

A highly efficient *ab initio* tight-binding-like approximate density-functional theory quantum mechanical method

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Abstract. A highly efficient *ab initio* tight-binding-like approximate density-functional quantum mechanical method is developed by us recently. Based on the outline first proposed by O.sankey and D.J. Niklewski (*Phys. Rev. B*, 40: 3979–3995, 1989.) and an improvement by Horsfield (*Phys. Rev. B*, 56: 6594–6602, 1997.), we have made some significant improvements. In our approach, the integrals related to the exchange-correlation part are obtained by higher order many-center expansions and all the integrals can be obtained by interpolations of the look-up tables. The performance of the calculation is also improved by using a better way to choose the integrals in the look-up tables. It is shown that the calculated molecular equilibrium geometries, dipole moments, and the reaction energies for hydrogenation reactions are very close to those from the accurate results based on the density functional theory.

1 Theoretical Approach

Ab initio tight-binding-like (AITB) methods usually start from the Harris-Foulkes functionals[1, 2], which is equivalent to expanding the electron-electron interactions in the Kohn-Sham energy functional with respect to a reference density $\tilde{\rho}$, keeping only the first order correction and neglecting the second order and higher order corrections. In order to make the calculations simpler and faster, we made a further simplification of the Harris-Foulkes functional. The simplified Harris-Foulkes functional is given as

$$E_{HF} = \sum_i^{N_{occ}} \varepsilon_i - \frac{1}{2} \int \int \frac{\tilde{\rho}(\mathbf{r}_1) \tilde{\rho}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[\rho^{(0)}] - \int \rho^{(0)}(\mathbf{r}) V_{xc}(\rho^{(0)}(\mathbf{r})) d\mathbf{r} + V_{I-I}, \quad (1)$$

and the corresponding one-electron orbital equation is

$$\left[-\frac{1}{2} \nabla_1^2 + V_{ion}(\mathbf{r}_1) + \int \frac{\tilde{\rho}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{xc}(\rho^{(0)}(\mathbf{r}_1)) \right] | \psi_i(\mathbf{r}_1) \rangle = \varepsilon_i | \psi_i(\mathbf{r}_1) \rangle. \quad (2)$$

where E_{xc} is the exchange-correlation energy functional and V_{xc} the so-called exchange-correlation potential. V_{I-I} represents the ion-ion interaction term and V_{ion} the ionic potential. AITB methods often employ the frozen-core approximation. Thus, for a molecular system, V_{I-I} corresponds to core-core interaction and V_{ion} to the pseudopotential due to the nuclei and core electrons.

The reference electron densities $\tilde{\rho}$ and $\rho^{(0)}$ we used are superpositions of spherically distributed atomic-like densities having the forms

$$\tilde{\rho}(\mathbf{r}) = \sum_I \tilde{\rho}_I(r_I), \quad (3)$$

and

$$\rho^{(0)}(\mathbf{r}) = \sum_I \rho_I^{(0)}(r_I), \quad (4)$$

respectively, with

$$\tilde{\rho}_I(r_I) = \rho_I^{(0)}(r_I) + \Delta n_I f_I(r_I), \quad (5)$$

where $\rho_I^{(0)}$ is the valence electron density of neutral atom I and $f_I(r_I)$ corresponds to the density of a single electron in the highest occupied orbital. $r_I = |\mathbf{r} - \mathbf{R}_I|$ is the distance between \mathbf{r} and atomic site \mathbf{R}_I . Δn_I can be considered as the net number of electrons that atom I obtains in a molecular system and is determined by

$$\frac{\partial E_{HF}}{\partial \Delta n_I} = 0. \quad (6)$$

In this work, $\rho_I^{(0)}$ and $f_I(\mathbf{r})$ are all expressed as linear combinations of 1S type gaussians obtained by least fittings. V_{ion} corresponds to the norm-conserving separable dual-space pseudopotential devised by Goedecker, Teter, and Hutter[3] for DFT calculations.

Under the LCAO-MO approximation, that is,

$$\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}, \quad (7)$$

if we expand the atomic orbital ϕ_{μ} as a linear combination of primitive gaussian, then it is clear that all the integrals except for those related to the exchange-correlation potential and energy functional can be calculated analytically.

For the calculation of integrals related to the exchange-correlation potential or energy functional, we developed an improved many-center expansion scheme for the on-site integrals by including higher order terms in the original expression proposed by Horsfield[4]. The improved integrals are given as

$$\begin{aligned} \langle \phi_{I\alpha} | V_{xc}(\rho^{(0)}) | \phi_{I\beta} \rangle &= \langle \phi_{I\alpha} | V_{xc}(\rho_I^{(0)}) | \phi_{I\beta} \rangle \\ &+ \sum_{J(\neq I)} \langle \phi_{I\alpha} | V_{xc}(\rho_I^{(0)} + \rho_J^{(0)}) - V_{xc}(\rho_I^{(0)}) | \phi_{I\beta} \rangle \\ &+ \delta V_{I\alpha, I\beta}, \end{aligned} \quad (8)$$

$$\begin{aligned}
\int \rho_I^{(0)}(\mathbf{r}) \varepsilon_{XC}(\rho^{(0)}(\mathbf{r})) d\mathbf{r} &= \int \rho_I^{(0)}(\mathbf{r}) \varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r})) d\mathbf{r} \\
&+ \sum_{J(\neq I)} \int \rho_I^{(0)}(\mathbf{r}) [\varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r}) + \rho_J^{(0)}(\mathbf{r})) - \varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r}))] d\mathbf{r} \\
&+ \delta E_{XC,I}, \tag{9}
\end{aligned}$$

with

$$\begin{aligned}
\delta V_{I\alpha,I\beta} &\approx \frac{1}{2} \sum_{\substack{J(\neq I) \\ K(\neq I,J)}} \langle \phi_{I\alpha} | V_{xc}(\rho_I^{(0)} + \rho_J^{(0)} + \rho_K^{(0)}) + V_{xc}(\rho_I^{(0)}) \\
&- V_{xc}(\rho_I^{(0)} + \rho_J^{(0)}) - V_{xc}(\rho_I^{(0)} + \rho_K^{(0)}) | \phi_{I\beta} \rangle, \tag{10}
\end{aligned}$$

and

$$\begin{aligned}
\delta E_{XC,I} &\approx \frac{1}{2} \sum_{\substack{J(\neq I) \\ K(\neq I,J)}} \int \rho_I^{(0)}(\mathbf{r}) [\varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r}) + \rho_J^{(0)}(\mathbf{r}) + \rho_K^{(0)}(\mathbf{r})) + \varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r})) \\
&- \varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r}) + \rho_J^{(0)}(\mathbf{r})) - \varepsilon_{XC}(\rho_I^{(0)}(\mathbf{r}) + \rho_K^{(0)}(\mathbf{r}))] d\mathbf{r} \tag{11}
\end{aligned}$$

respectively. In the above equations, α and β denote atomic orbitals and I , J , and K atoms, respectively. ε_{XC} is the exchange-correlation energy density. $\delta V_{I\alpha,I\beta}$ and $\delta V_{I\alpha,J\beta}$ are the corrections for the on-site and off-site potential integrals, respectively. $\delta E_{XC,I}$ is the correction for the energy integral.

In many AITB calculations, the integrals required are often obtained by finding the corresponding integrals in local coordinate systems through the interpolation of the look-up tables and then by rotating the integrals from the local coordinate systems to those in the molecular system. Except in those for the one-center integrals, in look-up tables are integrals calculated on a pre-defined mesh of inter-atomic distances in the local coordinate systems. In this work, we devised a simple logarithmic mesh. The geometry used in the tables is shown in Figure 1. The point $(r_i; s_j; t_k)$ in the mesh is determined by the following equations

$$r_i = r_{\max} - (r_{\max} - r_{\min}) \frac{\ln(N_r + 1 - i)}{\ln(N_r)}, \tag{12}$$

$$s_j = s_{\max} - (s_{\max} - s_{\min}) \frac{\ln(N_s + 1 - j)}{\ln(N_s)}, \tag{13}$$

and

$$t_k = t_{\max} - (t_{\max} - t_{\min}) \frac{\ln(N_t + 1 - k)}{\ln(N_t)} \tag{14}$$

Usually, when $r_i = r_{\max}$, or $s_j = s_{\max}$, or $t_k = t_{\max}$, most of the integrals approach to some values that can be neglected. The exceptions are those of the form $\langle \phi_\mu(\mathbf{r}_1) | \int \frac{f_J(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 | \phi_\nu(\mathbf{r}_1) \rangle$. For these integrals, a similar treatment to that outlined in Ref([5]) is used.

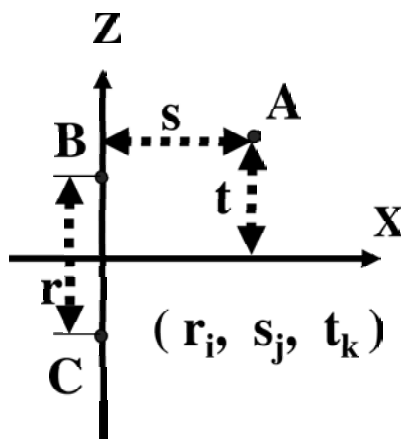


Fig. 1. The geometry used in the look-up tables in this work

Based on the above improvements, we have written a Fortran AITB calculation program which use BLYP [6,7] Generalized Gradient Approximation (GGA) for the exchange-correlational. It is shown that the calculated molecular equilibrium geometries, dipole moments, and the reaction energies for hydrogenation reactions are very close to those from the accurate results based on the density functional theory (DFT). However, our method is almost two orders faster than the normal DFT calculations. This method is now also incorporated into the molecular dynamic simulation program *M.DynaMix* for use in the study of nano and large scale molecular systems.

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