Giant Dzyaloshinskii-Moriya interaction (DMI) in magnetic bilayers and its microscopic origin

Priyamvada Jadaun,1Leonard F Register,1 and Sanjay K Banerjee1
1Department of Electrical and Computer Engineering,
The University of Texas at Austin, Austin, Texas. USA.
(Dated: March 25, 2019)

Skyrmions are widely regarded as promising candidates for emergent spintronic devices. Large Dzyaloshinskii-Moriya interaction (DMI) is critical to the realization of functional skyrmion technology. Here we present a comprehensive, first principles study of DMI in a series of metallic bilayers. We report four new materials systems with giant DMI and new designs for magnetic multilayers that are expected to outperform the best materials we have so far. We also derive a model to explain the microscopic mechanism of DMI and explain the trend of DMI values observed. These results not only advance skyrmion-based memory technology towards realization, but also demonstrate the physics behind it.

Introduction- As our society’s need to store data continuously increases, we will soon reach the performance limits of current magnetic devices such as hard disk drives. Magnetic skyrmions are widely believed to be one of the most promising candidates for next-generation memory technology. A magnetic skyrmion is a local whirl of spins in a magnetic material, with a fixed chirality and topological protection from deformation into other magnetic states. This topological protection enables skyrmions to be stable against disorder and perturbation, as well as display a quasiparticle-type response to magnetic-field gradients and currents of charge and heat. The stability of skyrmions, their small size, and their responsiveness to tiny electrical current densities ($10^6 A/m^2$), make these skyrmions ideal for enabling ultra-dense, low-energy memory devices. A skyrmion based racetrack memory promises to achieve lower operating power, higher device packing density and more robust data stability, than competing options like domain walls, which are also relevant to next-generation data storage devices. The smallest skyrmions obtained so far are in the 30 - 50 nm range, under fields of a few tens of milliTesla, whereas most memory devices would ideally require skyrmions of size $\leq 10$ nm. In this paper, we address this problem by reporting new HM/FM bilayers that show remarkable promise for hosting small-sized skyrmions, that are stable at RT, under very low or no magnetic fields. We also derive a model to explain the microscopic mechanism of DMI and predict the large values of Dzyaloshinskii-Moriya interaction (DMI) that researchers could obtain in HM/FM multilayers.

Despite the impressive strides made in the realization and manipulation of RT skyrmions, transformation of skyrmions into viable technology still faces many challenges. Skyrmion-based devices require stable, small, individual skyrmions in zero or very small applied fields. The smallest skyrmions obtained so far are in the 30 - 50 nm range, under fields of a few tens of milliTesla, whereas most memory devices would ideally require skyrmions of size $\leq 10$ nm. In this paper, we address this problem by reporting new HM/FM bilayers that show remarkable promise for hosting small-sized skyrmions, that are stable at RT, under very low or no magnetic fields. The key to generating such small and robust skyrmions is large DMI. Here we present a comprehensive study of DMI in HM/FM bilayers and predict giant DMI for four new materials systems. Our largest values for microscopic DMI ($d$) are twice as large as the state-of-the-art materials used for skyrmion generation, while our micromagnetic DMI ($D$) values are up to four times as large. Micromagnetic DMI relates more closely to skyrmion experiments. Large DMI also enables the formation of other chiral spin structures, like chiral domain walls, which are also relevant to next-generation data storage devices. These discoveries will directly impact the development of ultralow-energy spintronic devices. Additionally, we explain the microscopic physics behind the generation of DMI and trace its origin to specific terms in spin orbit coupling (SOC). Our model aims to clarify the essential physics behind DMI, which is a critically important yet poorly understood interaction.

Calculation details- We calculated the DMI using density functional theory (DFT) for a comprehensive series of HM/FM bilayers, constructed from a heavy metal and a ferromagnet. Our choice of HM varied through the 5d and 6p series of elements, starting from Hf and going...
The cutting edge materials for skyrmion generation so far have been Co/Pt ($d_{\text{theory}} = 1.5meV/atom\ [17]$) and Ir/Fe ($d_{\text{theory}} = -1.9meV/atom\ [17]$). While Simon et al.\ [16] had previously reported a large DMI in Re/Fe and Os/Fe, our predictions for Re/Co, Os/Co, Os/Ni and hBi/Ni are completely new and up to twice the cutting edge values. These results are even more impressive when considering the value of the micromagnetic DMI ($D$), which is more relevant to experiments. We report $D$ as large as $24.3mJ/m^2$ for hBi/Ni and $28.5mJ/m^2$ for Os/Ni which is approximately four times the known theoretical value for Pt/Co (6$mJ/m^2\ [17]$). Interestingly, the trend for $D$ differs from that for $d$, since $D$, the micromagnetic DMI, includes information about the crystal structure of the bilayer and magnetic moments in the FM. For instance, the magnetic moments in Ni are usually smaller than those in Fe and Co, thereby relatively enhancing the micromagnetic DMI for Ni bilayers.

It is also noteworthy that hBi or bismuthene is predicted to be a quantum spin Hall material\ [24] and, thus, can be a source of large spin Hall current. HMs with large spin Hall effects are ideal for driving skyrmions with the help of spin-orbit torques. Our results can also successfully explain the recent experimental finding of room temperature skyrmions in Pt/Co/Os/Pt thin films\ [25], by pointing out the large DMI expected from Co/Os interface. A useful design strategy for enhancing DMI has been the addition of DMI from opposite interfaces\ [10, 11]. This strategy requires combining successive interfaces that demonstrate DMI of opposite signs and is successfully implemented in Pt/Co/Fe/Ir multilayers. Owing to our prediction of giant negative DMI in Os/Co and Re/Co interfaces, our results make it possible to achieve even larger additive DMIs in simpler multilayer structures, such as Pt/Co/Os and Pt/Co/Re.

**Microscopic mechanism of DMI** - We now describe a model that explains our findings. Despite the importance of DMI to the generation and stability of skyrmions, the microscopic mechanism by which DMI acts is poorly understood. DMI was first phenomenologically proposed, as a relativistic spin-lattice interaction, by Dzyaloshinsky\ [26]. He used it to explain weak ferromagnetism in $\alpha - Fe_2O_3$. Later, Moriya showed that in magnetic insulators, DMI naturally resulted from the inclusion of spin-orbit coupling. Smith, Fert and Levy subsequently proposed that interfacial DMI could also exist in ultrathin magnetic films\ [28, 29]. Here DMI arose from an indirect exchange interaction between two magnetic atoms with moments, $S_1$ and $S_2$, and took the form $H_{DMI} = (S_1 \cdot \vec{S}_2) \cdot \vec{D}_{\alpha\beta}.$\ [2, 31]. While the Fert-Levy mechanism is very helpful in understanding the overall picture of interfacial DMI in magnetic bilayers, surprisingly little is known about its microscopic origin, the relationship of DMI with electronic orbitals, the mechanism by which it produces magnetic textures like skyrmions or even the trends observed in the variation of DMI values in materials. These are all critical questions that we address in this paper.
There are a few competing theories that aim to explain the microscopic origin of DMI in magnetic bilayers. One study reports that the proximity-induced magnetic moment in HM layers plays a critical role in determining the DMI value. However, this is contradicted by other reports. A first principles study by Belabbes et al. posits that the 3d band filling in the FM decides the sign and the strength of interfacial DMI. They also demonstrate the role played by SOC in the generation of DMI. The authors note the formal analogy between DMI and orbital magnetization. They also report that our DMI values do not follow this trend, our conclusion is that 3d bands alone are not decisive in determining the DMI value. Moreover, this picture cannot explain the changes in the sign of DMI values. Recently, the Berry phase theory of DMI has been developed, which is an important step towards understanding the origins of DMI. The authors note the formal analogy between DMI and orbital magnetization. They also show that DMI is related to the twisting of magnetic moments of a wavepacket. Here, we derive the microscopic mechanism that generates DMI, in an orbital picture. Critically, we demonstrate the role played by SOC in the generation of DMI, which has not been addressed before. We also explain the trend of DMI values obtained with changes in the sign of DMI. The qualitative trend of DMI values observed in our results can be explained by analyzing the projected density of states (p-DOS) of HM and FM atoms. The p-DOS for Hf/Co and Os/Co are shown in Fig.2. As we transition from early 5d elements (like Hf) to later ones like Os and Pt, the overlap of the 5d bands of HM with the 3d bands of FM, increases. This increase is because the energy alignment of the 5d bands with the 3d bands is optimal for Os, Pt etc., which leads to large DMI values. Beyond Pt as we approach Au and Hg, the HM/FM bands become misaligned again, leading to a decrease in DMI. This is similar in a sense to the band alignment picture put forth by Belabbes et al., except that in our model it is the relative alignment of 3d and 5d orbitals that determines DMI, amongst other factors.

We now present a derivation to better explain the microscopic mechanism behind DMI. Freimuth et al. derive DMI from the change in free energy due to oscillations in magnetization direction. The rotation of the magnetic moment of an electron perturbs the wavefunctions of the FM via the exchange interaction. The change in free energy due to this perturbation gives rise to the DMI term. Here we examine the mechanism by which the magnetic moment of an electron in an HM/FM bilayer oscillates. We report that it is the competition between three off-diagonal terms of SOC in the HM that lead to the rotation of magnetization in the FM. Magnetic multilayers with interfacial DMI are known to host hedgehog-like (Néel) skyrmions unlike bulk materials that host vortex-like (Bloch) skyrmions. A Néel skyrmion, in the Bloch sphere representation, is signified with a rotating polar angle $\theta$ and a fixed azimuthal angle $\phi$. A schematic for this skyrmion is shown in Fig.3. Our model thus specifically considers the SOC terms that rotate $\theta$. We leave the derivation of an analogous model for Bloch skyrmions for future work.

**DMI derivation** - We use first order perturbation theory to derive the mechanism by which SOC leads to the rotation of the magnetization of the FM, generating DMI. Consider a bilayer system comprised of a thin film of a FM and a HM. In the absence of SOC, the FM has a constant magnetization. Let $\psi_{kn}^0$ represent the unperturbed wavefunction of an electron delocalized over this bilayer.

$$\hat{H}_0|\psi_{kn}^0\rangle = E_{kn}^0|\psi_{kn}^0\rangle$$

We now turn on SOC, such that $\hat{H} = \hat{H}_0 + \hat{H}_{SOC}$. The new eigenstate representing the electron hopping between HM and FM is given by

$$|\psi_{kn}\rangle = |\psi_{kn}^0\rangle + \sum_{\vec{q},m} \frac{\langle \psi_{kn}^0 | \hat{H}_{SOC} | \psi_{kn}^0 \rangle}{E_{kn}^0 - E_{k+\vec{q}m}^0} |\psi_{k+\vec{q}m}^0\rangle$$

Without loss of generality, we can assume the unperturbed FM has a magnetization along the z axis and the perturbed magnetic moment rotates in the XZ plane. We now consider the component of magnetic moment of the perturbed state along x, up to first order

$$\langle \hat{s}_x \rangle = \sum_{\vec{q},m} \langle \psi_{kn}^0 | \hat{H}_{SOC} | \psi_{kn}^0 \rangle \frac{\langle \psi_{k+\vec{q}m}^0 | \hat{H}_{SOC} | \psi_{kn}^0 \rangle}{E_{kn}^0 - E_{k+\vec{q}m}^0} + C.C.$$

Taking the long wavelength limit of $\vec{q} \to 0$.

$$\langle \hat{s}_x \rangle = \sum_{m \neq n} \langle \psi_{kn}^0 | \hat{s}_x | \psi_{kn}^0 \rangle \frac{\langle \psi_{kn}^0 | \hat{H}_{SOC} | \psi_{kn}^0 \rangle}{E_{kn}^0 - E_{km}^0} + C.C.$$
Writing \( \hat{s}_x \) and \( \hat{H}_{SOC} \) in the spin basis (|\( \uparrow \rangle \), |\( \downarrow \rangle \)):

\[
|\uparrow \rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad |\downarrow \rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \hat{s}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \hat{H}_{SOC} = \begin{bmatrix} \lambda_0/2 & \lambda_-/2 \\ \lambda_+/2 & -\lambda_0/2 \end{bmatrix}
\]

(5)

where \( \hat{l}_+ = \hat{l}_x + i\hat{l}_y \quad \hat{l}_0 = \hat{l}_z \). We can write \( \hat{l}_\pm \) in the d orbital basis \( \langle d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2} \rangle \) as,

\[
\hat{l}_+ = \begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 0 & \iota \end{bmatrix}, \quad \hat{l}_- = \begin{bmatrix} 0 & -\sqrt{3} & 0 & 0 \\ -\iota \sqrt{3} & 0 & 0 & 1 \end{bmatrix}
\]

(6)

For an unperturbed wavefunction \( \psi_{km}^0 \) in the spin up state, the only nonzero contributions to \( \langle \hat{s}_x \rangle \) come from \( \psi_{km}^0 \) in the spin down state:

\[
\langle \hat{s}_x \rangle = |\psi_{km}^0\rangle \sum_{m \neq n} \frac{\langle \phi_{km}^0 | \hat{l}_+ | \phi_{kn}^0 \rangle}{E_{kn}^0 - E_{km}^0} + C.C.
\]

(7)

where \( \phi_k^0 \) is the orbital part of the wavefunction. Similarly, for an unperturbed wavefunction \( \psi_{kn}^0 \) in the spin down state, we get:

\[
\langle \hat{s}_x \rangle = |\psi_{kn}^0\rangle \sum_{m \neq n} \frac{\langle \phi_{kn}^0 | \hat{l}_- | \phi_{km}^0 \rangle}{E_{km}^0 - E_{kn}^0} + C.C.
\]

(8)

Rotation of the magnetic moment of an electron, delocalized over the HM/FM interface, is thus caused by the spin orbit terms, \( \hat{l}_+ \cdot \hat{s}_- \) and \( \hat{l}_- \cdot \hat{s}_+ \). To obtain a continuous, self-sustained rotation in real space, spin up and spin down states should be rotated such that they pick up magnetic moments in opposite directions along the axis. This condition requires \( \langle \phi_{km}^0 | \hat{l}_+ | \phi_{kn}^0 \rangle \) to be opposite in sign to \( \langle \phi_{kn}^0 | \hat{l}_- | \phi_{km}^0 \rangle \). Inspecting Eq. (6) we conclude that there are only three such transitions, namely, \( \langle d_{xz} | \hat{l}_+ | d_{xz} \rangle \), \( \langle d_{xy} | \hat{l}_+ | d_{xy} \rangle \) and \( \langle d_{x^2-y^2} | \hat{l}_+ | d_{xz} \rangle \).

Our derivation clarifies the mechanism for DMI generation. Consider a wavefunction hopping across the HM/FM interface. In the absence of SOC, this electron exhibits a magnetic moment parallel to the magnetization of the FM. In the presence of SOC, whenever the electron hops to the HM atom, the three off-diagonal SOC terms cause d-orbital transitions and rotate its magnetic moment (creating a swirling spin texture). As this electron hops to the FM, its rotated magnetic moment perturbs the wavefunctions of the FM via exchange interaction. The change in free energy due to this perturbation gives rise to DMI [64]. Such a sustained magnetic rotation in real space (e.g., as seen in skyrmions), also requires the breaking of inversion symmetry, giving directionality to the magnetic rotation.

As further proof of our model for the rotation of magnetization from SOC, we present our analysis of projected band structures for some chosen magnetic bilayers. To simplify the analysis, we reduce the unit cells of our chosen bilayers along X and Y. For a band structure projected onto the 1st orbital, the size of a data point at a given \((E, \vec{k})\), signifies the strength of contribution from the 1st orbital of the state at that \((E, \vec{k})\). To study a given SOC transition term between orbitals \(d_1\) and \(d_2\), we compare the strength of contributions from \(d_1\) and \(d_2\), before and after SOC is switched on. For an \((E, \vec{k})\) point that shows the presence of \(d_1\) orbital in the absence of SOC, if switching on the SOC increases the presence of \(d_1\) orbital, one can surmise that SOC has caused an orbital transition from \(d_1\) to \(d_2\) at that point.

Fig. 3 compares the bandstructures for Pt/Co \((D = 5.3mJ/m^2)\) and Os/Fe \((D = -12.1mJ/m^2)\) with projections taken on the HM \(d_{xz}\) and \(d_{x^2-y^2}\) orbitals. Pt/Co, with a positive DMI, has a strong \(d_{x^2-y^2}\) presence around K, and a net transition of \(d_{x^2-y^2}\) into \(d_{xz}\) orbitals (shown in red). Os/Fe, with a negative DMI, has a weaker \(d_{x^2-y^2}\) presence around the K point, and shows the converse transition of \(d_{xz}\) into \(d_{x^2-y^2}\) orbitals (shown in deep blue). Re/Fe \((D = -7.8mJ/m^2)\) behaves similarly to Os/Fe, demonstrating \(d_{xz}\) to \(d_{x^2-y^2}\) transitions (see Fig. 6), whereas Os/Co \((D = -12.6mJ/m^2)\) shows transitions in both directions (see Fig. 6). Comparing the
strength of $d_{x^2-y^2}$ orbitals (see Fig. 6), one can clearly see that Pt/Co has a much stronger presence of $d_{x^2-y^2}$ orbitals at the K point than all 3 bilayers with negative DMI (Re/Fe, Os/Fe and Os/Co). This can explain why Pt/Co shows a net transition from $d_{x^2-y^2}$ to $d_{z^2}$, while the others do not.

A similar picture is seen for transitions between $d_{xy}$ and $d_{yz}$ orbitals. Pt/Co, with a positive DMI, shows a transition of $d_{xy}$ to $d_{yz}$ (shown in deep blue); while Os/Fe, with a negative DMI, shows the converse transition of $d_{yz}$ into $d_{xy}$ (shown in red in Fig. 7). We do not see significant signatures of transitions between $d_{z^2}$ and $d_{xz}$ orbitals. Both our derivation and band structure plots show that DMI is caused by off-diagonal terms of SOC which lead to transitions between the d-orbitals of the HM and rotate the magnetic moment of the electron in the process. The value and sign of the net DMI depends on the relative competition between three such SOC terms. Our model is in keeping with Moriya’s 2-site model for DMI in magnetic insulators, where the DMI term was a product of the spin mixing SOC term and a hopping term.

Summary- In this paper we present a systematic study of DMI in magnetic bilayers. An important result is the giant DMI predicted for four bilayers namely Re/Co, Os/Co, Os/Ni and hBi/Ni. We also put forth Os/Co/Pt and Re/Co/Pt as new candidates for magnetic multilayers. Another important result is the model that explains the microscopic mechanism which creates skyrmions in magnetic bilayers and generates interfacial DMI.

[1] Constance Moreau-Luchaire et al., “Additive interfacial chiral interaction in multilayers for stabilization of small individual skyrmions at room temperature”, Nature nanotechnology 11.5 (2016), p. 444.
[2] Albert Fert, Nicolas Reyren, and Vincent Cros, “Magnetic skyrmions: advances in physics and potential applications”, Nature Reviews Materials 2.7 (2017), p. 17031.
[3] Albert Fert, Vincent Cros, and Joao Sampaio, “Skyrmions on the track”, Nature nanotechnology 8.3 (2013), p. 152.
[4] Axel Hoffmann and Sam D Bader, “Opportunities at the Frontiers of Spintronics”, Physical Review Applied 4.4 (2015), p. 047001.
[5] Wang Kang et al., “Voltage controlled magnetic skyrmion motion for racetrack memory”, Scientific reports 6 (2016), p. 23164.
[6] Alexei N Bogdanov and DA Yablonskii, “Thermodynamically stable vortices in magnetically ordered crystals. The mixed state of magnets”, Zh. Eksp. Teor. Fiz 95.1 (1989), p. 178.
[7] UK Rössler, AN Bogdanov, and C Pfeidereri, “Spontaneous skyrmion ground states in magnetic metals”, Nature 442.7104 (2006), p. 797.
[8] Stefán Heinze et al., “Spontaneous atomic-scale magnetic skyrmion lattice in two dimensions”, Nature Physics 7.9 (2011), p. 713.
[9] Niklas Romming et al., “Writing and deleting single magnetic skyrmions”, Science 341.6146 (2013), pp. 636-639.
[10] B Dupe et al., “Engineering skyrmions in transition metal multilayers for spintronics”, Nature communications 7 (2016), p. 11779.
[11] A Hrabec et al., “Measuring and tailoring the Dzyaloshinskii-Moriya interaction in perpendicularly magnetized thin films”, Physical Review B 90.2 (2014), p. 020402.
[12] Seonghoon Woo et al., “Observation of room temperature magnetic skyrmions and their current driven dynamics in ultrathin metallic ferromagnets”, Nature materials 15.5 (2016), p. 501.
[13] Anjan Soumyanarayanan et al., “Tunable room temperature magnetic skyrmions in Ir/Fe/Co/Pt multilayers”, Nature materials 16.9 (2017), p. 898.
[14] Olivier Boule et al., “Room-temperature chiral magnetic skyrmions in ultrathin magnetic nanostructures”, Nature nanotechnology 11.5 (2016), p. 449.
[15] Anjan Soumyanarayanan et al., “Emergent phenomena induced by spin orbit coupling at surfaces and interfaces”, Nature 539.7630 (2016), p. 509.
[16] E Simon et al., “Spin-correlations and magnetic structure in an Fe monolayer on 5d transition metal surfaces”, Journal of Physics: Condensed Matter 26.18 (2014), p. 186001.
[17] Hongxin Yang et al., “Anatomy of Dzyaloshinskii-Moriya interaction at Co/Pt interfaces”, Physical review letters 115.26 (2015), p. 267210.
[18] Hongxin Yang et al., “Controlling Dzyaloshinskii-Moriya interaction via chirality dependent atomic-layer stacking insulator capping and electric field”, Scientific reports 8 (2018), 12356.
[19] Gong Chen et al., “Tailoring the chirality of magnetic domain walls by interface engineering”, Nature communications 4 (2013), p. 2671.
[20] Georg Kresse and Jürgen Hafner, “Ab initio molecular dynamics for liquid metals”, Physical Review B 47.1 (1993), p. 558.
[21] Georg Kresse and Jürgen Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set”, Computational materials science 6.1 (1996), p. 15-50.
[22] Georg Kresse and Jürgen Furthmüller “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”, Physical review B 54.16 (1996), p. 11169.
[23] Georg Kresse and D Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method”, Physical Review B 59.3 (1999), p. 1758.
[24] F Reis et al., “Bismuthene on a SiC substrate: A candidate for a high-temperature quantum spin Hall material”, Science 357.6348 (2017), pp. 287-290.
[25] R Tolley, SA Montoya, and EE Fullerton, “Room-temperature observation and current control of skyrmions in Pt/Co/Os/Pt thin films”, Physical Review Materials 2.4 (2018), p. 044404.
[26] Igor Dzyaloshinsky, “A thermodynamic theory of ‘weak’ ferromagnetism of antiferromagnetics”, Journal of Physics and Chemistry of Solids 4.4 (1958), pp. 241-255.
Figure 4. (a,b) Schematic of our structure of Pt/Co bilayer. (a) The front view of the pre-relaxed structure, which includes 10 Å of vacuum. (b) Top view of the post-relaxed structure. (c) Schematic of a Néel skyrmion
Figure 5. Bandstructure of bilayers calculated without spin orbit coupling, projected onto $d_{x^2-y^2}$ orbitals. The presence of $d_{x^2-y^2}$ orbitals around K is much stronger for (a) Pt/Co than (b-d) Re/Fe, Os/Fe and Os/Co. Fermi level is at 0 eV.

Figure 6. Bandstructure of Re/Fe and Os/Co projected onto $d_{xz}$ (cyan) and $d_{x^2-y^2}$ (magenta) orbitals. Calculations without (with) spin orbit coupling are shown in the left (right) column. Areas where we see orbital transitions from $d_{xz}$ to $d_{x^2-y^2}$ are plotted in deep blue, and the converse transition is marked in red. Fermi level is at 0 eV.
Figure 7. Bandstructure of Pt/Co and Os/Fe projected onto $d_{xy}$ (cyan) and $d_{yz}$ (magenta) orbitals. Calculations without (with) spin orbit coupling are shown in the left (right) column. Areas where we see orbital transitions from $d_{xy}$ to $d_{yz}$ are plotted in deep blue, and the converse transition is marked in red. Fermi level is at 0 eV.