Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Periodic DFT Calculations to Compute the Attributes of a Quantum Material: Honeycomb Ruthenium Trichloride – Supporting Information

Ashlyn M. Koval[a,b], Glen R. Jenness[c], Timothy C. Schutt[c], Gilbert K. Kosgei[c], P.U. Ashvin I. Fernando[b], and Manoj K. Shukla[c]

[a]*Oak Ridge Institute for Science and Education (ORISE), Oak Ridge, Tennessee 37830 United States*

[b]*Current affiliation: Simetri, Inc., 7005 University Blvd, Winter Park, Florida 32792, United States*

[c]*Environmental Laboratory, US Army Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, Mississippi 39180, United States*

*Corresponding authors; Email: timothy.c.schutt@usace.army.mil; manoj.k.shukla@usace.army.mil

Table of Contents

EXPERIMENTAL UV-VIS SPECTRA 3

LATTICE PARAMETER CONVERGENCE 4

Non-Gamma Shifted Grid 4
Gamma-Shifted Grid 4

BANDGAP CONVERGENCE VS K-POINT DENSITY 5

CHEMICAL POTENTIAL VS K-POINT DENSITY 6

RELATIVE ENERGY OF THE AFM STATES 7

Rec3D with Plane Waves 7
RhomMono with Differing Ruthenium Valency 7

Experimental UV-Vis Spectra

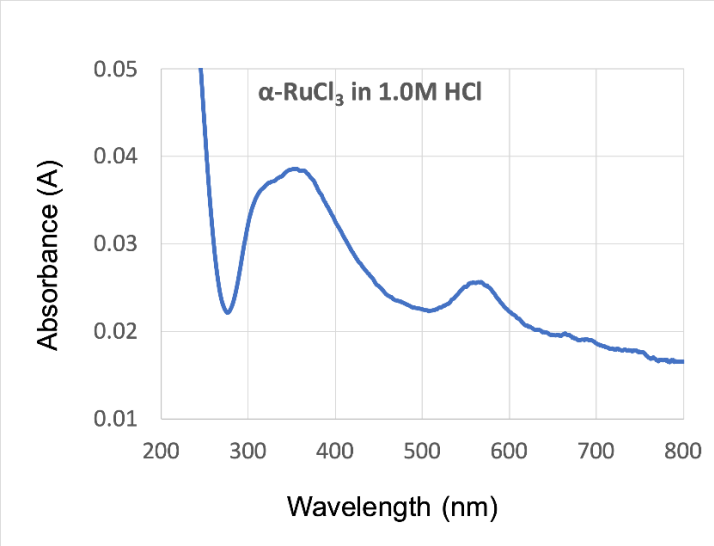

Figure S1. The UV-Vis absorption spectrum of α-$RuCl_3$ was obtained using a freshly prepared solution in 1.0M HCl.

Lattice Parameter Convergence

Non-Gamma Shifted Grid

Table S1. Lattice parameters (Å) computed with respect to k-point density & Hubbard correction (U) using a non-gamma-shifted grid for the ferromagnetic spin state of Rec3D. Calculations completed using optPBE-vdW and plane waves cut off (600 eV). When the k-point density was varied (left side of the table) the U was kept at a static value of 2.5 eV and when the U was varied (right side of the table) the k-point density was kept at a static value of 3.0 points per Å^{-1}.

k-point Density (points per Å^{-1})	**k-point Grid**	**a (Å)**	**b (Å)**	**c (Å)**	**Hubbard Correction (eV)**	**a (Å)**	**b (Å)**	**c (Å)**
2.0	3 × 2 × 1	16.91	10.59	6.13	**1.5**	16.89	10.52	6.11
3.0	4 × 2 × 2	16.90	10.59	6.13	**2.5**	16.90	10.59	6.13
4.0	5 × 3 × 2	16.90	10.59	6.13	**3.5**	16.80	10.61	6.14
*from neutron scattering[70] α-$RuCl_3$ lattice is: a = 17.05 b = 10.32 c = 5.96								

Gamma-Shifted Grid

Table S2. Lattice parameters (Å) computed with respect to k-point density using a gamma-shifted grid for the ferromagnetic spin state of Rec3D. Calculations completed using optPBE-vdW and plane waves cut off (600 eV). When the k-point density was varied the U was kept at a static value of 2.5 eV.

k-point Density (points per Å^{-1})	**k-point Grid**	**a (Å)**	**b (Å)**	**c (Å)**
2.0	3 × 2 × 1	16.90	10.59	6.13
3.0	4 × 2 × 2	16.91	10.59	6.13
4.0	5 × 3 × 2	16.90	10.59	6.13
*from neutron scattering[70] α-$RuCl_3$ lattice is: a = 17.05 b = 10.32 c = 5.96				

Bandgap Convergence vs k-point Density

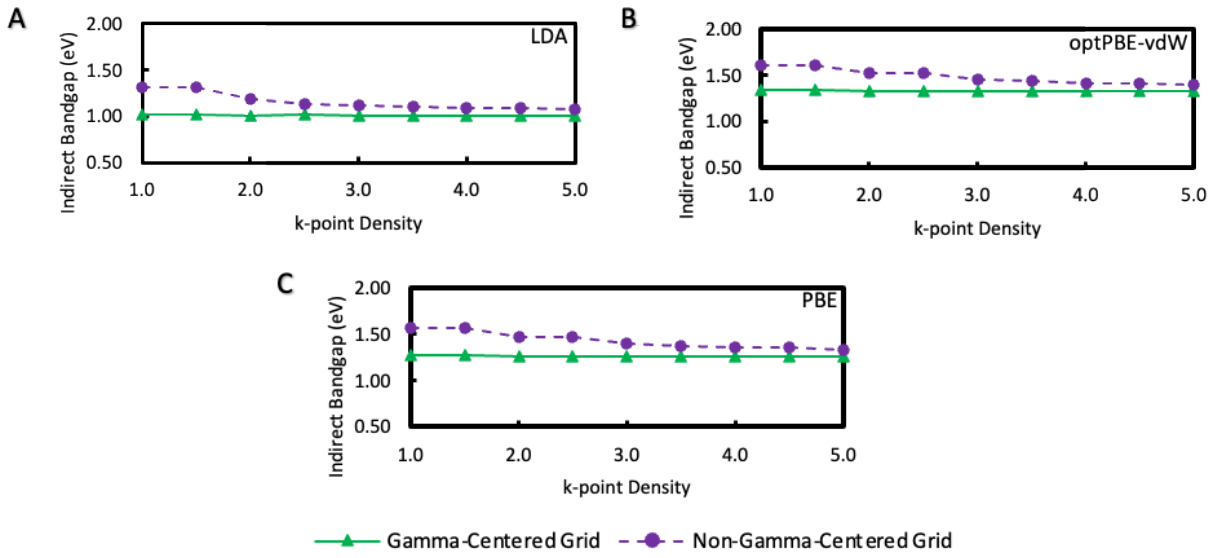

Figure S2. Band gap (E_g) convergence for the ferromagnetic spin state of Rec3D. Solid greenline is computed using a gamma-centered gric. Dashed blue line is computed using a non-gamma centered grid. A) E_g convergence with respect to k-point density computed using LDA & finite difference. B) E_g convergence with respect to k-point density computed using optPBE-vdW & finite difference. C) E_g convergence with respect to k-point density computed using PBE & finite difference.

Initial observations of the date presented in Figure S2 determined that when the grid was not specified to be gamma-centered the E_g started high at low k-point density before slowly decreasing towards higher k-point densities. Applying linear regression gives a slope of -0.0667 eV, -0.0616 eV, and -0.0642 eV for LDA, optPBE-vdW, and PBE, respectively. On the other hand, the gamma-centered grid specification results in a much more linear trend with linear regression slopes of -0.0042 eV, -0.0027 eV, and -0.0027 for LDA, optPBE-vdW, and PBE, respectively. This indicates that the gamma-centered grid is much faster to converge with respect to k-point density and that we do not need to consider large k-densities to achieve convergence. In fact, if we neglect to include the k-point densities of 1.0 points per $Å^{-1}$ and 1.5 points per $Å^{-1}$ the slope of the trend line for the data from 2.0 points per $Å^{-1}$ to 5.0 points per $Å^{-1}$ is only -0.0002 eV and -0.0006 eV for optPBE-vdW and PBE, respectively. In the case of LDA we see the exclusion of these data points only causes the slope to decrease to -0.0025 which is roughly half of the original slope. This indicates that LDA is reaching convergence with respect to k-point density more slowly than the other two functionals. It should also be noted that LDA underestimates the predicted E_g to be much lower (avg. 1.01±0.06 eV) than either optPBE-vdW (avg. 1.33±0.01 eV) or PBE (avg. 1.26±0.01 eV).

Chemical Potential vs k-point Density

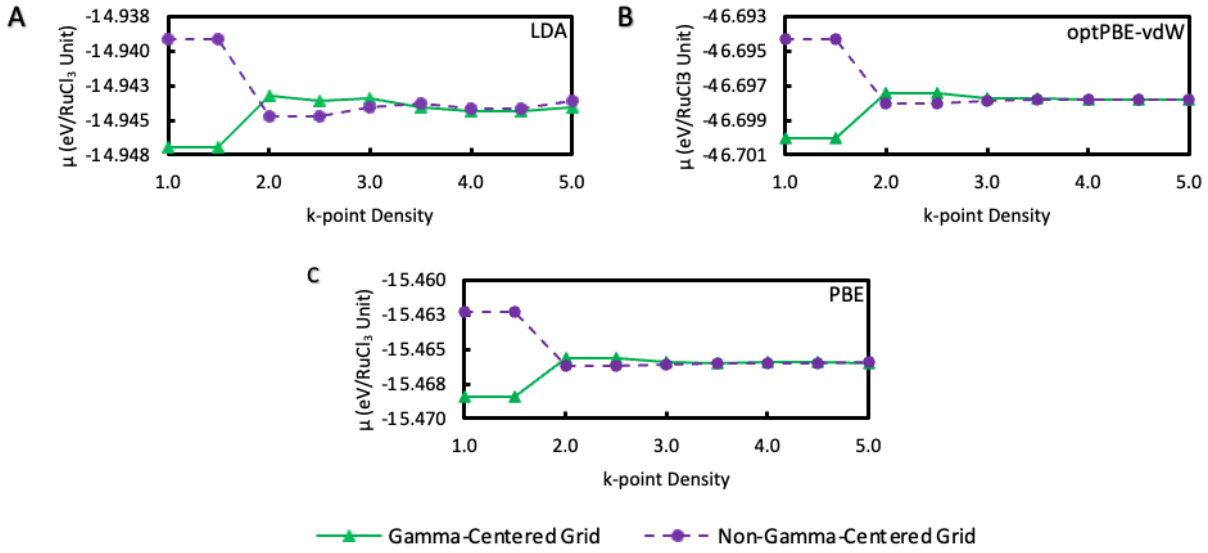

Figure S3. Chemical potential convergence for the ferromagnetic state of Rec3D. Solid greenline is computed using a gamma-centered gric. Dashed blue line is computed using a non-gamma centered grid. A) Chemical potential (μ) convergence with respect to k-point density computed using LDA & finite difference. B) Convergence of μ with respect to k-point density computed using optPBE-vdW & finite difference. C) Convergence of μ with respect to k-point density computed using PBE & finite difference.

The μ presented in Figure S3 with respect to k-point density has a different starting point depending on whether a gamma-centered grid is specified or a gamma-centered grid is not specified. At low k-point densities (1.0 — 1.5 points per $Å^{-1}$) the μ for the non-gamma shifted grid is higher in energy than the gamma-shifted grid. Then between k-point densities of 2.0 — 3.0 points per $Å^{-1}$ this trend flips so that the gamma-shifted grid is higher in energy than the non-gamma shifted grid. The LDA functional (Figure S3A) in particular starting from a k-point density of 3.0 points per $Å^{-1}$ and up continues to fluctuate rather than converging to a specific value. It is possible that a higher k-point density might be necessary in order to reach convergence with the use of the LDA functional. Nevertheless, in the case of both the PBE and optPBE-vdW functionals (Figure 5A & Figure5 B) we see that both the gamma-shifted and non-gamma grids appear to reach convergence around a k-point density of 3.0 points per $Å^{-1}$. This information combined with the previous analysis of E_g convergence in Section 3.1.2, and the lack of sensitivity of lattice to k-point density indicates that a k-point density of 3.0 points per $Å^{-1}$ should be a sufficient compromise on convergence and computational time. It can also be evaluated that the PBE and optPBE-vdW functionals are more appropriate as they calculate E_g closest to experimentally determined values and also reach convergence of thus far calculated properties.

Relative Energy of the AFM States

Rec3D with Plane Waves

Table S3. Relative energy of the AFM spin states to the ferromagnetic spin state (meV) using a gamma-shifted grid. Calculations completed using optPBE-vdW, U of 1.5 eV, and k-point density of 3.0 points per $Å^{-1}$.

Structure	Rec3D (3 layers)		
Method	PBE		optPBE-vdW
Basis Set	PW 400	PW 600	PW 600
FM	0	0	0
AFM-ZZ	133	132	221
AFM-ST	136	136	228
AFM-NE	67	67	75

RhomMono with Differing Ruthenium Valency

Table S4. Relative energy of the AFM spin states to the ferromagnetic spin state (meV). Calculations completed using optPBE-vdW and k-point density of 3.0 points per $Å^{-1}$.

Ru^{3+} Valency			16 e^-					8 e^-		
U (eV)	1.5	2.0	2.5	3.0	3.5	1.5	2.0	2.5	3.0	3.5
FM	0	0	0	0	0	0	0	0	0	0
AFM-ZZ	6.0	5.7	3.0	2.4	3.7	-0.55	1.87	-1.84	2.83	-0.88
AFM-ST	1.5	-1.2	-3.9	-1.6	-1.4	2.19	3.27	-2.23	-1.57	-0.02
AFM-NE	9.2	5.6	2.2	2.2	1.6	9.57	5.00	2.19	2.62	2.61