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Comparison of Finite Element Approach and LCAO Analysis with SIWB Method for a Molecule Including an Anion in a Discrete Variational Density Functional Theory

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Since the 1930s, antiferromagnetism in metal oxides, which is a special case of ferrimagnetism, has been unsuccessfully attempted to be described using the density functional theory (DFT) or similar theories; this hitherto unsolved problem in solid state physics has only recently been solved. The difficulty in solving this problem stems from a peculiar property exhibited by electrons on a negative ion like oxygen. The anion O^{2-} is stable in a solid and molecule; however, O^{2-} in a vacuum is not observed, although the experimental observation of O^{-} in a vacuum has been achieved. In order to describe this peculiar property of electrons on an anion, the author developed the SIWB method (**s**urround or solid Coulomb-potential-**i**nduced **w**ell for **b**asis set) [1-5] for a linear combination of atomic orbitals (LCAO), calculated numerically via a discrete variational (DV) method in a DFT. The DV method usually adds a relatively deep well potential within a radius of about 3.5 a.u. to the potential on electrons in an anion for generating atomic orbital basis functions, where the depth and radius of the well are not definitely determined. On the other hand, in the author's SIWB method mentioned above, the well depth for an anion is determined using the spherically averaged Coulomb potential from quantum electron clouds and nuclei around the central anion in a solid/molecule. The well depth is measured from the minimum energy level, over which electrons move freely when the potential except for the potential constructing the well does not exist. The well radius is determined from the anion radius, whose value at the first step was equivalent to the Shannon ionic radius (crystal radius), based on Pauling's theory considering Goldschmidt's experimental data. At the second step, the SIWB method self-consistently derives an anion radius as a well radius, which is the distance from the anion nucleus to the point where the electron charge density of the anion is equal to that of the nearest neighboring cation [4]. The well radius value obtained with this method is shallower than that obtained with the conventional DV method, and leads to the insulating antiferromagnetic state for periodic copper (Cu) oxides (cuprates), lowering the total energy to less than that of the non-magnetic metallic state [2]. This presentation reports that the wave function of electrons on an anion H of a small ionic LiH molecule via SIWB bears closer resemblance to that obtained from the finite-element approach than that obtained from the conventional LCAO (DV) method [6]; it should be noted that the finite-differential approach is reliable because it involves microscopic analysis, similar to the finite-difference approach.

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