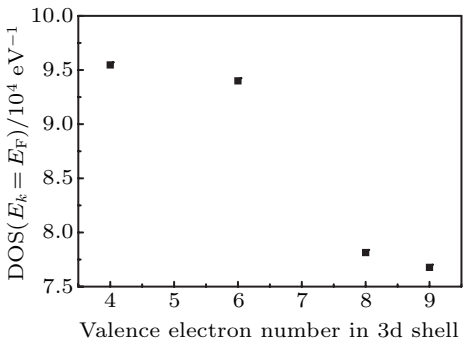


Fig. 2. Values of DOS at Fermi level.

4. Conclusions

Solving an integral–differential equation through its strictly equivalent PDE is stricter and more efficient than directly applying an iterative method to it. For the HF equation, that its Coulomb-type integral kernel function obeys the Poisson equation determines its equivalence to a 4th-order nonlinear PDE. According to the standard theory of the PDE,the solution of such a 4th-order PDE depends on its boundary conditions. Having converted the differential–integral equation into its equivalent higher-order differential counterpart according to the standard strict procedure described in the text, we can find that the equivalent differential equation contains "potentials" of space singularity $\sim 1/r$ and $1/r^2$. As shown in Eqs. (16) and (17), this space singularity will affect the allowed values of the space boundary conditions of an analytic wavefunction. By analyzing the allowed values of the space boundary conditions from Eqs. (22)–(26), we obtain a detailed formula reflecting the dependence of the wavefunction energy on the space boundary conditions of the wavefunction modulus, and finally obtain the dispersion relation of modulated plane-waves, which are the allowed solutions of the HF equation. This corresponds to a stricter method of calculating electronic structures within the framework of the single-electron problem.

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