Evaluation of atomic integrals for hybrid Gaussian type and plane-wave basis functions via the McMurchie-Davidson recursion formula

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A convenient formalism is developed for the evaluation of atomic integrals composed of a hybrid Gaussian type function and plane-wave (GTF-PW) basis set, based upon the recursion scheme proposed by McMurchie and Davidson [L. E. McMurchie and E. R. Davidson, J. Comput. Phys. **26**, 218 (1978)] which was originally for Gaussian type basis functions. We show that revisions of recursion relations in the original article are necessary in order to allow systematic production of overlap, kinetic energy, nuclear attraction, and electron repulsion integrals in compact forms. Involving easy calculation of complex incomplete gamma functions, the recursion relations enable the use of hybrid GTF-PW basis functions with arbitrarily large angular momentum. This basis function can be applied to the first-principle calculation for solids involving localized electron orbitals.

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I. INTRODUCTION

For several decades, the Cartesian Gaussian type function (GTF) has achieved its popularity as a basis function for localized electron orbitals owing to its simplicity in computing the atomic integrals within the framework of the linear combination of atomic orbitals. Among some convenient methods contrived for computing GTF atomic integrals [1–6], one of the most efficient algorithms has been suggested by McMurchie and Davidson (MD) [1]. The MD scheme has an attractive feature in its recursion relations in terms of auxiliary functions, which enables the generation of GTF atomic integrals systematically with arbitrarily large angular momentum. Besides, the MD formula is also practically useful in the evaluation of sophisticated atomic integrals such as two-electron integrals involving r_{12} [7], and three-electron integrals [8]. For these reasons, the MD method has been widely used in current *ab initio* program packages.

On the other hand, the plane-wave (PW) basis function has been successful for describing delocalized Bloch orbitals in the condensed phase, such as periodic crystals and metallic solids. PW's as a basis set have advantages in simple formulas of atomic integrals and its derivatives, and they are suitable for molecular-dynamics calculations. In this context, it is a natural choice to adopt both localized GTF and delocalized PW's as basis functions at the same time [9–11]. Thus, it is encouraging to set up a systematic treatment for the evaluation of atomic orbitals in hybrid GTF-PW's.

The aim of the present report is the generalization of this efficient MD formalism to hybrid GTF-PW basis functions of the form

$$\begin{aligned}\chi_A &= \prod_{k=x,y,z} (r_k - R_{Ak})^{n_k} \exp\{-\alpha_A(\mathbf{r}-\mathbf{R}_A)^2\} \\ &\quad \times \exp\{i\mathbf{K}_A\cdot(\mathbf{r}-\mathbf{R}_A)\} \\ &= \prod_{k=x,y,z} (r_k - R_{Ak})^{n_k} \\ &\quad \times \exp\left[-\alpha_A\left\{\mathbf{r}-\left(\mathbf{R}_A+\frac{i\mathbf{K}_A}{2\alpha_A}\right)\right\}^2\right]\exp\left(-\frac{|\mathbf{K}_A|^2}{4\alpha_A}\right),\end{aligned} \tag{1}$$

where α_A gives the Gaussian exponent and $\mathbf{r}=(r_x,r_y,r_z)$, $\mathbf{R}_A=(R_{Ax},R_{Ay},R_{Az})$, and $\mathbf{K}_A=(K_{Ax},K_{Ay},K_{Az})$ denote the electronic Cartesian coordinate space, the center coordinate of GTF, and the PW vector, respectively. In Eq. (1), we note that setting $\mathbf{K_A}=0$ reduces to conventional GTF, while setting $n_k=\alpha_A=0$ corresponds to the PW function.

In Sec. II, we describe the way to obtain desired atomic integrals from one- and two-electron basic integrals. As an example, we give the expressions of overlap, nuclear-attraction, and electron-repulsion integrals. The recursion relations for auxiliary functions which is necessary in nuclear-attraction and electron-repulsion integrals, are also shown. In Sec. III, we explain the prescriptions to obtain their derivatives. Finally, in Sec. IV, we give some remarks on the applications of the present work to be expected in the future.

II. EXPANSION OF ATOMIC INTEGRALS

In this section, we seek convenient formulas for the one-electron integral

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$$I_1=\int d\mathbf{r}\chi_A(\mathbf{r})^*\theta(\mathbf{r})\chi_B(\mathbf{r}), \tag{2}$$

and the two-electron integral

$$I_2=\int\int d\mathbf{r}_1 d\mathbf{r}_2\chi_A(\mathbf{r}_1)^*\chi_B(\mathbf{r}_1)\theta(\mathbf{r}_1,\mathbf{r}_2)\chi_C(\mathbf{r}_2)^*\chi_D(\mathbf{r}_2). \tag{3}$$

To begin with, let us introduce the product of two basis functions in Eq. (1),

$$\chi_A^*\chi_B=E_{AB}\exp\{i(\mathbf{K}_A\cdot\mathbf{R}_A-\mathbf{K}_B\cdot\mathbf{R}_B)\}\times\prod_{k=x,y,z}(r_k-R_{Ak})^{n_k}(r_k-R_{Bk})^{m_k}\times\exp\{-\alpha_P(\mathbf{r}-\mathbf{P})^2+i\mathbf{K}\cdot\mathbf{r}\}, \tag{4}$$

where we have defined $\mathbf{K}=-\mathbf{K}_A+\mathbf{K}_B$, $\alpha_P=\alpha_A+\alpha_B$, $\mathbf{P}=(\alpha_A\mathbf{R}_A+\alpha_B\mathbf{R}_B)/\alpha_P$, and $E_{AB}=\exp(-\alpha_A\alpha_B|\mathbf{R}_A-\mathbf{R}_B|^2\alpha_P)$. Following the procedure similar to MD, we also introduce the function Λ_{N_k} as an N_kth order polynomial of r_k,

$$\Lambda_{N_k}(r_k-P_k;\alpha_p)\exp\{-\alpha_P(\mathbf{r}-\mathbf{P})^2+i\mathbf{K}\cdot\mathbf{r}\}=(\partial/\partial P_k)^{N_k}\exp\{-\alpha_P(\mathbf{r}-\mathbf{P})^2+i\mathbf{K}\cdot\mathbf{r}\}. \tag{5}$$

Now, we consider the expansion of

$$(r_k-R_{Ak})^{n_k}(r_k-R_{Bk})^{m_k}=\sum_{N_k=0}^{n_k+m_k}d_{N_k}^{n_k,m_k}\Lambda_{N_k}(r_k-P_k;\alpha_p). \tag{6}$$

Using the nature of

$$(r_k-R_{Ak})\Lambda_{N_k}=N\Lambda_{N_k-1}+(P_k-R_{Ak})\Lambda_{N_k}+\frac{1}{2\alpha_p}\Lambda_{N_k+1}, \tag{7}$$

we are able to use the recursion relations to obtain the coefficient $d_{N_k}^{n_k,m_k}$ by

$$d_{N_k}^{n_k+1,m_k}=(2\alpha_p)^{-1}d_{N_k-1}^{n_k,m_k}+(P_k-R_{Ak})d_{N_k}^{n_k,m_k}+(N_k+1)d_{N_k+1}^{n_k,m_k}, \tag{8}$$

$$d_{N_k}^{n_k,m_k+1}=(2\alpha_p)^{-1}d_{N_k-1}^{n_k,m_k}+(P_k-R_{Bk})d_{N_k}^{n_k,m_k}+(N_k+1)d_{N_k+1}^{n_k,m_k}, \tag{9}$$

with the initial condition $d_0^{00}=1$. Equations (8) and (9) remain the same as those defined in the original article [1]. Using the relation of Eq. (6), we are left with the evaluation of the basic integrals for one- and two-electron integrals as

$$[N_xN_yN_z|\theta]=\int d\mathbf{r}\theta(\mathbf{r})\prod_{k=x,y,z}(\partial/\partial P_k)^{N_k}\times\exp\{-\alpha_P(\mathbf{r}-\mathbf{P})^2+i\mathbf{K}\cdot\mathbf{r}\}, \tag{10}$$

$$[N_xN_yN_z|\theta|M_xM_yM_z]=\int d\mathbf{r}_1 d\mathbf{r}_2\theta(\mathbf{r}_1,\mathbf{r}_2)\times\prod_{k=x,y,z}(\partial/\partial P_k)^{N_k}(\partial/\partial Q_k)^{M_k}\times\exp\{-\alpha_P(\mathbf{r}_1-\mathbf{P})^2-\alpha_Q(\mathbf{r}_2-\mathbf{Q})^2+i(\mathbf{K}\cdot\mathbf{r}_1+\mathbf{L}\cdot\mathbf{r}_2)\}, \tag{11}$$

respectively, where we have defined $\mathbf{L}=-\mathbf{K}_C+\mathbf{K}_D$, $\alpha_Q=\alpha_C+\alpha_D$, and $\mathbf{Q}=(\alpha_C\mathbf{R}_C+\alpha_D\mathbf{R}_D)/\alpha_Q$.

A. Overlap integrals

By setting $\theta(\mathbf{r})$ to 1 in Eq. (10), the basic integral of the overlap integral is given by

$$[N_xN_yN_z|1]=\left(\frac{\pi}{\alpha_P}\right)^{3/2}\exp\left\{-\frac{\mathbf{K}^2}{4\alpha_P}\right\}\prod_{k=x,y,z}(iK_k)^{N_k}. \tag{12}$$

We note that since Eq. (12) depends on N_k, the overlap integrals will need the summation as to N_k in Eq. (6) (in contrast to the case of the pure GTF basis $\mathbf{K}=0$, where only the terms for $N_k=0$ survive).

B. Nuclear-attraction integrals

By setting $\theta(\mathbf{r})$ to r_C^{-1} in Eq. (10), the basic integral of the nuclear-attraction integral is expressed by

$$[N_xN_yN_z|\ r_C^{-1}]=\left(\frac{2\pi}{\alpha_P}\right)R_{N_x,N_y,N_z}(\alpha_P\overline{PC}^2), \tag{13}$$

where C is the nuclear coordinate, and

$$R_{N_x,N_y,N_z}(\alpha_P\overline{PC}^2)=(\partial/\partial P_x)^{N_x}(\partial/\partial P_y)^{N_y}\times(\partial/\partial P_z)^{N_z}F_0(\alpha_P\overline{PC}^2), \tag{14}$$

where

$$F_0(T)=\int_0^1 dt\exp(-t^2T), \tag{15}$$

$$\overline{PC}^2=(\tilde{P}_x-C_x)^2+(\tilde{P}_y-C_y)^2+(\tilde{P}_z-C_z)^2, \tag{16}$$

and

$$\tilde{\mathbf{P}}=\frac{\alpha_A(\mathbf{R}_A-(i\mathbf{K}_A/2\alpha_A))+\alpha_B(\mathbf{R}_B+(i\mathbf{K}_A/2\alpha_A))}{\alpha_A+\alpha_B}. \tag{17}$$

In order to compute R_{N_x,N_y,N_z} for a set of $\{N_k\}$, we have to derive a table of all R_{N_x,N_y,N_z} up to maximum angular moment number $N_x+N_y+N_z$. Thus, we introduce the more general integral

$$R_{N_x,N_y,N_z,j}(\alpha_P\overline{PC}^2)$$

$$=(-2\alpha_P)^j\int_0^1 du u^{2j}\prod_{k=x,y,z}(\partial/\partial P_k)^{N_k}\times\exp\left[-\alpha_P u^2\left\{\left(C_k-P_k-i\frac{K_k}{2\alpha_P}\right)^2\right\}\right]\times\exp\left\{-\frac{K_k^2}{4\alpha_P}\right\}\exp\{iK_k(P_k-P_k')\}\Big|_{P_k'=P_k}, \quad (18)$$

where $|_{P_k'=P_k}$ is applied after the differentiation by P_k. Using the incomplete gamma function for the complex argument

$$F_j(T)=\int_0^1 u^{2j}\exp(-Tu^2)du, \quad (19)$$

the first term of $R_{0,0,0,j}(\alpha_P\overline{PC}^2)$ is given by

$$R_{0,0,0,j}(T)=(-2\alpha_P)^j F_j(T). \quad (20)$$

Then, we may able to use the recursion formulas

$$R_{0,0,N_z+1,j}(\alpha_P\overline{PC}^2)=-\left(C_z-P_z-i\frac{K_z}{2\alpha_P}\right)R_{0,0,N_z,j+1}+N_zR_{0,0,N_z-1,j+1}+iK_zR_{0,0,N_z,j}, \quad (21)$$

$$R_{0,N_y+1,N_z,j}(\alpha_P\overline{PC}^2)=-\left(C_y-P_y-i\frac{K_y}{2\alpha_P}\right)R_{0,N_y,N_z,j+1}+N_yR_{0,N_y-1,N_z,j+1}+iK_yR_{0,N_y,N_z,j}, \quad (22)$$

$$R_{N_x+1,N_y,N_z,j}(\alpha_P\overline{PC}^2)=-\left(C_x-P_x-i\frac{K_x}{2\alpha_P}\right)R_{N_x,N_y,N_z,j+1}+N_xR_{N_x-1,N_y,N_z,j+1}+iK_xR_{N_x,N_y,N_z,j}, \quad (23)$$

and the upward recursion relation

$$F_{j+1}(T)=\frac{(2j+1)F_j(T)-\exp(-T)}{2T}, \quad (24)$$

to obtain $R_{N_x,N_y,N_z}(T)[=R_{N_x,N_y,N_z,0}(T)]$. The computational algorithm and the routine for complex error function $F_0(T)$ is available [12,13].

C. Electron-repulsion integrals

By setting $\theta(\mathbf{r}_1,\mathbf{r}_2)$ to r_{12}^{-1} in Eq. (11), the basic integral of the electron-repulsion integral is expressed by

$$[N_xN_yN_z|r_{12}^{-1}|M_xM_yM_z]=\frac{2\pi^{5/2}}{\sqrt{\alpha_P+\alpha_Q}\alpha_P\alpha_Q}\times R_{N_x,M_x,N_y,M_y,N_z,M_z}(\rho\overline{PQ}^2), \quad (25)$$

where $\rho=\alpha_P\alpha_Q/(\alpha_P+\alpha_Q)$, and

$$\overline{PQ}^2=(\tilde{P}_x-\tilde{Q}_x)^2+(\tilde{P}_y-\tilde{Q}_y)^2+(\tilde{P}_z-\tilde{Q}_z)^2, \quad (26)$$

$$\tilde{\mathbf{Q}}=\frac{\alpha_C(\mathbf{R}_C-(i\mathbf{K}_C/2\alpha_C))+\alpha_D(\mathbf{R}_D+(i\mathbf{K}_D/2\alpha_D))}{\alpha_C+\alpha_D}. \quad (27)$$

The values of $R_{N_x,M_x,N_y,M_y,N_z,M_z}(=R_{N_x,M_x,N_y,M_y,N_z,M_z,0})$ are obtained in the recursion formulas as

$$R_{N_x+1,M_x,N_y,M_y,N_z,M_z,j}(\rho\overline{PQ}^2)=\left(P_x-Q_x+i\frac{K_x}{2\alpha_P}-i\frac{L_x}{2\alpha_Q}\right)R_{N_x,M_x,N_y,M_y,N_z,M_z,j+1}+N_xR_{N_x-1,M_x,N_yM_y,N_z,M_z,j+1}-M_xR_{N_x,M_x-1,N_y,M_y,N_z,M_z,j+1}+iK_xR_{N_xM_x,N_y,M_y,N_z,M_z,j}, \quad (28)$$

$$R_{N_x,M_x+1,N_y,M_y,N_z,M_z,j}(\rho\overline{PQ}^2)=-\left(P_x-Q_x+i\frac{K_x}{2\alpha_P}-i\frac{L_x}{2\alpha_Q}\right)\times R_{N_x,M_x,N_y,M_y,N_z,M_z,j+1}-N_xR_{N_x-1,M_x,N_yM_y,N_z,M_z,j+1}+M_xR_{N_x,M_x-1,N_y,M_y,N_z,M_z,j+1}+iL_xR_{N_xM_x,N_y,M_y,N_z,M_z,j}, \quad (29)$$

where $R_{0,0,0,0,N_z+1,M_z,j}(\alpha_P\overline{PC}^2)$, $R_{0,0,0,0,N_z,M_z+1,j}(\alpha_P\overline{PC}^2)$, $R_{0,0,N_y+1,M_y,N_z,M_z,j}(\alpha_P\overline{PC}^2)$, and $R_{0,0,N_y,M_y+1,N_z,M_z,j}(\alpha_P\overline{PC}^2)$ are given in a similar manner.

III. INTEGRAL DERIVATIVES

Integral derivatives can be obtained using the analytic expression of one- and two-electron integrals derived above. For instance, kinetic-energy integrals are expressed by the second derivative with respect to r_x:

$$\frac{d^2}{dr_x^2}\chi_A=[n_x(n_x-1)(r_x-R_{Ax})^{n_x-2}+2iK_{Ax}n_x(r_x-R_{Ax})^{n_x-1}$$
$$-\{2\alpha_P(2n_x+1)+K_{Ax}^2\}(r_x-R_{Ax})^{n_x}$$
$$-4i\alpha_P(r_x-R_{Ax})^{n_x+1}+4\alpha_P^2(r_x-R_{Ax})^{n_x+2}]$$
$$\times\prod_{k=y,z}(r_k-R_{Ak})^{n_k}\exp\left[-\alpha_A\left\{\mathbf{r}-\left(\mathbf{R}_A+\frac{i\mathbf{K}_A}{2\alpha_A}\right)\right\}^2\right]$$
$$\times\exp\left(-\frac{|\mathbf{K}_A|^2}{4\alpha_A}\right). \tag{30}$$

Similarly, the gradients with respect to R_{Ax} and K_{Ax} are given by

$$\frac{d}{dR_{Ax}}\chi_A=[-n_x(r_x-R_{Ax})^{n_x-1}-iK_{Ax}(r_x-R_{Ax})^{n_x}$$
$$+2\alpha_P(r_x-R_{Ax})^{n_x+1}]\prod_{k=y,z}(r_k-R_{Ak})^{n_k}$$
$$\times\exp\left[-\alpha_A\left\{\mathbf{r}-\left(\mathbf{R}_A+\frac{i\mathbf{K}_A}{2\alpha_A}\right)\right\}^2\right]\exp\left(-\frac{|\mathbf{K}_A|^2}{4\alpha_A}\right) \tag{31}$$

and

$$\frac{d}{dK_{Ax}}\chi_A=i(r_x-R_{Ax})^{n_x+1}\prod_{k=y,z}(r_k-R_{Ak})^{n_k}$$
$$\times\exp\left[-\alpha_A\left\{\mathbf{r}-\left(\mathbf{R}_A+\frac{i\mathbf{K}_A}{2\alpha_A}\right)\right\}^2\right]\exp\left(-\frac{|\mathbf{K}_A|^2}{4\alpha_A}\right), \tag{32}$$

respectively. The above formulas can be used for energy derivative expressions in terms of one- and two-electron integrals. Other integrals, such as higher-order gradients, multiple moments can be derived in a similar manner. We should note that the derivatives of χ_A with respect to r_k and R_{Ak} are not equal as in the pure GTF case.

IV. CONCLUDING REMARKS

In this report, we have dealt with the systematic derivation of atomic integrals for the hybrid GTF-PW basis set by generalizing the McMurchie-Davidson method. Although this type of basis function is not yet common in *ab initio* studies at present, it is expected to have a wide range of applications in physics and chemistry, such as nonadiabatic dynamics of electronic structures [14], the electron scattering problems [15], and electronic band structures in solids [16]. In particular, the GTF-PW basis set should have great advantages for systems in which both localized and delocalized electrons exist, such as metal surfaces, conducting polymers, etc. Using the present algorithm for the GTF-PW basis set, a simulation study on plasma oscillationlike behavior in the electronic structure of molecules is in progress [17].

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