Theoretical study of complex susceptibility of Pd and Pt

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Abstract. Spin transfer torque in a multilayer magnetic system can be understood in terms of interaction between a normal metal and a ferromagnetic layer on the multilayer, in which the interaction is characterized by the magnetic susceptibility. Most of experimental studies on this subject utilizes heavy metals, such as Pd and Pt, while a recent theory assumes a light metal as the normal metal. We aim to reconcile this discrepancy and achieve consistency with the experiments by studying magnetic susceptibility of Pd and Pt. We theoretically investigate the complex magnetic susceptibility of Pd and Pt by combining Tight-binding Approximation, Hubbard Model, and Density Functional Theory. We calculate a single band susceptibility for Pd and Pt. Our results show that the band structure is dominated by the d-orbitals and the susceptibility is enhanced by its large repulsive interaction.

1. Introduction

Technologies grow rapidly, as technology develops, the amount of data that can be processed has also increased. These data require a bigger memory capacity. Computer memory consists of many small transistors and capacitors which store data using binary states 1 and 0, the states become 1 when the capacitor charged and 0 when the capacitor discharged. In developing memory technology, people try to develop a small and compact memory with the hope to achieve a fast and energy-efficient device. The more compact and smaller the device requires the smaller transistor and capacitor. A Smaller capacitor and transistors have consequences of charge leakage, which can affect data stored in memory [1, 2, 3], to resolve this charge leakage problem, many scientists try to develop spin-based memory using magnetic multilayer material. This memory can be made in small size and without any charge leakage because it works by changing the direction of magnetization in a magnetic multilayer. Since there are no charge leakages, Spin-based memory consumes less power than conventional memory [3, 4].

In a magnetic multilayer structure, the magnetization of a ferromagnetic layer can be modulated by a spin-polarized current by means of spin transfer torque, as seen in figure 1. The spin transfer torque generated by an exchange interaction between the spin of the conducting electron and the localized spin that give rise to the magnetization of the ferromagnetic layer. The origin of spin-transfer torque and other spin current related effects in magnetic metallic multilayers are by now relatively well
understood as the spin-dependent interaction between non-magnetic metal and ferromagnetic metal [5].

![Figure 1. Spin-transfer torque occurs when a spin current ($J_S$) flows from non-metallic layer (N) to ferromagnetic layer (F).]

Interaction between normal metal and ferromagnetic layer determined by complex susceptibility of non-magnetic metal [6, 7]. Although the theory of complex susceptibility for simple metal has been studied [7], the complex susceptibility of heavy metals that requires complex modelling has not been understood very well [8]. In our research, we focus on Pd and Pt metal, because they are often used in the experiments. These materials are heavy metal and have strong coulomb repulsive that can affect the susceptibility. To be able to understand the magnetic properties of materials, one of which is susceptibility [9], one need to accurately model the band structure [10]. In this article, we theoretically discuss the theoretical modelling of the band structure of Pd and Pt. The susceptibility of the heavy metals can be studied using tight-binding approximation [10, 11].

2. Method

In non-magnetic layers, the ferromagnetic layers influence the magnetic moment density of conduction electron $\sigma(\mathbf{r})$ as magnetic field $H(\mathbf{r}, t)$ according to:

$$H_{\text{ext}} = -\int H(\mathbf{r}, t) \cdot \mathbf{\sigma}(\mathbf{r}) d^3 \mathbf{r},$$

(1)

where $\mathbf{\sigma}(\mathbf{r})$ denotes spin density of conduction electron at point $\mathbf{r}$ [12,13]. By implementing linear response theory, one can obtain the spin susceptibility $\chi$ that relates $\mathbf{\sigma}$ and $\mathbf{\sigma}$:

$$\langle \sigma_i(\mathbf{r}, t) \rangle_H = \langle \sigma_i(\mathbf{r}, t) \rangle_{H=0} + \sum_j \int dt' \int d^3 r' \chi_{ij}(\mathbf{r}, \mathbf{r}' = \mathbf{r} - \mathbf{r}', t - t'),$$

(2)

The susceptibility $\chi_{ij}(\mathbf{x} - \mathbf{x}', t - t')$ can be written in term of its Fourier transform $\chi_{ij}(\mathbf{q}, \omega)$

$$\chi_{ij}(\mathbf{x} - \mathbf{x}', t - t') = i\theta(t - t')\langle [\sigma_i(\mathbf{x}, t), \sigma_j(\mathbf{x}', t')] \rangle = \int \frac{d^3 q}{(2\pi)^3} \chi_{ij}(\mathbf{q}, \omega).$$

(3)

When we include the repulsive interactions between the electrons within Hubbard model and Hartree-Fock (mean-field) approximation, the formula for complex magnetic susceptibility in momentum space is given by [13]:

$$\chi_{ij}(\mathbf{q}, \omega) = \delta_{ij} \frac{\Gamma(\mathbf{q}, \omega)}{1 - U \Gamma(\mathbf{q}, \omega)}$$

(4)

where

$$\Gamma(\mathbf{q}, \omega) = \lim_{\eta \to 0^+} \int \frac{d^3 p}{(2\pi)^3} \frac{f_p - f_{p+q}}{\epsilon_{p+q} - \epsilon_p + \omega + i\eta}$$

(5)

Here $U$ is Hubbard parameter that characterize the Coulomb repulsive interaction, $\Gamma(\mathbf{q}, \omega)$ is retarded particle-hole propagator for wave vector $\mathbf{q}$ and frequency $\omega$. Wave vector $\mathbf{q}$ defines momentum interaction, $\omega$ is dynamic magnetization frequency, $\eta \to 0^+$ is retardation constant. Pd and Pt are both
paramagnetic metals, for paramagnetic metal, the unperturbed energy dispersion of up-spin and down-spin are equal [13]. For small dynamic frequency, equation 5 can be expanded using Taylor expansion to the first order of $\omega$ as:

$$
\Gamma(q, \omega) = \int \frac{d^3p}{(2\pi)^3} \left( f_p - f_{p+q} \right) \left( \frac{1}{\varepsilon_{p+q} - \varepsilon_p + \omega} - i\pi\delta(\varepsilon_{p+q} - \varepsilon_p + \omega) \right)
$$

$$
= \Gamma_{\text{r}}(q) + i\omega \Gamma_{\text{i}}(q)
$$

The real part of $\Gamma$ corresponds with the paramagnetic reactive response, which should be proportional to the density of states at Fermi energy $N(\varepsilon_F)$.

$$
\lim_{\varepsilon_q \approx \varepsilon_F} \Gamma_{\text{r}}(q) = \lim_{\varepsilon_q \approx \varepsilon_F} \int \frac{d^3p}{(2\pi)^3} \left( f_p - f_{p+q} \right) \varepsilon_q = \lim_{\varepsilon_q \approx \varepsilon_F} \int \frac{d^3p}{(2\pi)^3} \frac{\partial f_p}{\partial \varepsilon_p} = N(\varepsilon_F)
$$

On the other hand, the imaginary part of $\Gamma$ corresponds to the energy loss due to two-body interactions and for sum $q$ it scales like the square of DOS($\varepsilon_F$).

$$
\int \frac{d^3q}{(2\pi)^3} \Gamma_{\text{i}}(q) = -\pi \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3p}{(2\pi)^3} \left( f_p - f_q \right) \frac{\partial}{\partial \varepsilon_q} \delta(\varepsilon_q - \varepsilon_p)
$$

$$
= \pi \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3p}{(2\pi)^3} \delta(\varepsilon_q - \varepsilon_p) \frac{\partial f_p}{\partial \varepsilon_p} = \pi(N(\varepsilon_F))^2
$$

Therefore, we should focus on the modelling the band structure near the Fermi energy. To be able to do that we replace $\varepsilon_p$ with the energy dispersion of Pd and Pt electrons.

### 2.1. Tight-binding approximation

Electrons in Pd and Pt metals can move (jump/hop) from one orbital-state to other in the same or different atoms. In the crystal system, the electrons perceive a periodic potential, so that the electron wave functions can be expressed in terms of Bloch functions. A crystal consists of $N$ unit cells and every unit cell is labeled by index $i$. In the unit cell, there are several atoms labeled by $n$ and each atom has some orbitals labeled by $\alpha$. The Bloch functions can be expressed by [14]:

$$
\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i,n,\alpha} \phi_{i,n,\alpha}(\mathbf{r} - \mathbf{R}_n) e^{i\mathbf{k} \cdot \mathbf{R}_n}
$$

where $\mathbf{k}$ is the electron wave vector. $\phi_{i,n,\alpha}$ is the $\alpha$-orbital wave function at the unit cell $i$ for atom $n$, which is located at $\mathbf{R}_n$. The energy (eigenvalue) can be obtained by solving the expectation value of Hamiltonian as:

$$
\langle \mathbf{k} | H | \mathbf{k} \rangle = \int d^3r \psi^*_{\mathbf{k}}(\mathbf{r}) H \psi_{\mathbf{k}}(\mathbf{r})
$$

$$
= \sum_{n,\alpha} \sum_{n',\alpha'} \sum_i (-t_{i,n,\alpha,n',\alpha'}) e^{-i\mathbf{k} \cdot \mathbf{R}_{n,n'}}
$$

Here $-t_{i,n,\alpha,n',\alpha'}$ is the hopping parameter and is given by:

$$
-t_{i,n,\alpha,n',\alpha'} = \int d^3r \phi^*_{i,n,\alpha}(\mathbf{r} - \mathbf{R}_n) H \phi_{i,n',\alpha}(\mathbf{r} - \mathbf{R}_{n'})
$$

For FCC unit cell the energy dispersion $\varepsilon_p$ has the following form:

$$
\varepsilon_p = \varepsilon_0 - 4t \left( \cos \left( \frac{\alpha}{2} p_x \right) \cos \left( \frac{\alpha}{2} p_y \right) + \cos \left( \frac{\alpha}{2} p_x \right) \cos \left( \frac{\alpha}{2} p_y \right) + \cos \left( \frac{\alpha}{2} p_x \right) \cos \left( \frac{\alpha}{2} p_y \right) \right)
$$

Where $\varepsilon_0$ is on-site energy, $p_x$, $p_y$, and $p_z$ are the wave vector. The information about $\varepsilon_p$ can then be used to calculate the magnetic susceptibility of Pd and Pt metals. The tight-binding parameter for energy dispersion calculation can be obtained from computational calculation.
Our computational calculation using Quantum Espresso (QE) [15] started from variational cell relax (VC-relax) calculation. The aim to run this calculation is to get the lattice constant of FCC lattice of Pd and Pt by relaxing the unit cell. For Pd metal, we use Local Density Approximation (LDA) – type pseudopotential with k-points grid $16 \times 16 \times 16$, kinetic energy cutoff 100 Ry, and 360 Ry for wavefunction and charge densities, respectively, and the energy convergence criterion was set to $10^{-10}$ a.u. From VC-relax result we obtained lattice constant for Pd metal 7.2715 Bohr (3.84785917 Å). The ground-state density is then calculated using the self-consistent field (SCF) and non-self-consistent field (NSCF) approaches. Both SCF and NSCF calculations use the same pseudopotential type, energy, and wavefunction cutoff value with VC-relax, with $k$-points grid. The Density of States (DOS) can be used to obtain tight-binding parameters. For Pt metal, we use Local Density Approximation (LDA) – type pseudopotential with k-points grid $16 \times 16 \times 16$, kinetic energy cutoff 50 Ry, and 450 Ry for wavefunction and charge densities, respectively, and the energy convergence criterion was set to $10^{-10}$ a.u. From VC-relax result we obtained lattice constant for Pd metal 7.3957 Bohr (3.9136359 Å). The ground-state density is then calculated using the self-consistent field (SCF) and non-self-consistent field (NSCF) approaches. Both SCF and NSCF calculations use the same pseudopotential type, energy, and wavefunction cutoff value with VC-relax, with $32 \times 32 \times 32$ k-points grid. The density of States (DOS) can be used as a guide for obtaining tight-binding parameters. The crystal structure for Pd and Pt can be observed from Figure 2.

**Figure 2.** The crystal structure of (A) metallic Palladium and (B) metallic Platinum. Both heavy metals have face-centered cubic crystal structure [16].

### 3. Result and Discussion

Using data from DFT calculation for SCF and NSCF calculation we can obtain the value of Fermi level and produce Projected Density of States (PDOS) for Pd and Pt metal. Since the magnetic susceptibility focused on the area near the Fermi level, using the value of the Fermi level we can decide which orbitals we must focus on when calculating the magnetic susceptibility. From Figure 3, we can observe that d-orbitals have dominant contributions in electronic structure compared to s and p orbitals, thus the susceptibility calculation must take place on the d-orbitals.
Figure 3. Orbital-specified Partial DOS for metallic Pd.

Figure 4. Orbital-specified Partial DOS for metallic Pt.

From Figure 4, we can observe that for the area near the Fermi level, d-orbitals have dominant contributions in electronic structure compared to s and p orbitals, thus the susceptibility calculation for Pt must take place on the d-orbitals too. Since the complex susceptibility is closely related to the density of states at the Fermi energy (see Equations 8 and 10), in determining the tight-binding parameters, we should choose the value of on-site energy and hoping parameter very carefully. We use the tight-binding calculation to produce PDOS for tight-binding for the area near the Fermi level. The parameters are chosen so that PDOS from tight-binding can mimic PDOS of d-orbitals from DFT calculation. The result for Pd and Pt metal will be shown in Figure 5 and Figure 6 respectively.

Figure 5 shows the result of the Tight-binding calculation for d-orbitals DOS using a single-band model. We use DFT result as a guide to choose tight-binding parameters to mimic d-orbitals DOS, in this calculation we assume calculation in low temperature (5K), with k-points grid 24 × 24 × 24, and on-site energy 13.9367 eV and hoping parameter 0.11055 eV. These values are chosen because resulting small difference between Tight-Binding calculation and DFT result for near Fermi level.
Figure 5. DFT vs Tight-Binding for d-orbital DOS of Pd metal.

Figure 6. DFT vs Tight-Binding for d-Orbitals DOS of Pt Metal.

Figure 6 shows the result of the Tight-binding calculation for d-orbitals DOS using a single-band model. We use DFT result as a guide choosing the right tight-binding parameters to mimic d-orbitals DOS, with k-points grid $24 \times 24 \times 24$, and on-site energy 16.9878 eV and hoping parameter 0.16308 eV. These values are chosen because resulting small difference between Tight-Binding calculation and DFT result of Pt for the area near Fermi level.

After obtaining the value of tight-binding parameters for Pd and Pt metal, the next steps to study complex susceptibility of Pd and Pt are calculating real and imaginary part of complex magnetic susceptibility. Using Tight-binding parameters for Pd and Pt from previous processes, we observe the energy dispersion for Pd and Pt. Using these formulism, we calculate $\Gamma(q)$ to obtain complex susceptibility. We then compare their value when there is no repulsive Coulomb interaction ($U=0$) and with repulsive Coulomb interaction ($U\neq0$).

Since Pd and Pt have similar values of $\varepsilon_0/4t$. By writing the energy dispersion as

$$\frac{\varepsilon_p}{4t} = \frac{\varepsilon_0}{4t} - \left\{\cos k_x \cos k_z + \cos k_y \cos k_y + \cos k_x \cos k_z\right\}$$  \hspace{1cm} (16)

We can write the complex susceptibility into a dimensionless integral because
\[ \Gamma(q) = \frac{1}{(\pi a)^2} \lim_{\eta \to 0} \int dk_x \, dk_y \, dk_z \frac{f_{k} - f_{k + qa}}{\varepsilon_{k + qa}^2 - \varepsilon_{k}^2 + \omega + i\eta} \]  

(17)

While the values of complex susceptibility for Pd and Pt for all values of \( q \) required a computationally high cost, we obtain the value for small \( q \) as follows

\[
\lim_{\varepsilon_{q} \to \varepsilon_{F}} \chi_{r}(q) = \frac{N(\varepsilon_{F})}{1 - UN(\varepsilon_{F})} \]

(18)

\[
\lim_{\varepsilon_{q} \to \varepsilon_{F}} \chi_{i}(q) = \frac{\pi N(\varepsilon_{F})}{4q v_{F}} \left(1 - UN(\varepsilon_{F})\right)^{-1} \]

(19)

Where the Fermi velocity

\[ v_{F} = \left|\nabla_{\varepsilon_{q}} \varepsilon_{q}\right|_{\varepsilon_{q} = \varepsilon_{F}} \]

(20)

Equation 18 and 19 shows that the Hubbard parameter \( U \), that characterized the repulsive electron–electron interaction largely contribute to the magnetic susceptibility of Pd and Pt. The value of \( UN(\varepsilon_{F}) \) of Pd and Pt are 0.89 and 0.72, respectively [17].

| Table 1. Parameters for Pd and Pt metal, with energy relative to \( E_{f} \) |  |
|-------------------|------------------|------------------|-------------------|------------------|
| Heavy metal       | Lattice Constant (Å) | \( E_{f} \) (eV) | \( \varepsilon_{0} \) (eV) | \( t \) (eV) | \( \varepsilon_{0} \) \( 4t \) | \( UN(\varepsilon_{F}) \) |
| Pd                | 3.8478592        | 0                | -0.4252           | 0.11055         | -0.96156       | 0.8925       |
| Pt                | 3.9136359        | 0                | -0.6276           | 0.16308         | -0.96210       | 0.7297       |

From Table 1 we can see that Pd and Pt have similar values of \( \varepsilon_{0} / 4t \). Because of that the dimensionless part of the integral in Equation 17 should not vary much and the susceptibility is proportional to the inverse of the lattice volume.

\[ \chi(q, \omega) \propto \frac{1}{d^3} \]

(21)

This proportionality indicates that the susceptibility of Pd is 5% larger than Pt. Equation 18 and 19 show that electron–electron repulsive interaction parameter \( U \) dominates the complex susceptibility.

\[ \frac{\chi_{r}(Pd)}{\chi_{r}(Pt)} = 2.51 \times 1.05 = 2.65 \]  

(22)

\[ \frac{\chi_{i}(Pd)}{\chi_{i}(Pt)} = 6.32 \times 1.05 = 6.65 \]  

(23)

4. Conclusion

We have calculated PDOS for each orbital (s, p, and d orbitals) for Pd and Pt metals using DFT calculation. From these DFT results, for Pd and Pt metal, d-orbitals have the dominant contribution for the states near the Fermi Level. Susceptibility occurs for the area near the Fermi level, and proportional to DOS and square of DOS, thus choosing the right tight-binding parameters in modelling single-band structure for energy dispersion for magnetic susceptibility calculation is crucial. For Pd, on-site energy is 13.9367 eV with hoping parameter 0.11055 eV. For Pt, on-site energy is 16.9878 eV, and the hoping parameter is parameter 0.16308 eV.

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