Heitler-London Type Start Functions in Real-Space Electronic State Calculations

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Real-space calculation methods develop lately in density functional theories (DFT) for investigating the electronic states in various materials. As for the k-space methods, projected augmented (plane) wave (PAW) methods have established successful processes as the main theory in such studies, but these methods drag several weak points as like problems in non-crystalline systems. The r-space DFT clear such problems, and one of them is proposed in this paper as a method for requiring the precision of semi-empirically calculated results.

The linear combination of valence bonds (LCVB) method is adapted here as a simple and easy semi-empirical method, which uses the corrected Heitler and London (H-L) type basis functions. The old H-L theory cannot satisfy the virial coefficients where the potential U over the kinetic T energy is equal to -2 as the first principle. In this paper, this H-L theory is corrected to satisfy the virial theory by taking account of the molecular Bohr radius (MBR) $b_0 = a_0 / \alpha$, where a_0 is (atomic) Bohr radius and $\alpha = 1.1661$. This manipulation correct the system energy E ftom -30.4 to -30.9 at the observation -31.9 eV, the atomic distance R from ~1.51 to 1.43 at 1.40 a_0 and the virial coefficient rate U/T from -2.26 to -2.00 at -2.00 as shown in Fig.1. In this calculation, the Hartree- Fock exchange energy cannot appear because of the only two-electron system. The exchange terms in the H-L theory are realized as the modified quantities of the atomic orbitals, which are optimized with a mixing parameter 1 (atomic) :1 (exchange) as a two particle system.

The concept of the MBR is born from a new idea of the quantum states in molecules, where the spaces of the quantum cyclic motion sized by b_0 as $mv \times 2\pi b_0 = nh$ in molecules are smaller than the atomic one sized by a_0. The minimum state energy of a hydrogen molecule is estimated from the coupled derivatives with the factor α and with the atomic distance R in the energy equation of the H-L theory. The results in the LCVB method (using only analytical functions) satisfy the first principle of the virial theory under this manipulation and produce good starting states of the density functional calculations for estimating highly precise results.

By means of a r-space DFT, the precise results can be derived from the start functions calculated with this LCVB method. The processes of such r-space DFT are also based on the virial theory and the momentums (kinetic energies) derived as the gradient of the wave (density) functions. The details are discussed in the main paper.
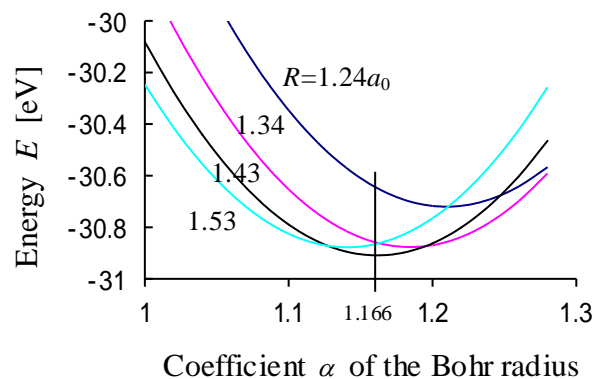

Fig.1 Energy minimum point at MBR in H_2.

Keywords: hydrogen molecule, virial theory, LCVB method, first principle, DFT.