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4 October - 8 October 2010:

I read the section 3 Approximations of many-electron integrals. It introduced the methods to reduce many-electron integrals into two- and three-electron integrals. But the evaluation of three-electron integrals was still expensive. Thus they still needed to reduce three-electron integrals. The author approximated integrals using an approximate resolution of the identity(RI) and used partial wave analysis to establish requirements on the RI basis. They also introduced RI, Density fitting(DF) and DF combined with RI.

11 October - 15 October 2010:

This week I focused on section 3.3 Resolution of the identity and section 3.5 Density fitting. I did a lot of work on the notation and definition of the words on Chemistry and Physics. For example, I tried to find the definition or explanation for an resolution of the identity, angular momentum, orthogonal projector, an orthonormal RI basis, Hartree-Fock method, density fitting and DF-MP2-R12 theory. During the week, I also read 6 papers such reference 69,73, 153. Next week I will try to understand the standard approximation such as

$$\langle ijm \left| r_{12} r_{13}^{-1} r_{23} \right| kml \rangle \approx \Sigma_{p'} \left\langle ij \left| r_{12} \right| p'q' \right\rangle \left\langle p'm \left| r_{12}^{-1} \right| mr' \right\rangle \left\langle q'r' \left| r_{12} \right| kl \right\rangle.$$

18 October - 22 October 2010:

This week I was still working on Resolution of the identity approximation and figured out more than last week. Resolutions of the identity

Given a complete orthonormal basis set of functions φ_n in a separable Hilbert space, for example, the normalized eigenvectors of a compact self-adjoint operator, any vector f can be expressed as:

$$f = \sum_n \alpha_n \varphi_n.$$

The coefficients α_n are found as:

$$\alpha_n = \langle \varphi_n, f \rangle,$$

which may be represented by the notation:

$$\alpha_n = \varphi_n^\dagger f,$$

a form of the bra-ket notation of Dirac. Adopting this notation, the expansion of f takes the dyadic form:

$$f = \sum_n \varphi_n \left(\varphi_n^\dagger f \right).$$

Letting I denote the identity operator on the Hilbert space, the expression

$$I = \sum_n \varphi_n \varphi_n^\dagger,$$

is called a resolution of the identity. When the Hilbert space is the space $L^2(D)$ of square-integrable functions on a domain D, the quantity:

$$\varphi_n \varphi_n^\dagger,$$

is an integral operator, and the expression for f can be rewritten as:

$$f(x) = \sum_n \int_D (\varphi_n(x)\,\varphi_n^*(\xi))\, f(\xi)\, d\xi.$$

The right-hand side converges to f in the L^2 sense. It need not hold in a pointwise sense, even when f is a continuous function. Nevertheless, it is common to abuse notation and write

$$f(x) = \int \delta(x-\xi)\, f(\xi)\, d\xi.$$

resulting in the representation of the delta function:

$$\delta(x-\xi) = \sum_n \varphi_n(x)\,\varphi_n^*(\xi).$$

With a suitable rigged Hilbert space $(\phi, L^2(D), \phi^*)$ where $\phi \subset L^2(D)$ contains all compactly supported smooth functions, this summation may converge inϕ^*, depending on the properties of the basis ϕ_n. In most cases of practical interest, the orthonormal basis comes from an integral or differential operator, in which case the series converges in the distribution sense.

25 October - 29 October 2010:

During the last week I read a paper about RI, which name is the impact of the resolution of the identity approximate integral method on modern ab initio algorithm development. Actually I focused on RI approximation on R12 method. The reason that I read this paper is that I try to compare the cost of RI approximation on different method. Furthermore, I was still working on the impact of RI approximation on R12 method. The result is that the basic approach is the factorization of the four-center integral into two parts:

$$(ij|kl) = \sum_\gamma^N L_{ij\gamma} R_{\gamma kl}.$$

The details vary in each application but the ultimate goal is qualitatively the same e.g., the reduction in computational cost. The factorization is beneficial for any Coulomb interaction summation. The cost is now $O(n^3)$, as opposed to the $O(n^4)$ for traditional integral evaluation. Unfortunately, this factorization does not formally reduce the scaling of an exchange interaction summation. The time to compute the quantities used in the Coulomb or exchange interaction summations will vary but the cost of the summation remains $O(n^4)$ for the exchange term.

1 November - 5 November 2010:

During the last week I was preparing for final presentation for this quater's reseach, which is mainly about Resolution of the Identity. I also continued to read the paper about RI, which name is the impact of the resolution of the identity approximate integral method on modern ab initio algorithm development. I figured out that the basic approach was the factorization of the four-center integral into two parts:

$$(ij|kl) = \sum_\gamma^N L_{ij\gamma} R_{\gamma kl}.$$

The details varied in each application but the ultimate goal is qualitatively the same e.g., the reduction in computational cost. The factorization was beneficial for any Coulomb interaction summation. The cost iss now $O(n^3)$, as opposed to the $O(n^4)$ for traditional integral evaluation. However, the factorization doesn't work for an exchange interaction summation. The time to compute the quantities used in the Coulomb or exchange interaction summations will vary but the cost of the summation remains $O(n^4)$ for the exchange term. It means that we only can use RI method to reduce the computation cost of any Coulomb interaction summation, not any exchange interaction summation.

8 November - 12 November 2010:

Worked on preparation for Final presentation.

Papers

R12 methods in explicitly correlated molecular electronic structure theory

In this article[1], I focused on the section 3 (Approximations of many-electron integrals). I mainly studied Resolution of the identity and Density fitting. Later I read more papers to understand what is Resolution of the identity. In this section, the conclusion is that Density fitting with RI is the best way to approximate.

An explicitly correlated second order Mller-Plesset theory using a frozen Gaussian geminal

In this article[2], the author showed a variant of the MP2-R12 class of theories was introduced using an arbitrary geminal function in the place of r_{12}. Integrals are derived for the case where the geminal is expanded in a basis of Gaussian functions in the interelectronic distance. Recurrence relations are derived that do not depend on the exponents of the Gaussian geminals, allowing much of the integration work to be performed after summations over the geminal expansion.

Density fitting in second-order linear-r_{12} MllerPlesset perturbation theory

I read this article[3] to try to find more information about Density fitting. Density fitting is used to approximate all of the 4-index 2-electron integrals in the explicitly correlated MP2-R12 theory of Kutzelnigg and Klopper. Because I focused on Resolution of the identity this quarter, this paper is not that important.

Explicitly correlated second-order MllerPlesset methods with auxiliary basis sets

In this article[4], the author talked about correlated MllerPlesset MP2-R12! methods. My goal was to understand the notation and definition such as auxiliary basis sets. This paper helped me to be more familiar with RI and MP method, which are very important methods this quarter.

The impact of the resolution of the identity approximate integral method on modern ab initio algorithm development

This article[5] is the most important one for me in this quarter. The author showed The impact of the resolution of the identity method. The conclusion is that the basic approach is the factorization of the four-center integral into two parts:

$$(ij|kl) = \sum_{\gamma}^{N} L_{ij\gamma} R_{\gamma kl}.$$

The details vary in each application but the ultimate goal is qualitatively the same e.g., the reduction in computational cost. The factorization is beneficial for any Coulomb interaction summation. The cost is now $O(n^3)$, as opposed to the $O(n^4)$ for traditional integral evaluation. Unfortunately, this factorization does not formally reduce the scaling of an exchange interaction summation. The time to compute the quantities used in the Coulomb or exchange interaction summations will vary but the cost of the summation remains $O(n^4)$ for the exchange term.

Reference:

[1] R12 methods in explicitly correlated molecular electronic structure theory. WIM KLOPPER. International Reviews in Physical Chemistry, Vol.25, No.3, JulyCSeptember 2006, 427C468

[2] An explicitly correlated second order Mller-Plesset theory using a frozen Gaussian geminal. Andrew J. May, Frederick R. Manby. JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 10

[3] Density fitting in second-order linear-rr_{12} MllerPlesset perturbation theory. Frederick R. Manby. JOURNAL OF CHEMICAL PHYSICS VOLUME 119, NUMBER 9

[4] Explicitly correlated second-order MllerPlesset methods with auxiliary basis sets. Wim Kloppera, Claire C. M. Samson. JOURNAL OF CHEMICAL PHYSICS VOLUME 116, NUMBER 15

[5] The impact of the resolution of the identity approximate integral method on modern ab initio algorithm development. Rick A. Kendall, Herbert A. Fru chtl. Theor Chem Acc (1997) 97:158163