

4E07 Gauss 軌道を用いて良好な相対論効果の計算が可能か？

(その3) Slater 軌道に対する分子積分公式

所属なし 石田和弘

Can the Gaussian-type orbital describe the relativistic calculation well?

III. Molecular integrals over the Slater-type orbitals

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Abstract: The relativistic effect is important especially to describe the magnetic resonance spectroscopy. We extend the Kutzelnigg theory and solve the relativistic and gauge invariant Dirac equation for the hydrogen atom with using the Foldy-Wouthuysen transformation. For our aim to apply our theory to molecules, we try to use the Gaussian-type orbitals (GTO) and have reached to the title doubt. In order to resolve our doubt, we develop new methods for calculating molecular integrals over the Slater-type orbitals (STO) and derive the necessary molecular integrals over STOs.

Introduction: The relativistic usual Dirac equation for the hydrogen atom can be extended to that for including the vector potential of the proton source. The extended Dirac equation is gauge invariant as shown by Sun et al. [1]. However, the gauge invariant Dirac equation has not been solved yet. We try to solve it numerically with using the Foldy-Wouthuysen transformation. We extend the formulation by Kutzelnigg [2] to that for including the vector potential. Divergent integrals are arising in the theory. Then we use the finite nucleus model to avoid the divergence. To extend our theory to the molecular system, we first derive molecular integrals over the STOs.

Theory: The reader may refer ref. 3 for the extension of the Kutzelnigg theory.

Category of molecular integrals: We consider integrals arising from the operator

$(\sigma \pi)(\sigma \pi)$ and $(\sigma \pi)V(\sigma \pi)$, where σ is the Pauli spin matrices, $\pi = \vec{p} + \vec{A}$,

$$\vec{p} = -i\nabla, \quad \vec{A} = \frac{1}{c^2} \frac{4}{\sqrt{\pi} r_0^3} F_1\left(\frac{r^2}{r_0^2}\right) \vec{\mu} \times \vec{r} \quad (c=137.035999139, \quad r_0 = 0.2169394461(-4)),$$

$$V = \frac{2}{\sqrt{\pi} r_0} F_0\left(\frac{r^2}{r_0^2}\right), \quad F_m(z) = \int_0^1 ds s^{2m} \exp(-zs^2). \quad \text{Among them, divergent integrals}$$

(within the point charge nucleus) are for the following operators, $(\sigma A)(\sigma A) = A^2$,

$$i\sigma \cdot (\vec{p} \times V \vec{A} + \vec{A} V \times \vec{p}) = \sigma \cdot (\nabla \times V \vec{A} + \vec{A} V \times \nabla), \quad \text{and} \quad (\sigma A) V (\sigma A) = \vec{A} \cdot V \vec{A}.$$

Development: In order to derive molecular integrals over STOs, we first extend the Gaussian transform formula by Shavitt and Karplus given by [4]

$$\exp(-\zeta_A r_A) = \frac{\zeta_A}{2\sqrt{\pi}} \int_0^\infty ds s^{-3/2} \exp\left(-\frac{\zeta_A^2}{4s} - s r_A^2\right). \quad (1)$$

Differentiating both side of Eq. (1) with respect to ζ_A (n-1) times, we have the extended Gaussian transform formula given by

$$r_A^{n-1} \exp(-\zeta_A r_A) = \frac{1}{2\sqrt{\pi}} \sum_{k=0}^{n-1} (-)^k (2k-1)!! \binom{n-1}{2k} \int_0^\infty ds \left(1 - (n-1-2k) \frac{2s}{\zeta_A^2}\right) \frac{\zeta_A^{n-2k}}{(2s)^{n-1-k} s^{3/2}} \exp\left(-\frac{\zeta_A^2}{4s} - s r_A^2\right). \quad (2)$$

Using the solid harmonic gradient operator [5], we have the generalized Gaussian transform formula for the general STO centered at A, given by

$$r_A^{n_A - \ell_A - 1} S_{\ell_A m_A}(\vec{r}_A) \exp(-\zeta_A r_A) = S_{\ell_A m_A}(\nabla_A) \frac{1}{\sqrt{\pi}} \sum_{k=0}^{n_A - \ell_A - 1} (-)^k (2k-1)!! \binom{n_A - \ell_A - 1}{2k} \frac{\zeta_A^{n_A - \ell_A - 2k}}{2^{n_A - k}} \int_0^\infty ds \left(1 - (n_A - \ell_A - 1 - 2k) \frac{2s}{\zeta_A^2}\right) \frac{1}{s^{n_A - k + 1/2}} \exp\left(-\frac{\zeta_A^2}{4s} - s r_A^2\right) \nabla_A = \left(\frac{\partial}{\partial A_x}, \frac{\partial}{\partial A_y}, \frac{\partial}{\partial A_z}\right) \quad (3)$$

We also use the Sack's formula for GTO centered at B, given by [6]

$$\exp(-\alpha r_B^2) = 4\pi \exp(-\alpha \overline{BA}^2 - \alpha r_A^2) \sum_{\ell=0}^{\ell} i_\ell (2\alpha \overline{BA} r_A) \sum_{m=-\ell}^{\ell} Y_\ell^m(B\hat{A}) Y_\ell^m(\hat{r}_A)^*. \quad (4)$$

Using Eq.(3) and (4), we can derive all necessary formula for our integrals.

Alternatively, we can use the mixed solid harmonics (MSH) [7]; i.e., it holds

$$S_{\ell_B m_B}(\vec{r}_B) = S_{\ell_B m_B}(\overline{BA} + \vec{r}_A) = \sum_{t=0}^{\ell_B} S_{\ell_B m_B}(\overline{BA} \vec{r}_A; t). \quad (5)$$

Note that MSH, $S_{\ell_B m_B}(\overline{BA} \vec{r}_A; t)$, is centered at A. Using Eq. (2), (4), and (5), we can also derive all necessary formula for our integrals. Thus we have two new methods for deriving molecular integrals over STOs. We find that each results of two methods coincides each other.

- [1] W-M Sun, X-S Chen, X-F Lü, and F. Wang, Phys. Rev. **A82**, 012107 (2010). [2] W. Kutzelnigg in "Relativistic electronic structure theory" Part 1, edited by P. Schwerdtfeger, (Elsevier Amsterdam 2002) pp.664. [3] K. Ishida, 1F04 at Japanese Symposium on Molecular Science (Sendai, 2017). [4] I. Shavitt and M. Karplus, J Chem Phys, **43**, 398-414 (1965). [5] K. Ishida, J Comput Chem, **23**, 378-393 (2002). [6] R. A. Sack, J Math Phys, **5**, 245-251 (1964). [7] K. Ishida, J Chem Phys, **111**, 4913-4922 (1999).