

Multiple order asymptotic expansion for approximation of atomic orbital electron repulsion integral

Tomonori Yamada, So Hirata

*Department of Chemistry, University of Illinois at Urbana-Champaign, 600 South Mathews Avenue,
Urbana, Illinois 61801, USA*

CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

We have developed an accurate, fast, and easily implemented approximation for atomic orbital-electron repulsion integrals (AO-ERI's), which is called as asymptotic expansion (AE) [1]:

$$(\mu\nu|\kappa\lambda) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\chi_\kappa^*(\mathbf{r}_2)\chi_\lambda(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \quad (1)$$

$$\approx \frac{S_\nu^\mu S_\lambda^\kappa}{|\mathbf{r}_{\mu\nu}-\mathbf{r}_{\kappa\lambda}|} \quad (2)$$

Eq. (1) is an AO-ERI, and Eq. (2) is the AE, χ_μ^* is the μ th AO basis function, \mathbf{r}_1 is the coordinate of electron 1, $\mathbf{r}_{\mu\nu}$ is the average position of the centers of χ_μ^* and χ_ν , and S_ν^μ is the overlap integral of χ_μ^* and χ_ν . AE becomes more accurate when the distributions of two electrons are more distant to each other. This has been shown numerically in ref [1] and is also analytically proven by performing the Taylor expansion of Coulomb operator $1/r_{12}$ in the Eq. (1) as follows.

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \approx \frac{1}{|\mathbf{r}_0|} + \mathbf{r} \cdot \nabla_{\mathbf{r}} \left(\frac{1}{|\mathbf{r}_0+\mathbf{r}|} \right)_{\mathbf{r}=\mathbf{0}} + \dots \quad (3)$$

Eq. (3) can be accurate if $|\mathbf{r}_0| > |\mathbf{r}|$. By taking \mathbf{r}_0 as $\mathbf{r}_{\mu\nu} - \mathbf{r}_{\kappa\lambda}$, and considering only the first term of Eq. (3), Eq. (2) is obtained. Eq. (3) manifests that the accuracy of AE is to be improved by including the second and higher order terms. In this work we implement AE including those higher order terms in a program of ab initio crystalline orbital Hartree-Fock theory, and show the actual improvements and efficiency of calculation for solid state systems. Note that the potential applicability of AE is not limited to solid state systems but it is also applicable to large molecules where long range interactions cannot be ignored in AO-ERI's. Namely, AE can be an efficient method for calculations of large molecules such as proteins with ab initio molecular orbital theory.

References

- [1] T. Yamada, R. P. Brewster, S. Hirata, J. Phys. Chem. 139 (2013) 184107. [2] L. Piela, J. Delhalle, Int. J. Quantum Chem. 13 (1978) 605. [3] J. Delhalle, L. Piela, J.-L. Brédas, J.-M. André, Phys. Rev. B 22 (1980) 6254.