

Basis Function Corrections in the LCVB Method

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Start functions of a real-space density functional (RDF) approach are proposed using the results of the linear combination of valence bonds (LCVB) method. As the first step basis data of the DF calculations, spatial electron densities in molecules are determined with the LCVB method. For increasing precision of these data, the atomic orbitals are corrected with modification functions by means of the improved Rosen's method, where the precision is fairly increased and the virial coefficient is satisfied.

Key words: density functional theory, LCVB method, molecular orbitals, real space.

1. INTRODUCTION

Quantum Monte Carlo (QMC) methods have excellent for accurately investigating electronic states of molecules and solids except for loads of a large amount of computations.^[1] Opposite to such methods, our theory has purpose to perform the works in brief calculations using simple and analytical functions. In this paper, simple formulations (ignored for a long-long time) are introduced as the modified Heitler-London (HL) theories^{[2]-[5]}, which results are adaptable to start up calculations of the density functional theories (DFT)^[6]. HL^[2] formulated the hydrogen molecule using two direct hydrogen atomic orbitals. These results have not enough accuracy as like the ground state of -30.4 eV, the atomic distance $1.51a_0$ and the virial coefficients $U/T=-2.32$ for the observed values $E_0=-31.96=-27.21-4.75$ eV, $1.40a_0$ and -2, respectively. The quantities are a_0 : the Bohr radius, U : the potential energy and T : the kinetic energy. After this, N. Rosen^[3] improved this formulation and showed the good results (-31.23 eV, $1.416a_0$ and -2.0) with the brief corrections. Then, H. M. James and A. S. Coolidge (JC)^[4] showed the almost exact results (-31.90 eV, $1.40a_0$ and -2.0) using the two-electron orbitals consisted of 13 terms applied the Hylleraas variational calculations. In recent studies, J. S. Sims and S. A. Hagstrom (SH)^[5] showed the very precise results (-31.958 eV, $1.40a_0$ and -2.0) using the 7034 term orbitals followed the above JC algorithm. Thus, the algorithms based on the HL theory build up the excellent molecular orbital theories beside the Gaussian, the DFT and the QMC theories.

The Hamiltonian of two-atom molecules becomes

$$\hat{H}_{AB} = \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{a_0}{2} (\nabla_1^2 + \nabla_2^2) + \left(\frac{z_A z_B}{R_{AB}} + \frac{1}{r_{12}} - \frac{z_A}{r_{A1}} - \frac{z_B}{r_{B1}} - \frac{z_A}{r_{A2}} - \frac{z_B}{r_{B2}} \right) \right\} \quad \dots\dots(1)$$

and satisfies the quantum theory:

$$\hat{H}_{AB} \Psi_{AB}(r_1, r_2) = E \Psi_{AB}(r_1, r_2) \quad \dots\dots\dots(2)$$

This equation (2) becomes the driving algorithm in most of molecular orbital theories as the first principle. In N electron systems, the N kinetic energies and the full potential interactions are taken into account in the Hamiltonian, and the N -electron wave function satisfies

the equation (2). The wave function must satisfy the same energy minimum state everywhere. The above theories should give this result at the final precision stage.

Thus, these molecular orbital theories have the each purpose as how to get the exact results, how to calculate easily, how to represent simply etc.. Our theory i.e. the linear combination of valence bonds (LCVB) method^{[7]-[9]} has the purpose as how to get the good results in simple and short calculations. The basis processes of the modifications are represented in §2 and the results are compared with each other in §3. In §4, the density of states in a nanotube is shown as an example of the LCVB method.

2. BASIC FORMULATION

2.1 Basic algorithm for adapting atomic orbitals

The atomic orbitals are directly obtained from the Schrödinger equations of atoms;

$$\hat{H}_A = \frac{e^2}{4\pi\epsilon_0} \left\{ -\frac{a_0}{2} \nabla_1^2 - \frac{z_A}{r_{A1}} \right\}, \quad \dots\dots\dots(3)$$

$$\hat{H}_A \phi_A(r_1) = E \phi_A(r_1) \quad \dots\dots\dots(4)$$

By superposing the modification functions $f(r)$ to these, the corrected atomic orbitals functions

$$\phi_A(r_1) = f(r_1) \phi_A(r_1) \quad \dots\dots\dots(5)$$

are obtained analytically. The molecular orbitals of the bonded A - B atoms are equated using these functions as the bonding state

$$\Psi_{AB}(1,2) = \frac{1}{\sqrt{2(1+s_{AB}^2)}} \{ \phi_A(r_1) \phi_B(r_2) + \phi_A(r_2) \phi_B(r_1) \} \quad \dots\dots(6)$$

under the HL algorithm, where the front term is determined with the normalization condition

$$\iint \Psi_{AB}^*(r_1, r_2) \Psi_{AB}(r_1, r_2) dV_1 dV_2 = \langle \Psi_{AB} | \Psi_{AB} \rangle = 1 \quad \dots\dots\dots(7)$$

and the overlap integrals

$$s_{AB} = \int \phi_A(r_1) \phi_B(r_1) dV_1 \quad \dots\dots\dots(8)$$

In (6), the anti-bonding state is equated by setting the sign as - in the bracket.

2.2 Examples of the hydrogen molecule

As simple examples, several cases of the hydrogen

molecule are discussed below. The coordinates and the distances are represented using the atomic position vector of *A B* atoms being $R_{AB}=Ri$ as

$$r_{A1} = \sqrt{x_1^2 + y_1^2 + z_1^2}, \quad r_{B2} = \sqrt{(R-x_2)^2 + y_2^2 + z_2^2} \quad \dots\dots(9)$$

Using these coordinates, the orbitals of hydrogen atoms are equated as

$$\phi_A(r_1) = \frac{1}{\sqrt{\pi b^3}} e^{-r_{A1}/b}, \quad \phi_B(r_2) = \frac{1}{\sqrt{\pi b^3}} e^{-r_{B2}/b} \quad \dots\dots(10)$$

where $b=z/a_0$ means the molecular Bohr radius including the effective charge z .

Simplest case

The simplest case of $f(r)=1$ in (5) has already the minimum energy $E=-31.00$ eV, distance $R=1.416a_0$ and the virial coefficient $U/T=-2.0$ at $z=1.167$ ($b=0.857a_0$). This effective charge z is larger than 1 and should be realized as the space shrinkage effect of the quantum motion in the molecule.

N. Rosen

Soon after the HL work, N. Rosen showed the improved results using the modified functions

$$f_A(r_1) = \frac{1}{\sqrt{1+a^2}} (1 + a \frac{x_1}{b}), \quad f_B(r_1) = \frac{1}{\sqrt{1+a^2}} (1 + a \frac{R-x_1}{b}) \quad \dots\dots(11)$$

as $E=-31.249$ eV, $R=1.416a_0$, and $U/T=-2.0$ at $a=0.095$ and $z=1.181$ ($b=0.8466a_0$).

This work

By improving the Rosen's functions as

$$f_A(r_1) = \frac{1}{\sqrt{A}} \{1 + (a \frac{x_1}{b} + c \frac{x_1^2}{b^2}) e^{-d(y^2+z^2)}\},$$

$$f_A(r_1) = \frac{1}{\sqrt{A}} \{1 + (a \frac{R-x_1}{b} + c \frac{(R-x_1)^2}{b^2}) e^{-d(y^2+z^2)}\}, \quad \dots\dots(12)$$

we obtain the more fitted results: $E=-31.290$ eV, $R=1.40a_0$, and $U/T=-2.0$ at $a=0.12$, $c=0.02$, $d=0.11$ and $z=1.186$ ($b=0.8432a_0$). The value A is the normalization constant being determined numerically.

2.3 Closely exact theory

The JC method is represented here as the final stage of the HL algorithm, but not adapted now with the above reasons. If one could find the simple modification rules with the style of (5) (6) in this method, one should apply such modifications. Using electron positions

$$\lambda_1 = (r_{A1} + r_{B1})/R, \quad \lambda_2 = (r_{A2} + r_{B2})/R, \quad \mu_1 = (r_{A1} - r_{B1})/R$$

$$\mu_2 = (r_{A2} - r_{B2})/R, \quad \rho = 2r_{12}/R, \quad \dots\dots(13)$$

the trial functions of the singlet spin state are equated as

$$F_{iAB}(r_1, r_2) = e^{-\delta(\lambda_1 + \lambda_2)} \lambda_1^m \lambda_2^n \mu_1^{j_1} \mu_2^{k_1} \rho^{p_1},$$

$$F_{iAB}(r_2, r_1) = e^{-\delta(\lambda_1 + \lambda_2)} \lambda_1^n \lambda_2^m \mu_1^{k_2} \mu_2^{j_2} \rho^{p_2},$$

$$\psi_i(r_1, r_2) = \frac{1}{\sqrt{a_i}} \{F_{iAB}(r_1, r_2) + F_{iAB}(r_2, r_1)\}, \quad \dots\dots(14)$$

where the integers m, n, j and p are selected in the natural numbers $\{0,1,2\}$. The first and the second terms have the exchange relation as in (3). The normalization constants a_i are determined with $S_{ii}=1$ in the overlap integrals

$$\iint \psi_i^*(r_1, r_2) \psi_i(r_1, r_2) dV_1 dV_2 = \langle \psi_i | \psi_i \rangle = S_{ii}, \quad \dots\dots(15)$$

and the molecular orbitals are produced as these linear combinations:

$$|\Psi_{AB}\rangle = \sum_{i=1}^{13} c_i |\psi_i\rangle \quad \dots\dots(16)$$

Using each energy evaluation

$$\iint \psi_i^*(r_1, r_2) \hat{H}_{AB} \psi_i(r_1, r_2) dV_1 dV_2 = \langle \psi_i | \hat{H}_{AB} | \psi_i \rangle = H_{ii} \quad \dots\dots(17)$$

and the above overlap integrals S_{ii} , the eigenvalues E and the coefficients c_i are obtained as the solution of the secular equation:

$$[H_{ii} - ES_{ii}] = 0 \quad \dots\dots(18)$$

In this solution, the lowest value E_0 gives the required minimum energy. The selected 13 terms of $[m_1 n_1 k_1 p_1]$ in (14) are $[00000]$, $[00020]$, $[00110]$, $[10000]$, $[10200]$, $[10020]$, $[10110]$, $[20000]$, $[00001]$, $[00021]$, $[00111]$, $[10001]$, $[00002]$. Recently, SH expand the molecular orbitals using such 7034-term 5-integer set and their results are almost exact.

2.4 The one-electron density and the local energy

Using the two-electron state-vectors in (7), we obtain the one-electron density functions with the coordinate r_2 integration as

$$\rho(r_1) = \int \Psi_{AB}^*(r_1, r_2) \Psi_{AB}(r_1, r_2) dV_2 = \langle \Psi_{AB} | \Psi_{AB} \rangle_2 \quad \dots\dots(19)$$

From this result and the energy value expectation, one can define the local energy fluctuations as like

$$E(r) = \frac{\langle \Psi | \hat{H} | \Psi \rangle_2}{\rho(r)} = \frac{T(r) + U(r)}{\rho(r)} \quad \dots\dots(20)$$

The seek out processes of the condition

$$E(r) \rightarrow E_{const} \quad \dots\dots(21)$$

in (20) become the principal methodology in most of molecular orbital theories, and the virial coefficient

$$\langle U \rangle / \langle T \rangle = -2 \quad \dots\dots(22)$$

is satisfied at the minimum expected value of the total E .

3. THE RESULTS AND COMPARISON

3.1 The HL theory and the virial theorem

The hydrogen molecular states by HL are represented in Fig.1 for clearing the situation of our theory. The 10

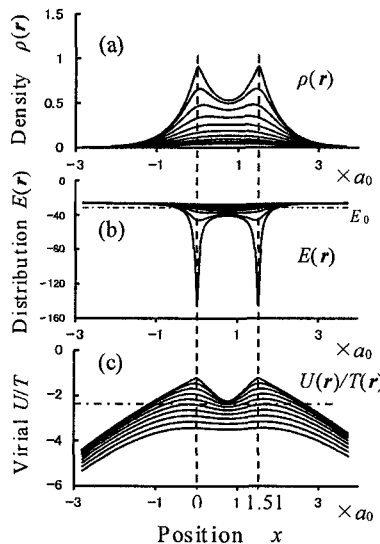


Fig.1 The HL results: $\rho(r)$, $E(r)$ and U/T . $\langle E \rangle = -30.4$ eV, $R=1.51 a_0$ and $\langle U \rangle / \langle T \rangle = -2.32$. The quantities are estimated with Eqs. (19)-(22).

lines in Fig.1 show the trace of the quantity on x-axis at $y_n = a_0(n+\Delta)_{n=0,1,\dots,9}$ with $z=0$ and $\Delta=0.025$. In these results, the local energy distribution and the virial coefficient are not good, but they are improved with the brief corrections in the next section.

3.2 Results in simple, Rosen's and our methods

In this paper, we try to get the good condition of the Eqs. (20) (21) using the atomic orbitals. In this stand, we do not perform the precise variational calculations in §2.3. It might be easy to turn to the DFT from our results for making up the precision.

The results of (19) and (20) in the hydrogen molecule using the modification functions in §2.2 are shown in Fig.2 and Fig.3. The simple and the Rosen's results do not give the observed value of R , but our result satisfies. The 10 trace lines in the figures are the same in Fig.1. The energy fluctuation $E(r)$ is required to be the flat constant under the adjustment of the density distribution $\rho(r)$. The problem is how to get such state in short calculations. In comparison of these in Fig.2, the density corrections are to say small, where the energy fluctuations are improved fairly well in our method as in Fig.3, where the modification of (c) is shifted to $z=1.20$ ($0.8315 a_0$) for the smoothness. Opposite to infinite aria fluctuations in the Rosen's results, our results converge into nearly E_0 . In all cases, the fluctuations in the space between two atoms are large and the electron densities are required to increase on the atomic space of the AB line.

The distributions of the virial coefficient do not change largely between Fig.1 (c) and Fig.4, and seem to have not important meaning in some applications.

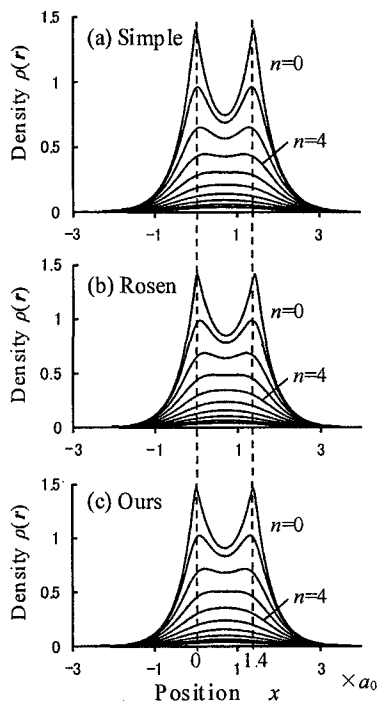


Fig.2 The calculated density distributions of H₂. The densities are results of (19). The modification functions are (a) (1), (b) (11) of N. Rosen and (c) (12) of ours. The right peaks of (a) and (c) are just different from $1.4a_0$ of the observed value, but (c) satisfies.

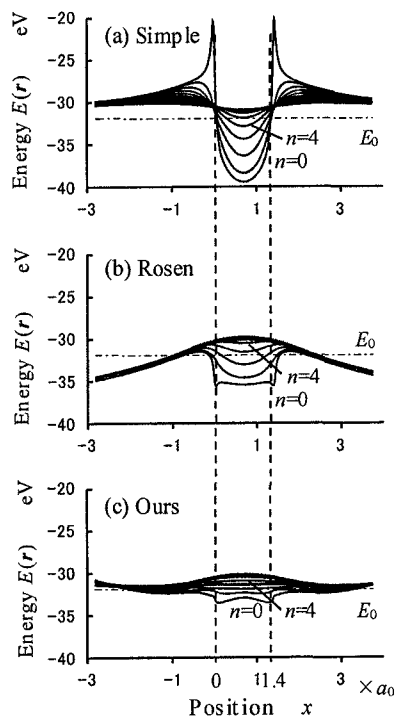


Fig.3 The calculated energy fluctuations of H₂

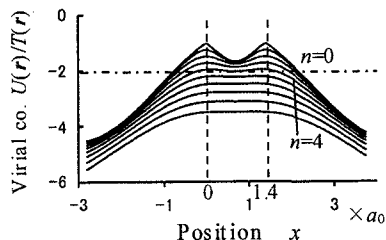


Fig.4 The calculated virial co. distributions of H₂. Our results are shown and other results are similar.

3.3 The practical functions in the LCVB method

One can find mysterious quantum phenomena as complex number fields represented in wave function $\psi = \psi_0(r) \exp(i(p \cdot r - Et)/\hbar)$, where the momentums are determined by $-\hbar \nabla \psi = p \psi$ with the phase factors. In the angular momentum quantization of hydrogen orbitals, the eigenfunction $Y_l^m(\theta, \phi)$ of spherical angular terms includes the angular function $e^{im\phi}$ which produces important relations in the quantum theory. Concerned with the angular momentum \hat{l} , the angular momentum kinetic energy is represented with $\hat{l}^2 \rightarrow l(l+1)$. Such total energy is equated using this and the function of the radius $r_k = |r - R_k|$ about the force center R_k as like

$$-\frac{\hbar^2}{2m_e} \nabla^2 \phi_k(r) = -\frac{\hbar^2}{2m_e} \left(\frac{d^2}{dr^2} + \frac{2}{r_k} \frac{d}{dr} - \frac{l^2}{r_k^2} \right) \phi_k(r) = T \phi_k(r) \quad (23)$$

In matters including valence p orbitals with the angular momentum $l=1$, electron motions of sp^2 and sp^3 hybrid orbitals become something circular near the force centers, and the T also include the rotational motion energies mixing with the divergent terms. In the LCVB method, these angular momentum factors are treated

with the complex number functions $e^{im\phi}$ in X - Y plane, and the needed interaction energies are determined semi-empirically. The basis eigenvectors $|\Phi_\alpha(r_1, r_2)\rangle$ are created from the bonding states as like the hydrogen molecule. The effective charges z_A in Eq. (3) is obtained with

$$z_A = k \sqrt{\frac{|E_A|}{13.6}}, \dots\dots\dots (24)$$

for the function of a principal quantum number k , where E_A is determined from the observed values. In this process, the simple case corrections in §2.2 are already included in such effective charges.

The sp^2 functions are composed of 2s and 2p hydrogen-like atomic orbitals $\phi_k(r)$ calculated from the Schrödinger equations in (3)-(4). Here, the 2s, 2p_x, 2p_y and 2p_z atomic orbitals are denoted by ϕ_s , ϕ_x , ϕ_y and ϕ_z , respectively. The hybrid orbitals χ_l of sp^2 are represented using the atomic orbitals $\phi_{l,j}$:

$$\chi_{1,k}(r) = \frac{1}{\sqrt{3}}\phi_{s,k}(r) + \sqrt{\frac{2}{3}}\phi_{x,k}(r), \dots\dots\dots (25)$$

$$\chi_{2,k}(r) = \frac{1}{\sqrt{3}}\phi_{s,k}(r) - \frac{1}{\sqrt{6}}\phi_{x,k}(r) + i\frac{1}{\sqrt{2}}\phi_{y,k}(r), \dots\dots (26)$$

$$\chi_{3,k}(r) = \frac{1}{\sqrt{3}}\phi_{s,k}(r) - \frac{1}{\sqrt{6}}\phi_{x,k}(r) - i\frac{1}{\sqrt{2}}\phi_{y,k}(r), \dots\dots (27)$$

$$\chi_{4,k}(r) = \phi_{z,k}(r), \dots\dots\dots (28)$$

where i is the imaginary number of $e^{im\phi}$. Here, instead of the atom number A and B in (3), we use the site number k and l for the bonding states of molecules;

$$\Psi_{kl}(r_1, r_2) = \frac{1}{\sqrt{a_{kl}}} \{ f(r_1, r_2) \chi_{i,k}(r_1) \chi_{j,l}(r_2) + \bar{f}(r_1, r_2) \chi_{i,k}(r_2) \chi_{j,l}(r_1) \} \dots\dots\dots (29)$$

where f and \bar{f} are the modification terms as like in (12). The related Hamiltonian in the least terms of two bonding states is composed of two kinetic energies, four atomic sites and two electrons. The each eigenvalue produced from the interactions in the system must satisfy the virial theorem, and then the interaction energies $H_{kl,mn}$ including $T_{kl,mn}$ and $U_{kl,mn}$ must satisfy the virial theorem i.e. $H_{kl,mn} < 0$.

4. AN EXAMPLE OF A NANOTUBE

As the basis functions of the LCVB method, the modification functions in §2.2 are applied and the density of states (DOS) in carbon nanotube (CN) is investigated. As long as using the semi-empirical parameters, the calculated DOS is not so largely different in the modifications, but electronic charge densities and detail arguments differ and follow the preciseness. As for CN and graphite, the DOS center generally must become -17.6 eV from the total of the atomic levels and the bonding energies. The Fermi level lays at -4.56 eV below the vacuum states as shown in the Fig. 5 of the experimental data.^[10] Adaptation of the JC method in §2.3 to the general molecular orbitals is not performed in this work because of the labors.

In our previous work [9], the conduction band structures near the vacuum level of CN was not explained with enough clearance, where the Hubbard

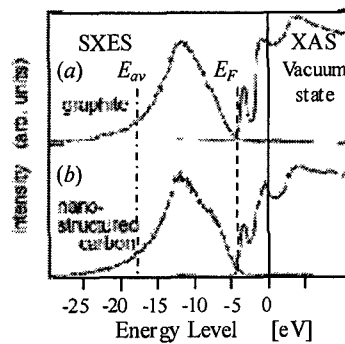


Fig. 5 SXES and XAS data of graphite by Hosokawa et al.^[10]

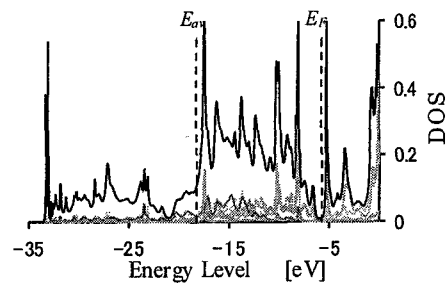


Fig. 6 Density of states in carbon nanotube. Calculated DOS using and the LCVB method with the simple correction. The conduction band and the gap states are based on the 3s excitation:

model excitation is adapted. In this work, the excitation level is altered to the 3s orbitals and the full DOS is obtained with the reliable structures in Fig. 6 (where the semi-empirical parameters are set to $\alpha_{\sigma-\sigma} = \alpha_{\pi-\pi} = 1.2$, $\beta_{\pi-ex} = 0.96$ and $\beta_{ex-ex} = 0.76$ adjusted in benzene)^[9], which are compared to the experimental data of Fig. 5 in nice fitting.

By improving the basis orbitals of the LCVB method, the charge density distributions become close to the practical states. Thus, the adaptations of these results to the DF calculations become reasonable, and such full real space DF calculations should be very easy and useful compared with a lot of k -space methods.

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