Description of delocalized negative ions leading to peculiar ionic material properties such as antiferromagnetism using the SIWB method in a density functional theory

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This paper reports on the description of delocalized negative ions (anions) such as \( \text{O}_2^\text{−} \) in a solid. These exist stably in a solid, despite the fact that an isolated \( \text{O}_2^\text{−} \) in a vacuum emits an electron, which causes peculiar ionic material properties, such as antiferromagnetism in copper oxides. The present study used the SIWB (surrounding- or solid-Coulomb-potential induced well for basis set) method [1-4], which was formulated by the present author for improving the anion basis set in the discrete variational (DV) method scheme [5,6] in a density functional theory (DFT). Since the 1930s, the antiferromagnetism prediction in a DFT had failed until recently; however, the SIWB method successfully reproduced the antiferromagnetism of copper oxides. The DV method employs linear combinations of atomic orbital basis functions calculated numerically, which add well potentials with an arbitrary depth within an arbitrary radius, to the potential in an isolated atom for generating the basis set. The SIWB method, used solely for negative ions, determined the depth of the well potential produced from the surrounding nuclei and electron clouds by using the Evjen method. The spherically symmetric average well depth is relative to the maximum of each average potential among divided thin spherical shell regions apart from the anion. The well radius adopted in the first version complied with the Shannon-Prewitt radius based on Pauling’s theory considering Goldschmidt’s experimental data. The anion radius employed as the well radius for the second version was \( R_{\text{eq}} \) (which is an iteratively converged value), at which point the charge of the cation (positive ion) and that of the anion are equal.

References