

学 位 論 文 の 要 旨

専 攻 名	材料科学 専 攻	ふ り が な 氏 名	な わ けんじ 名和 憲嗣	㊟
学位論文題目 First principles study on effective on-site Coulomb interaction from linear response approach and application to metal complexes (和訳 線形応答理論による有効オンサイトクーロン相互作用の第一原理計算と金属錯体への応用)				
<p>In investigations on electronic structures of correlated materials such as transition-metal oxides, rare-earth compounds, and organometallic molecules, first-principles calculations based on density functional theory (DFT) play a central role. However, there is a problem remaining to deal with correlation effects in the DFT for correlated materials. On a practical level, DFT+U method that introduces Hubbard-model parameters to represent screened on-site Coulomb (U) and exchange (J) interaction is one of the powerful and conventional tools suitable for calculations of large systems without expensive costs. The values of U and J are commonly chosen to match experimental observations, but optimal values depend on which exchange-correlation functional is used and the calculated material properties are very sensitive to values of on-site U and J even in the ground state. More recently the parameters have been calculated directly from first-principles calculations, but they vary over wide ranges of values even for the same ionic state in a given material. Unfortunately, this implies that choosing “good” values is problematic.</p> <p>In order to address this issue, here, non-empirical method for deriving scaled U parameters is developed and applied to the prototypical materials of correlated transition-metal monoxides and organometallic molecules. This dissertation consists of five chapters. After an introduction to electronic structures of correlated materials and general failures of the DFT-based first-principles calculations in chapter one, methodologies of the DFT and linear response approach to estimate an effective on-site Coulomb interaction, $U_{\text{eff}} = U - J$, of correlated elements are described in chapter two, where the U_{eff} values determined from the second derivative of the total energy with respect to the occupation numbers of localized d-electrons within the linear response theory. All calculations were carried out by means of the all-electron full-potential linearized augmented plane wave (FLAPW) method.</p> <p>Chapter three devotes to an application of this approach to the transition-metal monoxides, TMO (TM=Mn, Fe, Co, and Ni), where the variation of U_{eff} values by changing the muffin-tin (MT) sphere radius was examined. It is found that the U_{eff} value depends strongly on MT sphere size by more than 2~3 eV in all systems, for example, in MnO when the MT radius is 2.0 bohr, the U_{eff} value results in 10.1 eV but it decreases to 7.2 eV as the MT radius increases to 2.7 bohr.</p>				

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The same trend in the U_{eff} values was confirmed in other considered oxide systems. However, despite this large variation, essentially identical valence band structures are obtained, and I found an approximate scaling of U_{eff} with regard to size of MT sphere. Thus, although simple transferability of the U_{eff} value among different calculation methods is not allowed, guidelines for estimating U_{eff} are proposed.

In chapter four, this approach was applied to ground-state electronic structure calculations of correlated organometallic metallocens, TMCP_2 (TM=V, Cr, Mn, Fe, Co, and Ni). In these complexes, however, an additional difficulty intrinsically related to various electronic configurations of d electrons that nearly degenerate is raised, which may numerically trap in one of multiple local energy minima corresponding to meta-stable electronic configurations, instead of a global minimum of the ground state. The changes due to the presence of the ligand field of molecules further complicate theoretical analysis so that the DFT+U calculations may fail to search a ground-state electronic configuration truly. To overcome this problem, I implemented the constraint DFT+U approach that controls electronic configurations by introducing Lagrange multipliers to the d electron density matrix. Thus, the total energies of all electronic configurations allowed by a symmetric group were calculated self-consistently with the Lagrange multipliers and then the ground electronic configuration was energetically determined. The predicted results demonstrate precisely the experimentally observed grand-states, i.e., $^4A_{2g}$, $^3E_{2g}$, $^6A_{1g}$, $^1A_{1g}$, $^2E_{1g}$, and $^3A_{2g}$ for VCp_2 , CrCp_2 , MnCp_2 , FeCp_2 , CoCp_2 , and NiCp_2 , respectively, while the stability between different electronic configurations is found to be very sensitive depending on the U_{eff} values. Thus, an utility of constraint DFT+U method combined with non-empirical U_{eff} values for analyzing properties of correlated systems was demonstrated.

Chapter five concludes the thesis that by using the proposed methodology opens a new avenue toward reliable predictions of structures and physical properties in strongly correlated metal complexes and gives suggestions for future calculations.