Analysis of optimized effective potentials for multiplet states of 3d transition metal atoms

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Abstract. We apply the optimized effective potential method (OPM) to the multiplet energies of the 3d\textsuperscript{n} transition metal atoms, where the orbital dependence of the energy functional with respect to orbital wave function is the single-configuration HF form. We find that the calculated OPM exchange potential can be represented by the following two forms. Firstly, the difference between OPM exchange potentials of the multiplet states can be approximated by the linear combination of the potentials derived from the Slater integrals $F^2(3d, 3d)$ and $F^4(3d, 3d)$ for the average energy of the configuration. Secondly, the OPM exchange potential can be expressed as the linear combination of the OPM exchange potentials of the single determinants.

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1. Introduction

The density functional theory (DFT) has an important problem with the calculation of transition metal complexes. In spite of the recent development of the exchange-correlation functionals, it is difficult to evaluate the multiplet energies using the Kohn-Sham method, because these electronic structures are not always written in a single Slater determinant. Several methods have been proposed to calculate the multiplet energies using DFT. One of these methods has been proposed by Ziegler [26], Wood [24] and von Barth [25]. They have carried out the computation of the multiplet energies using the diagonal sum rule, in which the sum of the multiplet energies is equal to the corresponding sum of the single determinant energies. The method reproduces the multiplet energies of p electron system, but the method does not give correct multiplet energies for the d electron system. [4]

The time dependent density functional theory (TDDFT) has been recently developed to calculate excited states including the multiplet states. The method has been applied to p electron systems [23] within the adiabatic approximation. The non-adiabatic TDDFT calculation, in which the exchange-correlation kernel becomes frequency dependent, is still difficult.

Another method was formally discussed in the Görling’s paper [28] in which the energy functional depends on the multiplet states. They applied the optimized effective potential method to the calculation of the multiplet energies of p electron atoms. [14] The optimized effective potential method (OPM) was firstly proposed by Sharp and Horton [1]. The method was applied to the Neon and Carbon atoms by Talman et. al. [2]. Görling pointed out that OPM is formally regarded as DFT because the orbital dependent energy functional implicitly depends on the density [27]. The OPM potential can be evaluated by the singular integral equation called as the OPM equation. Talman et. al. [2, 5] and Engel et. al. [22] solved the one-dimensional OPM equation for an atom, in which the angular components of the OPM equation for an atom are integrated out using the spherical symmetry. To efficiently calculate the OPM potentials for atoms and molecules, Görling et. al. expanded the OPM potential using some base functions. [14, 15, 16, 21] The base expansion method gives the same total energy as calculated by Talman’s method. However, in the base expansion method, the OPM potential shows spurious oscillations. To solve the problem, some methods have been proposed but still are not applied to d electron atoms. [18, 19, 20]

An early work of OPM for the multiplet states is the OPM calculation by Aashamar [5] who applied OPM to the ground multiplet of the atom of which atomic number is less than 85. The OPM potentials for the p electron ground and excited state multiplets are calculated by Nagy [6] using the KLI method. [8, 9] Furthermore, Aashamar also applied OPM to the multiplet energies of p electron atoms using the multi-configuration HF form. [3] The total energies of the multiplet states have been discussed in these studies, but the potentials of the multiplet states are not presented. Sala and Görling have been developed the LHF method to approximately calculate the exchange only OPM
potential. Recently, the LHF method is extended to the open shell atoms and molecules. They applied the LHF method to the ground and excited multiplets of p electron atoms and molecules. However, in these papers, they did not treat the excited multiplet energies of the d electron atoms, which are difficult to calculate using the DFT. Furthermore, these studies give incorrect result caused by the approximation methods such as the KLI or the LHF method.

In the present paper, we apply OPM to the ground and excited state multiplets of the 3d\textsuperscript{n} electron atoms using the total energy functional of the single-configuration HF form. Following Talman and Engel, we solve the one-dimensional OPM equation correctly. The solution is considered to give the most reliable result among all the available methods. We show that the differences between the OPM potentials of the multiplet states can be approximated by the linear combination of the potentials derived from \( F^2(3d, 3d), F^4(3d, 3d) \) Slater integrals. We numerically show that the OPM exchange potential of multiplet state is approximated by the linear combination of the OPM exchange potentials of the single determinants.

2. Optimized Effective Potential Method

In the present paper, we calculate the OPM potential for eigenstates of a transition metal atom. Each state is characterized by a definite value of the total orbital angular momentum \( L \) and of the total spin angular momentum \( S \). These multiplet energies can be expressed as \( E^{L S, s} \), where \( s \) is the seniority number. The multiplet energy level is degenerate for possible directions of total momentums \( L \) and \( S \). Then, each multiplet wavefunction \( \Psi(L S L_z S_z, s) \) can be written as a linear combination of single Slater determinant functions \( \Phi(L_z S_z, \nu) \) which are not always eigenfunctions of the atom. \( L_z \) and \( S_z \) are \( z \) component of the total momentums \( L \) and \( S \), respectively, and \( \nu \) specifies different states with the same \( L_z \) and \( S_z \) component. Each total energy of the single determinant is represented as \( E^{L_z S_z, \nu} \).

Furthermore, we consider “average energy of the configuration” \( E^{av} \) defined by Slater. For the 3d\textsuperscript{n} multiplets, \( E^{av} \) is expressed as

\[
E^{av} = \frac{(10 - n)！n！}{10！} \sum_{LS, s}(2L + 1)(2S + 1)E^{LS, s}.
\]

To generally express these three kind of energies, \( E^{LS, s}, E^{L_z S_z, \nu} \) and \( E^{av} \), we introduce \( E^\xi \) where \( \xi \) stands for \{LS, s\}, \{LzSz, \nu\} and \{av\}. The total energy \( E^\xi \) is divided into the 1-body part \( E^\xi_1 \) and the 2-body part \( E^\xi_2 \);

\[
E^\xi = E^\xi_1 + E^\xi_2.
\]

The 1-body part is constructed from the kinetic energy of electrons and the electron-nucleus Coulomb energy.

\[
E^\xi_1 = \sum_i q_i I^\xi(n_i l_i),
\]
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\[ I^\xi(n_i,l_i) = \int P^\xi_{n_i,l_i}(r) L_i P^\xi_{n_i,l_i}(r) dr, \]  
\[ L_i = \left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{2r^2} - \frac{Z}{r}\right), \]

where \( q_i \) represents the number of the electrons in the orbital \( P^\xi_{n_i,l_i}(r) \). \( Z \) is the atomic number. \( n_i \) and \( l_i \) are the principal quantum number and the angular quantum number, respectively. In this study, we suppose that the OPM potential \( V^\xi_{OPM}(r) \) is spherically symmetric. The single electron orbital is determined by the following equation

\[ (L_i + V^\xi_{OPM}(r)) P^\xi_{n_i,l_i}(r) = \epsilon^\xi_i P^\xi_{n_i,l_i}(r), \]

where \( \epsilon^\xi_i \) is the single electron energy. \( P^\xi_{n_i,l_i}(r) \) is the product of the distance from the nucleus \( r \) and the radial component of the single electron wave function.

The 2-body part \( E^2_2 \) is composed of the electron-electron interaction energy expressed as

\[ E^2 = \frac{1}{2} \sum_{i,j,k} a^\xi_{ijk} F^k_\xi(ij) + \frac{1}{2} \sum_{i\neq j,k} b^\xi_{ijk} G^k_\xi(ij), \]

where the coefficients \( a^\xi_{ijk} \) and \( b^\xi_{ijk} \) depend on the multiplet states, the single determinants or the average energy of the configuration. The Slater integrals \( F^k_\xi(ij) \) and \( G^k_\xi(ij) \) are defined as

\[ F^k_\xi(ij) = \int dr \int dr' P^k_{n_i,l_i}(r) P^\xi_{n_i,l_i}(r) \frac{r^k_<}{r^k_>^{k+1}} P^k_{n_j,l_j}(r') P^\xi_{n_j,l_j}(r'), \]
\[ G^k_\xi(ij) = \int dr \int dr' P^k_{n_i,l_i}(r) P^\xi_{n_i,l_i}(r) \frac{r^k_<}{r^k_>^{k+1}} P^k_{n_j,l_j}(r') P^\xi_{n_j,l_j}(r'), \]

where \( r_< \) is the smaller of \( r \) , \( r' \) and \( r_> \) is the larger.

The OPM potential \( V^\xi_{OPM}(r) \) is determined by requiring that \( E^\xi \) be minimized for all \( P^\xi_{n_i,l_i} \) obtained from equation (6). This results in

\[ \frac{\delta E^\xi}{\delta V^\xi_{OPM}(r)} = \sum_i \int dr' \frac{\delta E^\xi}{\delta P^\xi_{n_i,l_i}(r')} \frac{\delta P^\xi_{n_i,l_i}(r')}{\delta V^\xi_{OPM}(r)} = 0, \]

where

\[ \frac{\delta E^\xi}{\delta P^\xi_{n_i,l_i}(r')} = 2q_i L_i P^\xi_{n_i,l_i}(r') + \frac{\delta E^2_2}{\delta P^\xi_{n_i,l_i}(r')} \]

Using equations (2),(3),(10), and the variation of the normalization condition \( \int P^\xi_{n_i,l_i}(r)^2 dr = 1 \) with respect to \( V^\xi_{OPM}(r') \), that is, \( \int P^\xi_{n_i,l_i}(r) \frac{\delta P^\xi_{n_i,l_i}(r)}{\delta V^\xi_{OPM}(r')} dr = 0 \), we can rearrange equation (10) as

\[ \sum_i \int dr' \left( 2q_i V^\xi_{OPM}(r) P^\xi_{n_i,l_i}(r') - \frac{\delta E^2_2}{\delta P^\xi_{n_i,l_i}(r')} \right) \frac{\delta P^\xi_{n_i,l_i}(r')}{\delta V^\xi_{OPM}(r)} = 0. \]

\[ (L_i + V^\xi_{OPM}(r)) P^\xi_{n_i,l_i}(r) = \epsilon^\xi_i P^\xi_{n_i,l_i}(r), \]
The functional derivative \( \frac{\delta P_{nili}^\xi(r')}{\delta \nu_{\text{OPM}}(r)} \) appeared in equation (10) is calculated using the perturbation theory:

\[
\frac{\delta P_{nili}^\xi(r')}{\delta \nu_{\text{OPM}}(r)} = -G_i^\xi(r, r') P_{nili}^\xi(r), \quad G_i^\xi(r, r') = \sum_{j \neq i} \frac{P_{njlj}^\xi(r') P_{nili}^\xi(r)}{\varepsilon_j^\xi - \varepsilon_i^\xi}. \tag{13}
\]

The functional derivative \( \frac{\delta E_i^\xi}{\delta P_{nili}^\xi(r')} \) in equation (12) is calculated as

\[
\frac{\delta E_i^\xi}{\delta P_{nili}^\xi(r')} = \sum_{jk} 2a_{ijk}^\xi X_k^\xi(jj, r') P_{nili}^\xi(r') + \sum_{jk} 2b_{ijk}^\xi X_k^\xi(ij, r') P_{nili}^\xi(r'), \tag{14}
\]

where \( X_k^\xi(ij, r) \) is defined as \( X_k^\xi(ij, r) = \int P_{nili}^\xi(r') P_{njlj}^\xi(r') \frac{r_k^\xi}{r_{\text{r}r'}} dr'. \) Substituting equations (13) and (14) into equation (12), we obtain

\[
\sum_i \int dr' \left( q_i V_{\text{OPM}}^\xi(r') - \sum_{jk} a_{ijk}^\xi X_k^\xi(jj, r') P_{nili}^\xi(r') \right) P_{nili}^\xi(r') G_i^\xi(r, r') P_{nili}^\xi(r) = \sum_i \sum_{jk} \int b_{ijk}^\xi X_k^\xi(ij, r') P_{njlj}^\xi(r') G_i^\xi(r, r') P_{nili}^\xi(r) dr'. \tag{15}
\]

Equation (15) is called as the OPM equation. The OPM potential can be obtained by self-consistently solving the OPM equation and the single electron equation (6).

### 3. Method of Calculations

To solve the OPM equation (15), we modified the code developed by Fischer et. al. \[31\]. For the calculation of the Green’s function, we use the following expression

\[
G_i^\xi(r, r') = P_{nili}^\xi(r >) Q_{nili}^\xi(r <) - P_{nili}^\xi(r') \Phi_{nili}^\xi(r) - P_{nili}^\xi(r) \Phi_{nili}^\xi(r'), \tag{16}
\]

where \( Q_{nili}^\xi(r) \) is the second solution of equation (6) satisfying \( \frac{dP_{nili}^\xi(r)}{dr} Q_{nili}^\xi(r) - \frac{dQ_{nili}^\xi(r)}{dr} P_{nili}^\xi(r) = 1 \), and

\[
\Phi_{nili}^\xi(r) = P_{nili}^\xi(r) \int_0^r P_{nili}^\xi(r') Q_{nili}^\xi(r') dr' + Q_{nili}^\xi(r) \int_r^\infty P_{nili}^\xi(r') P_{nili}^\xi(r') dr', \tag{17}
\]

with \( C_{nili}^\xi = \int P_{nili}^\xi(r) \Phi_{nili}^\xi(r) dr \). To evaluate \( P_{nili}^\xi(r) \) and \( Q_{nili}^\xi(r) \), we solve the single electron equation (6) using the Numerov’s method with the transformation \( h = \log(Zr) \) and \( P_{nili}(h) = P_{nili}(r)/\sqrt{r} \). The lower bound of \( h \) is set to -6.0 and the upper bound, which depends on the kind of atom, is set around 7. The step size \( \Delta h \) is 0.005. The integration in the OPM equation is approximated as the sum of the product of integrand and step size. Using this simple approximation with the step size \( \Delta h = 0.01 \), the OPM equation is approximated to the set of linear equations for...
the OPM potential. The OPM equation (15) determines the solution $V_{\xi}\text{OPM}(r)$ only up to a constant. The constant is fixed by the physical requirement $\lim_{r \to \infty} V_{\xi}\text{OPM}(r) = 0$. In our program, we fix the constant using the asymptotic form of the OPM potential $-\sum_k \int (a_{NNk}^\xi + b_{NNk}^\xi) \frac{P^\xi_{nNl}}{r_{k+1}} (r') dr'$ at $r = 9$ au, where $N$ is the index for HOMO.

In OPM, the single electron energy of HOMO $\epsilon_{\xi}\text{OPM}$ is equal to the HF single electron expectation value for HOMO $\epsilon_{\xi}\text{HF}$ [8]. In our results of the calculations for the 3d transition metal atoms, the differences between the single particle energies ($|\epsilon_{\xi}\text{OPM} - \epsilon_{\xi}\text{HF}|$) are less than 0.005 au.

4. Results and Discussions

The OPM exchange potential $V_{\xi}\text{ex}(r)$ is defined by subtracting spherical average of the Coulomb potential from the OPM potential $V_{\xi}\text{OPM}(r)$:

$$V_{\xi}\text{ex}(r) = V_{\xi}\text{OPM}(r) - \int \frac{\rho^\xi(r')}{r} dr',$$

where the radial density $\rho^\xi(r)$ is defined as

$$\rho^\xi(r) = \sum_i q_n P_{n_i}^\xi(r)^2.$$

Firstly, we apply OPM to the average energy $E_{\text{av}}^\xi$ defined by equation (1). The average OPM potential $V_{\text{av}}^\xi\text{OPM}(r)$ and average single electron orbital $P_{n_i}^\text{av}(r)$ are obtained by the self-consistent solution of the OPM equation (15) and the single electron equation (6). The average radial density $\rho_{\text{av}}(r)$ is calculated using equation (19). In DFT, the exchange energy is expressed as $E_{\text{DFTex}}[n(r)]$ where $n(r)$ is an electron density. To calculate averaged DFT potential, we used spherical averaged density $\rho_{\text{av}}(r)/4\pi r^2$ denoted as $n_{\text{av}}(r)$. Then, the average energy for DFT is defined as

$$E_{\text{DFT}}^\text{av} = \sum_i q_i I_{\text{av}}(n_i) + \int \frac{n_{\text{av}}(r)n_{\text{av}}(r')}{|r - r'|} d\mathbf{r} d\mathbf{r'} + E_{\text{DFTex}}[n_{\text{av}}(r)].$$

The average density is calculated by the self-consistent solution of the Kohn-Sham equation with spherical exchange potential $\frac{\delta E_{\text{DFTex}}[n_{\text{av}}(r)]}{\delta n_{\text{av}}(r)}$.

In the bottom part of figure 11 we show the X$\alpha$ exchange potential ($\alpha = 2/3$), the Becke’s GGA (B88) exchange potential [29], and the OPM exchange potential $V_{\text{av}}^\xi\text{ex}(r)$ of Mn$^{2+}$. The OPM exchange potential is close to the X$\alpha$ and B88 exchange potential. The B88 exchange potential diverges at the nucleus, whereas the OPM exchange potential does not diverge.

The radial density $\rho_{\text{av}}(r)$ is shown in the top part of figure 11. There are some kinks in the OPM exchange potential. The positions of the kinks correspond with the positions of troughs in the radial density. The kinks in the B88 exchange potential are
smoother than that in the OPM exchange potential. For the $X\alpha$ potential, the kinks are not appeared.

In table 1, we show the average total energies (Equation (11)) using HF method and OPM. The average total energy of DFT (Equation (20)) using $X\alpha$ and Becke’s GGA (B88) exchange functional is also tabulated in table 1. The total energy of the OPM method is more closer to the HF total energy than that of the B88 and $X\alpha$. The difference between the HF and OPM energies is order of 0.005 au throughout the transition metals.

Secondly, we discuss the OPM exchange potentials for the 3d$^n$ multiplet states. The 2-body part of the total energy of an atom (equation (7)) can be represented as the linear combination of $F^k_(\xi)(ij)$ and $G^k_(\xi)(ij)$. For the 3d$^n$ multiplet states, the coefficients $a^\xi_{3d,3d,2}$ and $a^\xi_{3d,3d,4}$ depend on the multiplet states, while the other coefficients do not. Therefore, the 2-body part of the total energy is expressed as

$$E^\xi_2 = E^\xi_0 + a^\xi_{3d,3d,2}F^2_(\xi)(3d,3d) + a^\xi_{3d,3d,4}F^4_(\xi)(3d,3d),$$  \tag{21}

where $E^\xi_0$ is the 3d$^n$ multiplet independent part of 2-body energy.

Since $E^\xi_2$, $F^\xi_0(ij)$ and $E^\xi_0$ are functionals of density $n^\xi(r) = \rho^\xi(r)/4\pi r^2$, we can define the potential for $E^\xi_2$, $F^\xi_0(ij)$ and $E^\xi_0$ as $V^\xi_2(r) = \frac{\delta E^\xi_2}{\delta n^\xi(r)}$, $V^\xi_0(ij)(r) = \frac{\delta F^\xi_0(ij)}{\delta n^\xi(r)}$ and $V^\xi_0(r) = \frac{\delta E^\xi_0}{\delta n^\xi(r)}$, respectively. In the following, we derive the equation to determine these potentials. We define $E^[\xi][P^\xi_{n,l,i}]$ as a general expression of $E^\xi_2$, $F^\xi_0(ij)$ and $E^\xi_0$. The corresponding potential is defined as $V^\xi_0 = \frac{\delta E^\xi}{\delta n^\xi(r)}$. From equation (3), the single electron orbital $P^\xi_{n,l,i}$ is considered to be a functional of $V^\xi_0$. Furthermore, we regard $V^\xi_0$ as a functional of $n^\xi$. Following chain rule of functional derivate, we get

$$V^\xi_0(r) = \int dr' \int dr'' \sum_i \frac{\delta E^\xi[P^\xi_{n,l,i}]}{\delta n^\xi(r')} \frac{\delta P^\xi_{n,l,i}(r')}{\delta V^\xi_0(r'')} \frac{\delta V^\xi_0(r'')}{\delta n^\xi(r')}. \tag{22}

$$

Multiplying the both sides of equation (22) by $\int dr \frac{\delta n^\xi(r)}{\delta V^\xi_0(r'')}$, and integrating the right-hand side over $r$ and $r''$, we obtain

$$\int dr \sum_i 2q_i P^\xi_{n,l,i}(r) \frac{\delta P^\xi_{n,l,i}(r)}{\delta V^\xi_0(r')} \frac{\delta V^\xi_0(r')}{\delta n^\xi(r)} = \int dr' \sum_i 2q_i P^\xi_{n,l,i}(r') \frac{\delta P^\xi_{n,l,i}(r')}{\delta V^\xi_0(r')} \frac{\delta V^\xi_0(r')}{\delta n^\xi(r')}, \tag{23}

$$

where we used the following relation: $\int dr \frac{\delta n^\xi(r)}{\delta V^\xi_0(r'')} = \int dr \sum_i 2q_i P^\xi_{n,l,i}(r) \frac{\delta P^\xi_{n,l,i}(r)}{\delta V^\xi_0(r')} \frac{\delta V^\xi_0(r')}{\delta n^\xi(r')}$. If we substitute $E^\xi_2$ for $E^[\xi][P^\xi_{n,l,i}]$ in equation (23), we get the OPM equation (12). Furthermore, if we substitute $F^\xi_0(ij)$ and $E^\xi_0$ for $E^[\xi][P^\xi_{n,l,i}]$, equation (23) defines the potential $V^\xi_0$ and $V^\xi_0$, respectively. Since equation (23) defines $V^\xi_0(r)$ only up to a constant, we set the boundary condition $\lim_{r \to \infty} V^\xi_0(r) = 0$. Equation (23) is solved using the method described in section 3

Functional derivative of equation (21) with respect to $n^{LS,s}(r)$ leads the decomposition of the OPM potential for the multiplet state $V^{LS,s}_{OPM}(r)$:

$$V^{LS,s}_{OPM}(r) = \frac{\delta E^\xi_2}{\delta n^{LS,s}(r)} = V^{LS,s}_{E_0}(r) + a^{LS,s}_{3d,3d,2}V^{LS,s}_{F^\xi_0}(3d,3d) + a^{LS,s}_{3d,3d,4}V^{LS,s}_{F^\xi_0}(3d,3d). \tag{24}

$$
In the top part of figure 2 we show the radial density $\rho^{LS,s}(r)$ of each multiplet states of V$^{2+}$. In the bottom part of figure 2 we display the difference of the radial density $\rho^{LS,s}(r) - \rho^{\text{av}}(r)$. Comparing the top and the bottom parts of figure 2, we find that the difference between the radial densities of the multiplet states are much smaller than the radial densities. So we neglect the difference of the radial components $\rho$ and substitute $V^\text{av}_{F_{3d,3d}}(r)$ for $V^{LS,4}_{F_{3d,3d}}(r)$ and $V^{LS,2}_{F_{3d,3d}}(r)$ in equation (24), respectively. The difference between the OPM exchange potential for the multiplet states $V^{\text{ex},LS,s}(r)$ and that for the average energy $V^{\text{ex},\text{av}}(r)$ can be approximated as a linear combination of $V^{\text{ex},\text{av}}_{F_{3d,3d}}(r)$ and $V^\text{av}_{F_{3d,3d}}(r)$:

$$V^{\text{ex},LS,s}(r) - V^{\text{ex},\text{av}}(r) \simeq \left(a^{LS,s}_{3d,3d,2} - a^{\text{av}}_{3d,3d,2}\right)V^{\text{av}}_{F_{3d,3d}}(r)$$

$$+ \left(a^{LS,s}_{3d,3d,4} - a^{\text{av}}_{3d,3d,4}\right)V^\text{av}_{F_{3d,3d}}(r). \quad (25)$$

Neglecting the multiplet dependence of the orbital, we can replace the orbital $P^\xi_{n_i,l_i}$ in equation (4) and (21) to $P^\text{av}_{n_i,l_i}$. Then, the 1-body and 2-body energies are approximated as

$$E^\xi_1 \simeq E^\text{av}_1 = \sum_i q_i I^{\text{av}}(n_i,l_i)$$

$$E^\xi_2 \simeq E^\text{av}_0 + a^\text{av}_{3d,3d,2} F^2_{\text{av}}(3d,3d) + a^\text{av}_{3d,3d,4} F^4_{\text{av}}(3d,3d). \quad (26)$$

In order to discuss the equality of equations (24) and (26), we compare the approximate OPM exchange potentials of V$^{2+}$ multiplets with exact ones. The dotted line of figure 3 exhibits the difference between the OPM exchange potential of the multiplet states and that of the average energy calculated from equation (25). In the solid line of figure 3 we show the same difference calculated from exact equation (24). The dotted line of figure 3 close to the solid line. Small differences come from the neglect of the multiplet dependence of the radial wave functions.

In third column of table 2 we show the approximate total energy of V$^{2+}$ multiplets calculated from equation (26). For comparison, the exact OPM total energies are shown in second column of table 2. If the total multiplet energies are deviate from the average of configuration, the approximate equation (26) poorly predicts the total energies. However, the differences between the approximate and the exact total energies are no more than 0.002 au. For the other 3d$^n$ transition metal atoms, the differences between the approximate and the exact energies are no more than 0.005 au. Therefore, we can conclude that the equation (25) and (26) work as the approximation formula of the exchange potential and the total energy for the multiplet states, respectively.

In stead of showing the OPM potentials for many multiplet states, we illustrated $V^\text{av}_{F_{3d,3d}}(r)$ and $V^\text{av}_{F_{3d,3d}}(r)$ multiplied by the occupation number $q_{3d}$ in the top parts of figure 4 and figure 5 respectively. As atomic number increases, the potentials $q_{3d} V^\text{av}_{F_{3d,3d}}(r)$ and $q_{3d} V^\text{av}_{F_{3d,3d}}(r)$ shrink and become high. This corresponds with the spread tendency of the electron density or the single electron orbital. In the bottom parts of figure 4 and figure 5 we show functional derivative of $F^2_{\text{av}}(3d,3d)$ and $F^4_{\text{av}}(3d,3d)$.
with respect to \( P_{3d}^{av} \), respectively. Maximum of \( \frac{\delta F_{k}^{(3d,3d)}}{\delta P_{3d}^{v}} \) is approximate to that of \( q_{3d} V_{F3d}^{av}(r) \), but the shapes of the potentials are different. The two peaks are observed in \( q_{3d} V_{F3d}^{av}(r) \), whereas, a single peak in \( \frac{\delta F_{k}^{(3d,3d)}}{\delta P_{3d}^{v}} \). Furthermore, at the nucleus, \( \frac{\delta F_{k}^{(3d,3d)}}{\delta P_{3d}^{v}} \) and \( q_{3d} V_{F3d}^{av}(r) \) are zero and nonzero value, respectively.

Finally, we discuss the relation between the OPM exchange potential for the multiplet state and that for the single determinant. The multiplet states \( \Psi(LS_{Z}S_{z}, \nu) \) are represented as the linear combination of the single determinants \( \Phi(L_{Z}S_{Z}, \nu) \). If the radial components of the wavefunctions do not depend on the multiplet states, the single determinant \( \Phi(L_{Z}S_{Z}, \nu) \) is represented as

\[
\Phi(L_{Z}S_{Z}, \nu) = \sum_{LS} \sum_{s} \alpha_{LS_{Z}S_{z},s}^{\nu} \Psi(LS_{Z}S_{z}, s).
\]

The 2-body energy of the single determinant \( E_{2}^{L_{Z}S_{Z}, \nu} \) is the expectation value of \( \sum_{i,j} \frac{1}{r_{ij}} \) with respect to \( \Phi(L_{Z}S_{Z}, \nu) \), which can be expressed as

\[
E_{2}^{L_{Z}S_{Z}, \nu} = \sum_{LS} \sum_{s,s'} \alpha_{LS_{Z}S_{z},s}^{\nu} \alpha_{LS_{Z}S_{z},s'}^{\nu} E_{2}^{L_{Z}S_{Z},s},
\]

where \( E_{2}^{L_{Z}S_{Z},s} = \int \Psi^{*}(LS_{Z}S_{Z}, s') \sum_{ij} \frac{1}{r_{ij}} \Psi(LS_{Z}S_{Z}, s) d\tau_{1} \cdots d\tau_{N} \), and \( \tau \) is the spatial and spin coordinates. Selecting some combination of single determinants, we solve simultaneous equations (28) with respect to the 2-body part of the multiplet state. The solution of the simultaneous equations is approximately valid because the orbital wavefunctions depend on multiplet states or single determinants.

\[
E_{2}^{L_{Z}S_{Z}, \nu} \approx \sum_{L_{Z}S_{Z}, \nu} \beta_{L_{Z}S_{Z}, \nu} E_{2}^{L_{Z}S_{Z}, \nu}.
\]

Replacing \( \sum_{i,j} \frac{1}{r_{ij}} \) appearing in the derivation of (29) with total Hamiltonian, we obtain approximate equation for the total energy.

\[
E_{LS, \nu}^{L_{Z}S_{Z}, \nu} \approx \sum_{L_{Z}S_{Z}, \nu} \beta_{L_{Z}S_{Z}, \nu} E_{LS, \nu}^{L_{Z}S_{Z}, \nu}.
\]

From the variation of equation (29) with respect to \( n_{LS}^{s}(r) \), the OPM potential for the multiplet state \( V_{OPM}^{LS_{Z}, \nu}(r) = \frac{\delta E_{LS, \nu}^{L_{Z}S_{Z}, \nu}}{\delta n_{LS}^{s}(r)} \) is expressed as the linear combination of the OPM potentials for the single determinants \( V_{OPM}^{L_{Z}S_{Z}, \nu}(r) = \frac{\delta E_{LS}^{L_{Z}S_{Z}, \nu}}{\delta n_{LS}^{s}(r)} \):

\[
V_{OPM}^{LS_{Z}, \nu}(r) \approx \sum_{L_{Z}S_{Z}, \nu} \beta_{L_{Z}S_{Z}, \nu} V_{OPM}^{L_{Z}S_{Z}, \nu}(r). \tag{31}
\]

Following equation (31), we evaluate the approximate OPM exchange potential for the multiplet state. Figure 6 presents the difference between the OPM potential for \( V_{2}^{+} \) multiplet state and that for the average energy. The dotted line exhibits the approximate difference potential calculated from equation (31). We select the single determinant appearing in equation (31) as \([2, 1, -2], [2, 1, 1], [2, 1, 0], [2, 1, -1], [2, -2, 2], [1, 0, 1], [2, 1, -2], [2, 1, 0], [2, 1, 2]\), where the number represents the z component of orbital angular momentum. The absence and presence of the line over the number stand...
for spin up and down state, respectively. In the solid line of figure 6, we show the difference potential calculated from exact equation (24). We find, from figure 6, that the approximate difference potential (dotted line) is very close to the exact one (solid line).

In the fourth column of table 2, we show the approximate total energy calculated from equation (30). We compare the approximate total energy with exact OPM total energy presented in second column of table 2. The difference between the approximate total energy and the exact one is no more than 0.004 au. For the other 3d transition metal atoms, the difference between two energies is no more than 0.01 au. Therefore, the exchange potential for the multiplet state can be evaluated using the theory such as the density functional theory, where the electronic structure is based on the single determinant.

5. Conclusion

We applied OPM to the multiplet energies of the 3d transition metal atoms using the total energy functional of the single-configuration HF [31] form. The calculated OPM exchange potential can be approximated by the $X\alpha$ and B88 exchange potentials in $r > 0.1$ au. For near nucleus region ($r < 0.1$ au), the OPM exchange potential strongly deviates from the $X\alpha$ and B88 exchange potentials. The difference between the OPM exchange potential for the multiplet states and that for the average energy is quite smaller than the OPM exchange potential. The OPM exchange potential for the multiplet state of the 3d transition metal atom can be represented as the linear combination of $V_{F_{3d,3d}}^{\xi}$, $V_{F_{3d,3d}}^{\xi}$ and $V_{E_{0}}^{\xi}$. We find that the OPM exchange potential can be approximated by the linear combination of multiplet independent potentials $V_{F_{3d,3d}}^{av}$ and $V_{F_{3d,3d}}^{av}$. This result indicates that the total energy functional can be represented as linear combination of the terms which are the product of the multiplet independent quantities derived from the Slater integrals ($F_{av}^{2}(3d,3d)$ and $F_{av}^{4}(3d,3d)$) and the multiplet dependent quantities ($a_{3d,3d,2}^{LS,s}$, $a_{3d,3d,4}^{LS,s}$).

As the representative of the potentials for the many multiplet states of the 3d transition metal atoms, we discussed the features of the potentials $V_{F_{3d,3d}}^{av}$ and $V_{F_{3d,3d}}^{av}$. We find that the potentials $V_{F_{3d,3d}}^{av}$ and $V_{F_{3d,3d}}^{av}$ shrink, and become high as the atomic number increases, which is the same trend as observed in the wave function of the 3d transition metals.

The multiplet state of the 3d transition metal atom is represented as the linear combination of the single determinants. From our calculation result, we find that the OPM exchange potential of the multiplet state can be approximated as the linear combination of the OPM exchange potentials of the single determinants. The result might be similar to the methods of Ziegler [26], Wood [24] and von Barth [25]. However, our result shows that the d electron multiplet state energy should be evaluated by including multiplet dependency to the total energy functional.
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**Table 1.** The average energy of the configuration (in au) for 3dⁿ multiplets calculated by Hartree-Fock \( (E_{HF}^{av}) \), OPM \( (E_{OPM}^{av}) \), Becke 88 \( (E_{B88}^{av}) \), and Xα \( (E_{Xα}^{av}, \alpha = 2/3) \) method.

| Multiplet | \( E_{HF}^{av} \) | \( E_{OPM}^{av} - E_{HF}^{av} \) | \( E_{B88}^{av} - E_{HF}^{av} \) | \( E_{Xα}^{av} - E_{HF}^{av} \) |
|-----------|-----------------|-----------------|-----------------|-----------------|
| Ti\(^{2+}\) | -847.6927 | 0.0061 | 0.0096 | 2.9047 |
| V\(^{2+}\)  | -942.0952 | 0.0063 | -0.0059 | 3.0478 |
| Cr\(^{2+}\) | -1042.4387 | 0.0065 | -0.0257 | 3.1876 |
| Mn\(^{2+}\) | -1148.8609 | 0.0066 | -0.0492 | 3.3252 |
| Fe\(^{2+}\) | -1261.4995 | 0.0067 | -0.0754 | 3.4613 |
| Co\(^{2+}\) | -1380.4916 | 0.0068 | -0.1034 | 3.5968 |
| Ni\(^{2+}\) | -1505.9743 | 0.0068 | -0.1320 | 3.7330 |

**Table 2.** The total energies (in au) of V\(^{2+}\) multiplet states calculated by the HF method, OPM, equation (26) and equation (30).

| Multiplet | HF | OPM | Eq. (26) | Eq. (30) |
|-----------|----|-----|---------|---------|
| \(^4\)F   | -942.1799 | -942.1733 | -942.1727 | -942.1733 |
| \(^4\)P   | -942.1128 | -942.1065 | -942.1065 | -942.1064 |
| \(^2\)H   | -942.0902 | -942.0840 | -942.0840 | -942.0840 |
| \(^2\)G   | -942.1124 | -942.1061 | -942.1060 | -942.1060 |
| \(^2\)F   | -942.0245 | -942.0181 | -942.0177 | -942.0161 |
| \(^2\)P   | -942.0902 | -942.0840 | -942.0840 | -942.0842 |
| \(^3\)D   | -941.9693 | -941.9628 | -941.9612 | -941.9606 |
| \(^3\)D   | -942.0507 | -942.0444 | -942.0442 | -942.0478 |

**Figure 1.** The radial density \( \rho^{av}(r) \) of Mn\(^{2+}\) calculated using the Xα, B88 and OPM exchange potentials for the average energy (top). The Xα, B88 and OPM exchange potentials for the average energy of Mn\(^{2+}\) (bottom).
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Figure 2. The radial densities $\rho^{LS,s}(r)$ of V$^{2+}$ multiplet states (top). The difference between the radial density of the multiplet state and that of the average energy: $\rho^{LS,s}(r) - \rho^{av}(r)$ (bottom).

Figure 3. The difference between the OPM exchange potential of V$^{2+}$ multiplet state ($V_{ex}^{LS,s}$) and that of the average energy ($V_{ex}^{av}$): $V_{ex}^{LS,s} - V_{ex}^{av}$. The dotted line is the difference potential calculated from equation (25). The solid line is the same difference calculated from exact equation (24).
Figure 4. The potential of the Slater integral $F_{av}^2(3d, 3d)$ multiplied by the occupation number: $q_{3d} V_{F_{av}^2(3d, 3d)}^{av}$ (top). The functional derivative of the Slater integral $F_{av}^2(3d, 3d)$ with respect to $P_{av}^{3d}$: $\frac{\delta F_{av}^2(3d, 3d)}{\delta P_{av}^{3d}}$ (bottom).

Figure 5. The potential of the Slater integral $F_{av}^4(3d, 3d)$ multiplied by the occupation number: $q_{3d} V_{F_{av}^4(3d, 3d)}^{av}$ (top). The functional derivative of the Slater integral $F_{av}^4(3d, 3d)$ with respect to $P_{av}^{3d}$: $\frac{\delta F_{av}^4(3d, 3d)}{\delta P_{av}^{3d}}$ (bottom).
Figure 6. The difference between the OPM exchange potential of the $V^{2+}$ multiplet state ($V_{\text{ex}}^{LS,s}$) and that of the average energy ($V_{\text{ex}}^{av}$): $V_{\text{ex}}^{LS,s} - V_{\text{ex}}^{av}$. The dotted line is the difference potential calculated from equation (31). The solid line is the same difference calculated from exact equation (24).