Analytical and Numerical Treatment of Molecular Integrals
Three-Center Nuclear Attraction Integrals

Hassan Safouhi

Campus Saint-Jean, University of Alberta

Edmonton (Alberta) Canada

hsafouhi@ualberta.ca

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The plan

- Introduction
- Molecular multicenter integrals (MMI)
- The Fourrier transform formalism for MMI
- Compact analytical development of the three-center nuclear attraction integrals
- Conclusion

Introduction
&
Motivations

Introduction & Motivation

- Molecular multicenter integrals (MMI):
  - Occur in an extremely large number even for small molecules.

    Thus, the need of an efficient numerical evaluation.

  - Contribute to the total energy of molecules.

    Thus, the need a highly accurate numerical evaluation (more than 10 correct digits).

- Analytic development of molecular integrals over exponential type functions (ETFs):
  - The Fourier integral transformation.
  - Difficulties in the numerical evaluation of molecular integrals arise from the presence of highly oscillatory semi-infinite spherical Bessel integrals with a large number of parameters.

Introduction & Motivation

- Classical methods, including numerical quadratures and convergence accelerators, were unable to provide sufficiently efficient and accurate algorithms for three- and four-center terms.
- Nonlinear transformations and extrapolation methods significantly improved convergence. However, these approaches did not fully resolve the computational challenges associated with multicenter molecular integrals.
- A complete analytic treatment of multicenter molecular integrals would represent a major breakthrough in computational quantum chemistry, providing highly accurate and efficient algorithms, reducing computational costs, and enabling the study of larger and more complex molecular systems with unprecedented precision.

  Numerical experiments show that the use of the analytic expressions is 10^3 times more efficient than the state-of-the-art.

Molecular integrals

Molecular Integrals

We consider two electrons separated from the origin by $\vec{R}$ and $\vec{R}'$, and four atomic orbitals centered on nuclei A, B, C and D, four arbitrary points of the euclidian space $\mathcal{E}_3$, while O is the origin of the fixed coordinate system.

Three-center nuclear attraction integrals:

$$\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2} = \int_{\vec{R}} \left[\varphi_{n_1,l_1}^{m_1}\left(\zeta_1, \vec{R} - \overrightarrow{OA}\right)\right]^* \frac{1}{|\vec{R} - \overrightarrow{OC}|} \varphi_{n_2,l_2}^{m_2}\left(\zeta_2, \vec{R} - \overrightarrow{OB}\right) d\vec{R},$$

$\varphi_{n,l}^{m}(\zeta, \vec{R})$ stand for an atomic orbitals, which are the **exact solutions** of the Schrödinger equation for one electron atoms.

n, l and m stand for the quantum numbers. ζ is the orbital exponent.

Molecular Integrals

Three-center two-electron Coulomb integrals:

$$\mathcal{K}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3} = \left[\varphi^{m_1}_{n_1,l_1}\left(\zeta_1, \vec{R} - \overrightarrow{OA}\right)\right]^* \left[\varphi^{m_3}_{n_3,l_3}\left(\zeta_3, \vec{R}\,' - \overrightarrow{OB}\right)\right]^* \frac{1}{|\vec{R} - \vec{R}\,'|} \varphi^{m_2}_{n_2,l_2}\left(\zeta_2, \vec{R} - \overrightarrow{OA}\right) \varphi^{m_4}_{n_4,l_4}\left(\zeta_4, \vec{R}\,' - \overrightarrow{OC}\right) d\vec{R}\, d\vec{R}\,'.$$

Four-center two-electron Coulomb integrals:

$$\mathcal{J}^{n_2 l_2 m_2, n_4 l_4 m_4}_{n_1 l_1 m_1, n_3 l_3 m_3} = \int_{\vec{R}, \vec{R}'} \left[\varphi^{m_1}_{n_1,l_1}\left(\zeta_1, \vec{R} - \overrightarrow{OA}\right)\right]^* \left[\varphi^{m_3}_{n_3,l_3}\left(\zeta_3, \vec{R}' - \overrightarrow{OC}\right)\right]^* \times \frac{1}{\left|\vec{R} - \vec{R}'\right|} \varphi^{m_2}_{n_2,l_2}\left(\zeta_2, \vec{R} - \overrightarrow{OB}\right) \varphi^{m_4}_{n_4,l_4}\left(\zeta_4, \vec{R}' - \overrightarrow{OD}\right) d\vec{R}\, d\vec{R}'.$$

Molecular Integrals

B functions [**Shavitt 1963, Filter and Steinborn 1978**]:

$$B^m_{n,l}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\ \hat{k}_{n-\frac{1}{2}}(\zeta r)\ Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}}),$$

$$\hat{k}_{n+\frac{1}{2}}(z) = \sqrt{\frac{2}{\pi}}(z)^{n+\frac{1}{2}} K_{n+\frac{1}{2}}(z) = z^n e^{-z}\sum_{j=0}^{n}\frac{(n+j)!}{j!(n-j)!}(2z)^{-j},$$

and $Y^m_l(\theta_{\vec{r}},\varphi_{\vec{r}})$ are spherical harmonics:

$$Y^m_l(\theta,\varphi) \;=\; i^{m+|m|}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{\frac{1}{2}} P^{|m|}_l(\cos\theta)\, e^{im\varphi},$$

$P^m_l(x)$ is the associated Legendre polynomial of l^{th} degree and m^{th} order.

Fourier transform of B function [**Filter 1978**]:

$$\bar{B}^m_{n,l}(\zeta,\vec{p}) = \sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1}\,\frac{(-i|\vec{p}|)^l}{(\zeta^2+|\vec{p}|^2)^{n+l+1}}\,Y^m_l(\theta_{\vec{p}},\varphi_{\vec{p}}).$$

The analytical development of molecular integrals

The analytical development of molecular integrals

By performing a translation of vector $\overrightarrow{OA}$, we can re-write:

$$\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2} = \int_{\vec{r}} \left[B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}) \right]^* \frac{1}{|\vec{r} - \vec{R}_1|} B_{n_2,l_2}^{m_2}\left(\zeta_2, \vec{r} - \vec{R}_2\right) d\vec{r}.$$

where $\vec{r} = \vec{R} - \overrightarrow{OA}$, $\vec{R}_1 = \overrightarrow{AC}$ and $\vec{R}_2 = \overrightarrow{AB}$.

Using the Fourier integral representation of the Coulomb operator:

$$\frac{1}{|\vec{r}|} = \frac{1}{2\pi^2} \int_{\vec{k}} \frac{e^{-i\vec{k}.\vec{r}}}{k^2} d\vec{k},$$

we obtain:

$$\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2} = \frac{1}{2\pi^2} \int_{\vec{x}} \frac{e^{i\vec{x}.\vec{R}_1}}{x^2} \left[\int \left[B_{n_i,l_i}^{m_i}(\zeta_1, \vec{r}) \right]^* e^{-i\vec{x}.\vec{r}} B_{n_j,l_j}^{m_j}\left(\zeta_2, \vec{r} - \vec{R}_2\right) d\vec{r} \right] d\vec{x}.$$

The analytical development of molecular integrals

The analytic expressions for the three-center nuclear attraction integrals:

$$\mathcal{I}_{n_1,l_1,m_1}^{n_2,l_2,m_2} = \frac{8(4\pi)^2(-1)^{l_1+l_2}(2l_1+1)!!(2l_2+1)!!(n_1+l_1+n_2+l_2+1)!\zeta_1^{2n_1+l_1-1}\zeta_2^{2n_2+l_2-1}}{(n_1+l_1)!(n_2+l_2)!}$$

$$\times \sum_{l_1'=0}^{l_1}\sum_{m_1'=-l_1'}^{l_1'}\sum_{l_2'=0}^{l_2}\sum_{m_2'=-l_2'}^{l_2'}\sum_{l=l'_{\min},2}^{l_2'+l_1'}\sum_{\lambda=l''_{\min},2}^{l_2-l_2'+l_1-l_1'}\sum_{j=0}^{\Delta l}(-i)^{\lambda}(i)^{l_1+l_1'+l_2+l_2'}\binom{\Delta l}{j}$$

$$\times \frac{\langle l_1 m_1 | l_1' m_1' | l_1 - l_1' m_1 - m_1' \rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!}(-1)^{l_2'}\frac{\langle l_2 m_2 | l_2' m_2' | l_2 - l_2' m_2 - m_2' \rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!}$$

$$\times \left\langle l_2' m_2' | l_1' m_1' | l m_2' - m_1' \right\rangle R_2^l \, Y_l^{m_2'-m_1'}(\theta_{\vec{R}_2}, \varphi_{\vec{R}_2})$$

$$\times \frac{(-1)^j \langle l_2 - l_2' m_2 - m_2' | l_1 - l_1' m_1 - m_1' | \lambda\mu \rangle}{2^{n_1+n_2+l_1+l_2-j+1}(n_1+n_2+l_1+l_2-j+1)!}$$

$$\times \int_{s=0}^{1} s^{n_2+l_2+l_1-l_1'}(1-s)^{n_1+l_1+l_2-l_2'} Y_\lambda^\mu(\theta_{\vec{v}}, \varphi_{\vec{v}})$$

$$\times \underbrace{\int_0^{+\infty} x^{n_x} \frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\,dx}_{\mathcal{I}(s)}\, ds,$$

The analytical development of molecular integrals

where the spherical Bessel function $j_n(z)$ is defined by:

$$j_n(z) = (-1)^n \, z^n \left(\frac{\mathrm{d}}{z \, \mathrm{d}z} \right)^n \left[\frac{\sin(z)}{z} \right],$$

and where:

$$[\gamma(s,x)]^2 = (1-s)\zeta_1^2 + s\zeta_2^2 + s(1-s)x^2$$

$$\vec{v} = (1-s)\vec{R}_2 - \vec{R}_1$$

$$n_\gamma = 2(n_1 + l_1 + n_2 + l_2) - (l_1' + l_2') - l + 1$$

$$\nu = n_1 + n_2 + l_1 + l_2 - l - j + \tfrac{1}{2}$$

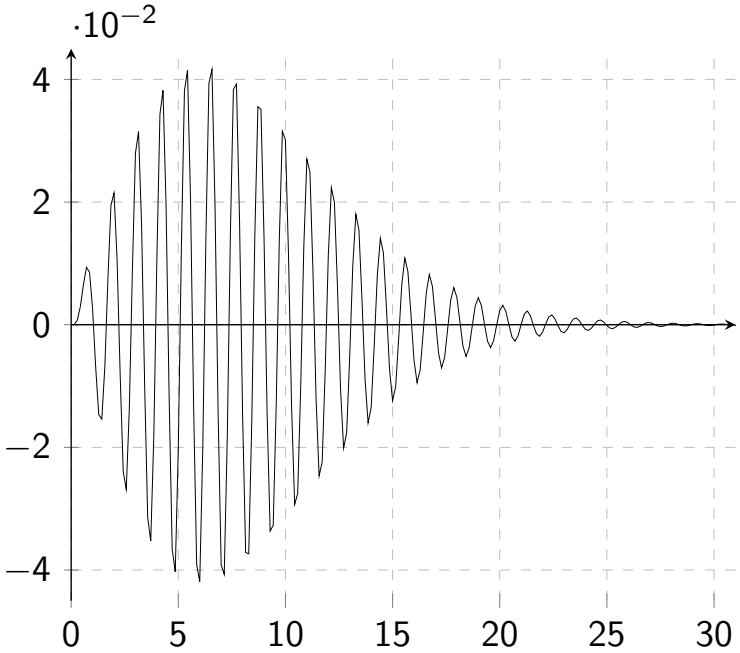
$$\mu = (m_2 - m_2') - (m_1 - m_1')$$

$$n_x = l_1 - l_1' + l_2 - l_2'$$

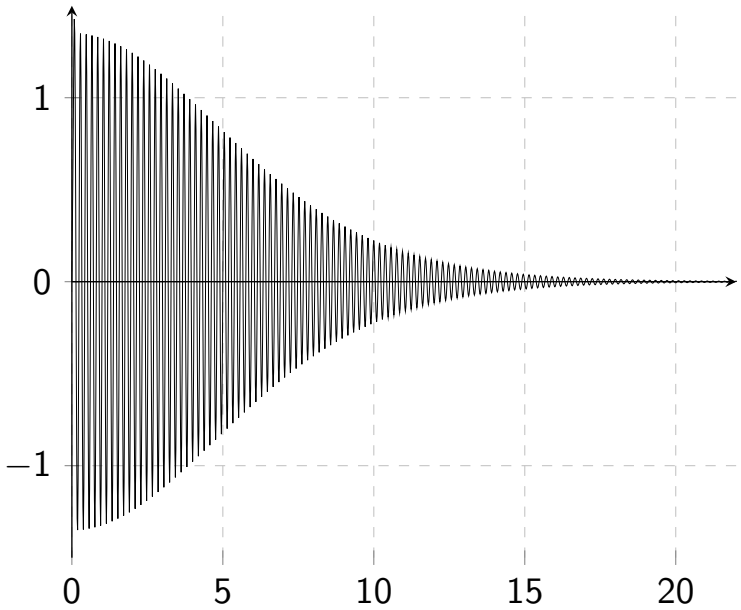
$$\Delta l = [(l_1' + l_2' - l)/2]$$

The analytical development of molecular integrals

Three-center terms



Four-center terms



Analytical development of three-center nuclear attraction integrals

Analytical development

We can easily prove that:

$$\int_0^\infty x^{\eta+1} \frac{K_\nu\left(\alpha\sqrt{x^2+z^2}\right)}{\sqrt{(x^2+z^2)^\nu}} J_\eta(\beta\, x)\, \mathrm{d}x$$

$$= \frac{\beta^\eta}{\alpha^\nu} \left(\frac{\sqrt{\alpha^2+\beta^2}}{z}\right)^{\nu-\eta-1} K_{\nu-\eta-1}\left(z\sqrt{\alpha^2+\beta^2}\right),$$

where $\nu \in \mathbb{R}$, $\mathrm{Re}\,\eta > -1$, $\alpha > 0$, $\beta > 0$, and $|\arg z| < \frac{\pi}{2}$.

In the above integral, cylindrical Bessel functions $J_\eta(z)$ are used instead of spherical Bessel functions, and the modified Bessel function $K_\nu(z)$ are used instead of reduced Bessel functions.

The semi-infinite integral in the analytic expressions for the three-center nuclear attraction integrals:

$$\mathcal{I}(s) = \int_0^{+\infty} x^{n_x} \frac{\hat{k}_\nu[R_2\gamma(s,x)]}{[\gamma(s,x)]^{n_\gamma}} j_\lambda(vx)\, dx,$$

Analytical development

The semi-infinite integral $\mathcal{I}(s)$ can be expressed as follows:

$$\mathcal{I}(s) = \frac{1}{\left[s\,(1-s)\right]^{\frac{n_\gamma}{2}}}\,\mathcal{T}^{\nu,\mu}_{\lambda,r}(R_2\sqrt{s(1-s)}, v, z),$$

where the integral $\mathcal{T}^{\nu,\mu}_{\lambda,r}(\alpha,\beta,z)$ is given by:

$$\mathcal{T}^{\nu,\mu}_{\lambda,r}(\alpha,\beta,z) = \int_0^\infty x^{\lambda+2r+2}\,\frac{\hat{k}_\nu\left[\alpha\sqrt{x^2+z^2}\right]}{(x^2+z^2)^{\nu-\mu}}\,j_\lambda(\beta\,x)\,\mathrm{d}x,$$

and where the integers μ and r, and the parameter z are given by:

$$r = \frac{n_x-\lambda}{2} - 1, \quad \mu = \frac{2\nu - n_\gamma}{2} \quad \text{and} \quad z = \frac{(1-s)\zeta_1^2 + s\zeta_2^2}{s(1-s)}.$$

Analytical development

The simpler case of $\mathcal{T}_{\lambda,r}^{\nu,\mu}(\alpha,\beta,z)$ is given by:

$$\begin{aligned}\mathcal{T}_{\lambda,0}^{\nu,0}(\alpha,\beta,z) &= \int_0^\infty x^{\lambda+2}\frac{\hat{k}_\nu\left[\alpha\sqrt{x^2+z^2}\right]}{(x^2+z^2)^\nu}j_\lambda(\beta\,x)\,\mathrm{d}x \\ &= \frac{\alpha^\nu}{\sqrt{\beta}}\int_0^\infty x^{\lambda+\frac{1}{2}+1}\frac{K_\nu\left[\alpha\sqrt{x^2+z^2}\right]}{\sqrt{(x^2+z^2)^\nu}}J_{\lambda+1/2}(\beta\,x)\,\mathrm{d}x.\end{aligned}$$

We can also write:

$$\mathcal{T}_{\lambda+r,0}^{\nu-\mu,0}(\alpha,\beta,z)=\int_0^\infty x^{\lambda+r+2}\frac{\hat{k}_{\nu-\mu}\left[\alpha\sqrt{x^2+z^2}\right]}{(x^2+z^2)^{\nu-\mu}}j_{\lambda+r}(\beta\,x)\,\mathrm{d}x,$$

This simpler case is the essential starting point because identities can be used to increase the r and μ parameters to obtain an expression for $\mathcal{T}_{\lambda,r}^{\nu,\mu}(\alpha,\beta,z)$.

Analytical development

If $r, \mu \geq 0$, then by applying the following identities:

$$\frac{1}{\beta^{\lambda+1}} \left(\frac{\partial}{\beta \partial \beta}\right)^r \left(\beta^{\lambda+r+1} j_{\lambda+r}(\beta x)\right) = x^r j_\lambda(\beta x),$$

$$(-1)^\mu \alpha^{2\nu} \left(\frac{\partial}{\alpha \partial \alpha}\right)^\mu \left(\alpha^{2\mu-2\nu} \hat{k}_{\nu-\mu}\left[\alpha\sqrt{x^2+z^2}\right]\right) = \hat{k}_\nu\left[\alpha\sqrt{x^2+z^2}\right],$$

to the integral $\mathcal{I}^{\nu-\mu,0}_{\lambda+r,0}(\alpha,\beta,z)$, we obtain:

$$\begin{aligned}\mathcal{T}^{\nu,\mu}_{\lambda,r}(\alpha,\beta,z) &= \frac{(-1)^\mu \alpha^{2\nu}}{\beta^{\lambda+1}} \left(\frac{\partial}{\alpha \partial \alpha}\right)^\mu \left(\frac{\partial}{\beta \partial \beta}\right)^r \\ &\quad \times \left(\alpha^{2\mu-2\nu}\, \beta^{\lambda+r+1}\, \mathcal{I}^{\nu-\mu,0}_{\lambda+r,0}(\alpha,\beta,z)\right).\end{aligned}$$

Analytical development

Now, let us consider:

$$\mathcal{T}^{\nu,0}_{\lambda,0}(\alpha,\beta,z) = \frac{\alpha^\nu}{\sqrt{\beta}}\int_0^\infty x^{\lambda+2-\frac{1}{2}}\frac{K_\nu\left[\alpha\sqrt{x^2+z^2}\right]}{\sqrt{(x^2+z^2)^\nu}}J_{\lambda+1/2}(\beta\,x)\,\mathrm{d}x.$$

Cylindrical Bessel functions are used instead of spherical Bessel functions.

By using the integral representation of the modified Bessel function, reversing the order of integration, and using the convergent series for the Bessel function, we obtain:

$$\mathcal{T}^{\nu,0}_{\lambda,0}(\alpha,\beta,z) = \frac{\beta^\lambda(\alpha^2+\beta^2)^{\frac{\nu-\lambda-3/2}{2}}}{z^{\nu-\lambda-3/2}}K_{\nu-\lambda-3/2}\left(z\sqrt{\alpha^2+\beta^2}\right),$$

$$\mathcal{T}^{\nu-\mu,0}_{\lambda+r,0}(\alpha,\beta,z) = \frac{\beta^{\lambda+r}(\alpha^2+\beta^2)^{\frac{\nu-\mu-\lambda-r-3/2}{2}}}{z^{\nu-\mu-\lambda-r-3/2}}K_{-\tau}\left(z\sqrt{\alpha^2+\beta^2}\right),$$

$$\tau = \lambda + r + \mu - \nu + 3/2.$$

Analytical development

Given the reflection formula $K_\tau(x) = K_{-\tau}(x)$, we obtain:

$$\begin{aligned}\mathcal{T}_{\lambda,r}^{\nu,\mu}(\alpha,\beta,z) &= \frac{(-1)^\mu \alpha^{2\nu} z^\tau}{\beta^{\lambda+1}} \left(\frac{\partial}{\alpha\partial\alpha}\right)^\mu \left(\frac{\partial}{\beta\partial\beta}\right)^r \\ &\quad \times \left(\alpha^{2\mu-2\nu}\beta^{2\lambda+2r+1}\frac{K_\tau(z\sqrt{\alpha^2+\beta^2})}{(\alpha^2+\beta^2)^{\tau/2}}\right),\end{aligned}$$

Evidently, all that remains to do is to expand the derivations, and the expression will be obtained:

$$\begin{aligned}\mathcal{T}_{\lambda,r}^{\nu,\mu}(\alpha,\beta,z) &= (-2)^r \alpha^{-2\nu} z^\tau \beta^{\lambda+1} \sum_{\sigma=0}^{r} \binom{r}{\sigma} \left(\frac{\beta^2 z}{2}\right)^\sigma (-\lambda-r-1/2)_{r-\sigma} \\ &\quad \times \sum_{m=0}^{\mu} \binom{\mu}{m} \left(\frac{\alpha^2 z}{2}\right)^m (\nu-\mu)_{\mu-m} \frac{K_{\tau+\sigma+m}(z\sqrt{\alpha^2+\beta^2})}{(\alpha^2+\beta^2)^{(\tau+\sigma+m)/2}}.\end{aligned}$$

Analytical development

If $\lambda \neq n_x$, we obtain:

$$\mathcal{I}(s) = \frac{(-2)^{\frac{n_x-\lambda}{2}-1}\left(\sqrt{z}\right)^{n_x+\lambda-n_\gamma+1} v^{\lambda+1}}{R_2^{2\nu}\left[s\,(1-s)\right]^{\nu+\frac{n_\gamma}{2}}}$$
$$\times \sum_{\sigma=0}^{\frac{n_x-\lambda}{2}-1} \binom{\frac{n_x-\lambda}{2}-1}{\sigma} \left(\frac{v^2\,z}{2}\right)^{\sigma} \left(\frac{-n_x-\lambda+1}{2}\right)_{\frac{n_x-\lambda}{2}-1-\sigma}$$
$$\times \sum_{m=0}^{\frac{2\nu-n_\gamma}{2}} \binom{\frac{2\nu-n_\gamma}{2}}{m} \left(\frac{R_2^2\,s\,(1-s)\,z}{2}\right)^{m} (\nu-\mu)_{\nu-m}$$
$$\times \frac{K_{\frac{n_x+\lambda-n_\gamma}{2}+\sigma+m+\frac{1}{2}}\left(z\sqrt{R_2^2\,s(1-s)+v^2}\right)}{\left(\sqrt{R_2^2\,s(1-s)+v^2}\right)^{\frac{n_x+\lambda-n_\gamma}{2}+\sigma+m+\frac{1}{2}}}.$$

Analytical development

Numerical experiments conducted for the three-center nuclear attraction integrals, show that the use of the analytic expressions is 10^3 times more efficient than the combination S and $\bar{D}$ and the combination of the W algorithm and the $\bar{D}$ transformation:

$$\frac{\text{Total time using} \quad S\bar{D}}{\text{Total time using the analytic formulae}} \approx 10^3$$

$$\frac{\text{Total time using} \quad W\bar{D}}{\text{Total time using the analytic formulae}} \approx 10^3.$$

Conclusion

- The analytic development let to an extremely efficient and highly accurate computation of the three-center nuclear attraction integrals.
- This approach could be generalized to multi-center two-electron Coulomb integrals, whcih can be expressed in terms of three-center integrals.
- We are hopeful this will lead to a software package for molecular structure calculation based on ETFs.

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