# Four center integrals for Coulomb interactions in small molecules 

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#### Abstract

In this work we make some progress on studying four center integrals for the Coulomb energy for both Hartree Fock (HF) and Density Functional Theory (DFT) calculations for small molecules. We consider basis wave functions of the form of an arbitrary radial wave function multiplied by a spherical harmonic and study four center Coulomb integrals for them. We reformulated these Coulomb four center integrals in terms of some derivatives of integrals of nearly factorable functions which then depend on the Bessel transform of the radial wave functions considered.


## I. INTRODUCTION

Small molecules water, carbon dioxide, ozone, ammonia, methane, ethane, ethene, ethyne to name a few have tremendous practical industrial applications so it is paramount that we study their electronic structures [1] 3]. To make progress with the many body Schrodinger equation for a small molecule a variety of different approximations need to be made. The most common ones for abinitio studies of electronic structures of small molecules are Hartree Fock (HF) or Density Functional Theory (DFT) [1-4] approximations (where DFT is then further approximated by the Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA) [2, 4]). As such it is of paramount importance to make progress in the study of small molecules both through Density Functional Theory (DFT) and Hartree Fock (HF) methods. One of the stumbling blocks towards implementing DFT or HF calculations on modern computers is the choice of the basis set. Indeed a significant practical improvement in the efficiency of solution of the HF equations was given by Roothaan [5] who mapped the HF integro-differential equations into a system of linear equations and unknowns using basis sets.Similarly the Khon Sham (KS) equations are a linear system of equations when considered within a fixed basis set [2, 4]. Recently substantial progress has been made [6] where it was argued that it is sufficient to consider basis sets of the form given by:

$$
\begin{equation*}
\varphi_{\alpha}(\mathbf{r})=Y_{l_{\alpha} m_{\alpha}}\left(\mathbf{r} \widehat{-\mathbf{R}_{\alpha}}\right) R_{l_{\alpha}}\left(\mathbf{r}-\mathbf{R}_{\alpha}\right) \tag{1}
\end{equation*}
$$

Here $Y_{l m}$ 's are spherical harmonics, $\mathbf{R}_{\alpha}$ is the position of a nucleus of an atom in the molecule and $R_{l}$ are arbitrary radial wave functions. In Ref [6] arguments were made as to the form of the optimal set of $R_{l}$ 's. Inspired by recent
progress in basis sets for small molecules [6] we study four center Coulomb integrals for specific types of wave functions given by Eq. (1) and in particular or those considered in Ref. [6]. Specifically we are interested in integrals of the form:
$I_{a b c d}=\int d^{3} \mathbf{r}_{1} \int d^{3} \mathbf{r}_{2} \frac{1}{\left|\mathbf{r}_{1}-\mathbf{r}_{2}\right|} \varphi_{a}^{*}\left(\mathbf{r}_{1}\right) \varphi_{b}\left(\mathbf{r}_{1}\right) \varphi_{c}^{*}\left(\mathbf{r}_{2}\right) \varphi_{d}\left(\mathbf{r}_{2}\right)$
which show up in calculations of the Coulomb energy both in DFT and HF methods. Previously evaluation of four center integrals was limited to $R_{l}$ 's being Gaussians [3, 7] which limited accuracy for small basis set sizes [3]. Evaluating these integrals for a large number of wave functions, with more complex structure then Gaussian, needed for an accurate basis is often the bottleneck in abinitio molecular electronic structures calculations [1, 3]. In this work we write these integrals in terms of derivatives of an integral in a nearly factorable form. The integrals depended on the Bessel transform of the radial wave function given by:

$$
\begin{equation*}
\mathcal{R}_{l}(U)=\int_{0}^{\infty} \frac{\pi}{2 U^{2}} d r J_{l}(U r) R_{l}(r) r^{2} \tag{3}
\end{equation*}
$$

as well as auxiliary integrals. This should lead to further abinitio studies of small molecules with basis sets more accurate then Gaussian.

## II. MAIN CALCULATION

We now calculate the integral considered in Eq. (2).

## A. Fourier transform

We begin by Fourier transforming the integral in Eq. (2). Now we have that

$$
\begin{equation*}
\frac{1}{\left|\mathbf{r}_{1}-\mathbf{r}_{2}\right|}=\int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i \mathbf{K} \cdot\left(\mathbf{r}_{1}-\mathbf{r}_{2}\right)\right) \tag{4}
\end{equation*}
$$

Furthermore we recall that [8]

$$
\begin{equation*}
\exp \left(i \mathbf{K}_{\alpha} \cdot \mathbf{r}\right)=\exp \left(i \mathbf{K}_{\alpha} \cdot \mathbf{R}_{\alpha}\right) \sum_{l m} i^{l} J_{l}\left(\left|\mathbf{K}_{\alpha}\right|\left|\mathbf{r}-\mathbf{R}_{\alpha}\right|\right) Y_{l m}^{*}\left(\hat{\mathbf{K}}_{\alpha}\right) Y_{l m}\left(\mathbf{r}-\widehat{\mathbf{R}}_{\alpha}\right) \tag{5}
\end{equation*}
$$

so that

$$
\begin{equation*}
\varphi_{\alpha}(\mathbf{r})=(-i)^{l_{\alpha}} \int \frac{d^{3} \mathbf{K}_{\alpha}}{(2 \pi)^{3}} \exp \left(-i \mathbf{K}_{\alpha} \cdot \mathbf{R}_{\alpha}\right) Y_{l_{\alpha} m_{\alpha}}\left(\hat{\mathbf{K}}_{\alpha}\right) \int_{0}^{\infty} \frac{\pi\left|\mathbf{K}_{\alpha}\right|^{2}}{2} d r_{\alpha} J_{l_{\alpha}}\left(\left|\mathbf{K}_{\alpha}\right| r_{\alpha}\right) R_{l_{\alpha}}\left(r_{\alpha}\right) r_{\alpha}^{2} \exp \left(i \mathbf{K}_{\alpha} \cdot \mathbf{r}\right) \tag{6}
\end{equation*}
$$

Here we have used orthogonality of Bessel functions (the Bessel transform [9]).

## B. Fourier transformed integral

As such we have that:

$$
\begin{align*}
I_{a b c d} & =\int d^{3} \mathbf{r}_{1} \int d^{3} \mathbf{r}_{2} \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{b}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{d}}{(2 \pi)^{3}} \times \\
& \times \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left(\mathbf{K}_{b}-\mathbf{K}_{a}+\mathbf{K}\right) \cdot \mathbf{r}_{1}\right) \exp \left(i\left(\mathbf{K}_{d}-\mathbf{K}_{c}-\mathbf{K}\right) \cdot \mathbf{r}_{2}\right) \times \\
& \times(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \exp \left(i\left[\mathbf{K}_{a} \cdot \mathbf{R}_{a}+\mathbf{K}_{c} \cdot \mathbf{R}_{c}-\mathbf{K}_{b} \cdot \mathbf{R}_{b}-\mathbf{K}_{d} \cdot \mathbf{R}_{d}\right]\right) \times \\
& \times Y_{l_{a}^{*} m_{a}}^{*}\left(\hat{\mathbf{K}}_{a}\right) Y_{l_{c} m_{c}}^{*}\left(\hat{\mathbf{K}}_{c}\right) Y_{l_{b} m_{b}}\left(\hat{\mathbf{K}}_{b}\right) Y_{l_{d} m_{d}}\left(\hat{\mathbf{K}}_{d}\right) \times \\
& \times \int_{0}^{\infty} d r_{a} \frac{\pi\left|\mathbf{K}_{a}\right|^{2}}{2} J_{l_{a}}\left(\left|\mathbf{K}_{a}\right| r_{a}\right) R_{l_{a}}\left(r_{a}\right) r_{a}^{2} \times \int_{0}^{\infty} d r_{b} \frac{\pi\left|\mathbf{K}_{b}\right|^{2}}{2} J_{l_{b}}\left(\left|\mathbf{K}_{b}\right| r_{b}\right) R_{l_{b}}\left(r_{b}\right) r_{b}^{2} \times \\
& \times \int_{0}^{\infty} d r_{c} \frac{\pi\left|\mathbf{K}_{c}\right|^{2}}{2} J_{l_{c}}\left(\left|\mathbf{K}_{c}\right| r_{c}\right) R_{l_{c}}\left(r_{c}\right) r_{c}^{2} \times \int_{0}^{\infty} d r_{d} \frac{\pi\left|\mathbf{K}_{d}\right|^{2}}{2} J_{l_{d}}\left(\left|\mathbf{K}_{d}\right| r_{a}\right) R_{l_{d}}\left(r_{d}\right) r_{d} \tag{7}
\end{align*}
$$

We now perform the integrals $\int d^{3} \mathbf{r}_{1} \int d^{3} \mathbf{r}_{2}$ to obtain some delta functions that simplify the integrations:

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \times \\
& \times \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{\mathbf{d}}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \times \\
& \times Y_{l_{a} m_{a}}^{*}\left(\hat{\mathbf{K}}_{a}\right) Y_{l_{c} m_{c}}^{*}\left(\hat{\mathbf{K}}_{c}\right) Y_{l_{b} m_{b}}\left(\mathbf{K}_{a} \widehat{-K}\right) Y_{l_{d} m_{d}}\left(\mathbf{K}_{c} \widehat{+} \mathbf{K}\right) \times \\
& \times \int_{0}^{\infty} d r_{a} \frac{\pi\left|\mathbf{K}_{a}\right|^{2}}{2} J_{l_{a}}\left(\left|\mathbf{K}_{a}\right| r_{a}\right) R_{l_{a}}\left(r_{a}\right) r_{a}^{2} \times \int_{0}^{\infty} d r_{b} \frac{\pi\left|\mathbf{K}_{b}\right|^{2}}{2} J_{l_{b}}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right| r_{b}\right) R_{l_{b}}\left(r_{b}\right) r_{b}^{2} \times \\
& \times \int_{0}^{\infty} d r_{c} \frac{\pi\left|\mathbf{K}_{c}\right|^{2}}{2} J_{l_{c}}\left(\left|\mathbf{K}_{c}\right| r_{c}\right) R_{l_{c}}\left(r_{c}\right) r_{c}^{2} \times \int_{0}^{\infty} d r_{d} \frac{\pi\left|\mathbf{K}_{d}\right|^{2}}{2} J_{l_{d}}\left(\left|\mathbf{K}_{b}+\mathbf{K}\right| r_{a}\right) R_{l_{d}}\left(r_{d}\right) r_{d}^{2} \tag{8}
\end{align*}
$$

Now we let

$$
\begin{equation*}
F_{\alpha}(K)=\int_{0}^{\infty} d r_{\alpha} K^{2} J_{l_{\alpha}}\left(K r_{\alpha}\right) R_{l_{\alpha}}\left(r_{\alpha}\right) r_{\alpha}^{2} \tag{9}
\end{equation*}
$$

so that

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{\mathbf{d}}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \times \\
& \times Y_{l_{a} m_{a}}^{*}\left(\hat{\mathbf{K}}_{a}\right) Y_{l_{c} m_{c}}^{*}\left(\hat{\mathbf{K}}_{c}\right) Y_{l_{b} m_{b}}\left(\widehat{K}_{a}-\mathbf{K}\right) Y_{l_{d} m_{d}}\left(\widehat{\mathbf{K}_{c}+\mathbf{K}}\right) \times F_{a}\left(\left|\mathbf{K}_{a}\right|\right) F_{c}\left(\left|\mathbf{K}_{c}\right|\right) F_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) F_{d}\left(\left|\mathbf{K}_{b}+\mathbf{K}\right|\right) \tag{10}
\end{align*}
$$

## C. Expansion in terms of derivatives

Now we write

$$
\begin{equation*}
\mathcal{F}_{\alpha}(K)=\frac{F_{\alpha}(K)}{K^{l_{\alpha}}} \tag{11}
\end{equation*}
$$

So that:

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{\mathbf{d}}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \\
& \times\left|\mathbf{K}_{a}\right|^{l_{a}} Y_{l_{a} m_{a}}\left(\hat{\mathbf{K}}_{a}\right)\left|\mathbf{K}_{c}\right|^{l_{x}} Y_{l_{c} m_{c}}\left(\hat{\mathbf{K}}_{c}\right)\left|\mathbf{K}_{a}-\mathbf{K}\right|^{l_{b}} Y_{l_{b} m_{b}}^{*}\left(\mathbf{K}_{a-\mathbf{K}}^{\mathbf{K}}\right)\left|\mathbf{K}_{c}+\mathbf{K}\right|^{l_{c}} Y_{l_{d} m_{d}}^{*}\left(\mathbf{K}_{c}+\mathbf{K}\right) \times \\
& \times \mathcal{F}_{a}\left(\left|\mathbf{K}_{a}\right|\right) \mathcal{F}_{c}\left(\left|\mathbf{K}_{c}\right|\right) \mathcal{F}_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) \mathcal{F}_{d}\left(\left|\mathbf{K}_{c}+\mathbf{K}\right|\right) \tag{12}
\end{align*}
$$

Furthermore:

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{\mathbf{d}}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \times \\
& \times \sum_{a b c d} C_{a, n, p, q}^{m} \mathbf{K}_{a x}^{m_{x}} \mathbf{K}_{a y}^{m_{y}} \mathbf{K}_{a z}^{m_{z}} \mathbf{K}_{c x}^{n_{x}} \mathbf{K}_{c y}^{n_{y}} \mathbf{K}_{c z}^{m_{z}}\left(\mathbf{K}_{a}-\mathbf{K}\right)_{x}^{p_{x}}\left(\mathbf{K}_{a}-\mathbf{K}\right)_{y}^{p_{y}}\left(\mathbf{K}_{a}-\mathbf{K}\right)_{z}^{p_{z}}\left(\mathbf{K}_{c}+\mathbf{K}\right)_{x}^{q_{x}}\left(\mathbf{K}_{c}+\mathbf{K}\right)_{y}^{q_{y}}\left(\mathbf{K}_{c}+\mathbf{K}\right)_{z}^{q_{z}} \times \\
& \times \mathcal{F}_{a}\left(\left|\mathbf{K}_{a}\right|\right) \mathcal{F}_{c}\left(\left|\mathbf{K}_{c}\right|\right) \mathcal{F}_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) \mathcal{F}_{d}\left(\left|\mathbf{K}_{c}+\mathbf{K}\right|\right) \tag{13}
\end{align*}
$$

Where we have transformed spherical harmonic into solid harmonics. Then

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{d}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \times \\
& \times \mathcal{F}_{a}\left(\left|\mathbf{K}_{a}\right|\right) \mathcal{F}_{c}\left(\left|\mathbf{K}_{c}\right|\right) \mathcal{F}_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) \mathcal{F}_{d}\left(\left|\mathbf{K}_{c}+\mathbf{K}\right|\right) \tag{14}
\end{align*}
$$

Where we have used the derivative property of exponentials to pull out the solid harmonics as derivatives. Whereby:

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} \exp \left(i\left[\mathbf{K}_{a} \cdot\left[\mathbf{R}_{a}-\mathbf{R}_{b}\right]+\mathbf{K}_{c} \cdot\left[\mathbf{R}_{c}-\mathbf{R}_{d}\right]+\mathbf{K} \cdot\left[\mathbf{R}_{b}-\mathbf{R}_{d}\right]\right]\right) \times \\
& \times \mathcal{F}_{a}\left(\left|\mathbf{K}_{a}\right|\right) \mathcal{F}_{c}\left(\left|\mathbf{K}_{c}\right|\right) \mathcal{F}_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) \mathcal{F}_{d}\left(\left|\mathbf{K}_{c}+\mathbf{K}\right|\right) \tag{15}
\end{align*}
$$

## D. A Bessel function expansion

Now [8]:

$$
\begin{equation*}
\exp \left(i \mathbf{K}_{a}\left(\mathbf{R}_{a}-\mathbf{R}_{b}\right)\right)=\sum_{L_{a} M_{a}} i^{L_{a}} J_{L_{a}}\left(\left|\mathbf{K}_{a}\right|\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) Y_{L_{a} M_{a}}^{*}\left(\hat{\mathbf{K}}_{\alpha}\right) Y_{L_{a} M_{a}}\left(\mathbf{R}_{a-\mathbf{R}_{b}}\right) \tag{16}
\end{equation*}
$$

As such:

$$
\begin{align*}
I_{a b c d} & =(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \sum_{L_{a} M_{a}} \sum_{L_{c}, M_{c}} \sum_{L, M} i^{L_{a}} Y_{L_{a} M_{a}}\left(\mathbf{R}_{a} \widehat{-} \mathbf{R}_{b}\right) i^{L_{c}} Y_{L_{c} M_{c}}\left(\mathbf{R}_{c} \widehat{-\mathbf{R}_{d}}\right) i^{L} Y_{L M}\left(\mathbf{R}_{b} \widehat{-\mathbf{R}_{d}}\right) \\
& \times \int \frac{d^{3} \mathbf{K}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{a}}{(2 \pi)^{3}} \frac{d^{3} \mathbf{K}_{c}}{(2 \pi)^{3}} \frac{4 \pi}{\mathbf{K}^{2}} J_{L_{a}}\left(\left|\mathbf{K}_{a}\right|\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) J_{L_{c}}\left(\left|\mathbf{K}_{c}\right|\left|\mathbf{R}_{c}-\mathbf{R}_{d}\right|\right) J_{L}\left(|\mathbf{K}|\left|\mathbf{R}_{b}-\mathbf{R}_{d}\right|\right) \\
& \times \mathcal{F}_{a}\left(\left|\mathbf{K}_{a}\right|\right) \mathcal{F}_{c}\left(\left|\mathbf{K}_{c}\right|\right) \mathcal{F}_{b}\left(\left|\mathbf{K}_{a}-\mathbf{K}\right|\right) \mathcal{F}_{d}\left(\left|\mathbf{K}_{c}+\mathbf{K}\right|\right) \tag{17}
\end{align*}
$$

and

$$
\begin{align*}
I_{a b c d} & =4 \pi(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \sum_{L_{a} M_{a}} \sum_{L_{c}, M_{c}} \sum_{L, M} i^{L_{a}} Y_{L_{a} M_{a}}\left(\mathbf{R}_{a} \widehat{-\mathbf{R}_{b}}\right) i^{L_{c}} Y_{L_{c} M_{c}}\left(\mathbf{R}_{c}-\mathbf{R}_{d}\right) i^{L} Y_{L M}\left(\mathbf{R}_{b} \widehat{-\mathbf{R}_{d}}\right) \\
& \times \int \frac{d|\mathbf{K}|}{2 \pi} \frac{d\left|\mathbf{K}_{a}\right| d u_{a}}{(2 \pi)^{2}} \frac{d\left|\mathbf{K}_{c}\right| d u_{c}}{(2 \pi)^{2}} \times J_{L_{a}}\left(\left|\mathbf{K}_{a}\right|\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) J_{L_{c}}\left(\left|\mathbf{K}_{c}\right|\left|\mathbf{R}_{c}-\mathbf{R}_{d}\right|\right) J_{L}\left(|\mathbf{K}|\left|\mathbf{R}_{b}-\mathbf{R}_{d}\right|\right) \\
& \times \mathcal{G}_{a}\left(\mathbf{K}_{a}^{2}\right) \mathcal{G}_{c}\left(\mathbf{K}_{c}^{2}\right) \mathcal{G}_{b}\left(\mathbf{K}_{a}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{a}\right||\mathbf{K}| u_{a}\right) \mathcal{G}_{d}\left(\mathbf{K}_{c}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{c}\right||\mathbf{K}| u_{c}\right)\left|\mathbf{K}_{a}\right|^{2}\left|\mathbf{K}_{c}\right|^{2} \tag{18}
\end{align*}
$$

The extra minus in $\mathcal{G}_{d}\left(\mathbf{K}_{c}^{2}+\mathbf{K}^{2}-\left|\mathbf{K}_{c}\right||\mathbf{K}| u_{c}\right)$ is because we are integrating $u_{c}$ between $[-1,1]$. Where

$$
\begin{equation*}
\mathcal{G}\left(K^{2}\right)=\mathcal{F}(K)=\frac{F_{\alpha}(K)}{K^{l_{\alpha}}}=\frac{\int_{0}^{\infty} d r_{\alpha} J_{l_{\alpha}}\left(K r_{\alpha}\right) R_{l_{\alpha}}\left(r_{\alpha}\right) r_{\alpha}^{2}}{K^{l_{\alpha}}} \tag{19}
\end{equation*}
$$

Now we write:

$$
\begin{align*}
I_{a b c d} & =4 \pi(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \sum_{L_{a} M_{a}} \sum_{L_{c}, M_{c}} \sum_{L, M} i^{L_{a}} Y_{L_{a} M_{a}}\left(\mathbf{R}_{a} \widehat{-\mathbf{R}_{b}}\right) i^{L_{c}} Y_{L_{c} M_{c}}\left(\mathbf{R}_{c} \widehat{-\mathbf{R}_{d}}\right) i^{L} Y_{L M}\left(\mathbf{R}_{b} \widehat{-\mathbf{R}_{d}}\right) \times \\
& \times \int \frac{d|\mathbf{K}|}{2 \pi} \frac{d\left|\mathbf{K}_{a}\right| d u_{a}}{(2 \pi)^{2}} \frac{d\left|\mathbf{K}_{c}\right| d u_{c}}{(2 \pi)^{2}} \times J_{L_{a}}\left(\left|\mathbf{K}_{a}\right|\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) J_{L_{c}}\left(\left|\mathbf{K}_{c}\right|\left|\mathbf{R}_{c}-\mathbf{R}_{d}\right|\right) J_{L}\left(|\mathbf{K}|\left|\mathbf{R}_{b}-\mathbf{R}_{d}\right|\right) \times \\
& \times \frac{\int_{0}^{\infty} d r_{a} J_{l_{a}}\left(\left|\mathbf{K}_{a}\right| r_{a}\right) R_{l_{a}}\left(r_{a}\right) r_{a}^{2} \int_{0}^{\infty} d r_{c} J_{l_{c}}\left(\left|\mathbf{K}_{c}\right| r_{c}\right) R_{l_{c}}\left(r_{c}\right) r_{c}^{2}}{\left|\mathbf{K}_{a}\right|^{l_{a}-2}} \times \\
& \times \frac{\int_{0}^{l_{c}-2} d r_{b} J_{l_{b}}\left(\left[\mathbf{K}_{a}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{a}\right||\mathbf{K}| u_{a}\right]^{1 / 2} r_{b}\right) R_{l_{b}}\left(r_{b}\right) r_{b}^{2} \int_{0}^{\infty} d r_{d} J_{l_{d}}\left(\left[\mathbf{K}_{c}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{c}\right||\mathbf{K}| u_{c}\right]^{1 / 2} r_{d}\right) R_{l_{d}}\left(r_{d}\right) r_{d}^{2}}{\left.\left[\mathbf{K}_{a}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{a}\right||\mathbf{K}| u_{a}\right]^{l_{b} / 2}-2\left|\mathbf{K}_{b}\right||\mathbf{K}| u_{c}\right]^{l_{d} / 2}} \tag{20}
\end{align*}
$$

## E. A global co-ordinate change

Now we use the co-ordinates:

$$
\begin{align*}
K_{a} & =\mathbf{K}_{a} \\
K_{c} & =\mathbf{K}_{c} \\
K & =\mathbf{K} \\
U_{a} & =\left[\mathbf{K}_{a}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{a}\right||\mathbf{K}| u_{a}\right]^{1 / 2} \\
U_{c} & =\left[\mathbf{K}_{c}^{2}+\mathbf{K}^{2}-2\left|\mathbf{K}_{c}\right||\mathbf{K}| u_{c}\right]^{1 / 2} \tag{21}
\end{align*}
$$

Now we have that the matrix of the transformation is upper triangular so the determinant of the Jacobian is given by:

$$
\begin{equation*}
\operatorname{det}(\mathcal{J})=\frac{K^{2} K_{a} K_{c}}{U_{a} U_{c}} \tag{22}
\end{equation*}
$$

As such we have that:

$$
\begin{align*}
I_{a b c d} & =4 \pi(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \sum_{L_{a} M_{a}} \sum_{L_{c}, M_{c}} \sum_{L, M} i^{L_{a}} Y_{L_{a} M_{a}}\left(\mathbf{R}_{a} \widehat{-\mathbf{R}_{b}}\right) i^{L_{c}} Y_{L_{c} M_{c}}\left(\mathbf{R}_{c} \widehat{-\mathbf{R}_{d}}\right) i^{L} Y_{L M}\left(\mathbf{R}_{b} \widehat{-\mathbf{R}_{d}}\right) \times \\
& \times \int \frac{1}{(2 \pi)^{5}} \frac{U_{a} U_{c}}{K^{2} K_{a} K_{c}} \times J_{L_{a}}\left(K_{a}\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) J_{L_{c}}\left(K_{c}\left|\mathbf{R}_{c}-\mathbf{R}_{d}\right|\right) J_{L}\left(K\left|\mathbf{R}_{b}-\mathbf{R}_{d}\right|\right) \times \\
& \times\left(\frac{2}{\pi}\right)^{4} \frac{\int_{0}^{\infty} d r_{a} J_{l_{a}}\left(K_{a} r_{a}\right) R_{l_{a}}\left(r_{a}\right) r_{a}^{2}}{K_{a}^{l_{a}}} \frac{\int_{0}^{\infty} d r_{c} J_{l_{c}}\left(K_{c} r_{c}\right) R_{l_{c}}\left(r_{c}\right) r_{c}^{2}}{K_{c}^{l_{c}}} \times \\
& \times \frac{\int_{0}^{\infty} d r_{b} J_{l_{b}}\left(U_{a} r_{b}\right) R_{l_{b}}\left(r_{b}\right) r_{b}^{2}}{U_{a}^{l_{b}+2}} \frac{\int_{0}^{\infty} d r_{d} J_{l_{d}}\left(U_{c} r_{d}\right) R_{l_{d}}\left(r_{d}\right) r_{d}^{2}}{U_{c}^{l_{d}+2}} \tag{23}
\end{align*}
$$

This factorizes to:

$$
\begin{align*}
I_{a b c d} & =4 \pi(-i)^{l_{b}+l_{d}} i^{l_{a}+l_{c}} \sum D_{a b c d}^{m, n, p} \frac{\partial^{m_{x}}}{\partial \mathbf{R}_{a}^{x}} \frac{\partial^{m_{y}}}{\partial \mathbf{R}_{a}^{y}} \frac{\partial^{m_{z}}}{\partial \mathbf{R}_{a}^{z}} \frac{\partial^{n_{x}}}{\partial \mathbf{R}_{c}^{x}} \frac{\partial^{n_{y}}}{\partial \mathbf{R}_{c}^{y}} \frac{\partial^{n_{z}}}{\partial \mathbf{R}_{c}^{z}} \frac{\partial^{p_{x}}}{\partial \mathbf{R}_{b}^{x}} \frac{\partial^{p_{y}}}{\partial \mathbf{R}_{b}^{y}} \frac{\partial^{p_{z}}}{\partial \mathbf{R}_{b}^{z}} \times \\
& \times \sum_{L_{a} M_{a}} \sum_{L_{c}, M_{c}} \sum_{L, M} i^{L_{a}} Y_{L_{a} M_{a}}\left(\mathbf{R}_{a} \widehat{-\mathbf{R}_{b}}\right) i^{L_{c}} Y_{L_{c} M_{c}}\left(\mathbf{R}_{c} \widehat{-\mathbf{R}_{d}}\right) i^{L} Y_{L M}\left(\mathbf{R}_{b} \widehat{-\mathbf{R}_{d}}\right) \\
& \times \int \frac{d K_{a}}{4} \frac{\int_{0}^{\infty} d r_{a} J_{l_{a}}\left(K_{a} r_{a}\right) R_{l_{a}}\left(r_{a}\right) r_{a}^{2}}{K_{a}^{l_{a}+1}} J_{L_{a}}\left(K_{a}\left|\mathbf{R}_{a}-\mathbf{R}_{b}\right|\right) \\
& \times \int_{0}^{\infty} \frac{d K_{c}}{4} \frac{\int_{0}^{\infty} d r_{c} J_{l_{c}}\left(K_{c} r_{c}\right) R_{l_{c}}\left(r_{c}\right) r_{c}^{2}}{K_{c}^{l_{c}+1}} J_{L_{c}}\left(K_{c}\left|\mathbf{R}_{c}-\mathbf{R}_{d}\right|\right) \\
& \times \int_{0}^{\infty} \frac{d K}{2 \pi} \frac{1}{K^{2}} J_{L}\left(K\left|\mathbf{R}_{b}-\mathbf{R}_{d}\right|\right) \\
& \times \int_{\left|K_{a}-K\right|}^{K_{a}+K} \frac{d U_{a}}{4} \frac{\int_{0}^{\infty} d r_{b} J_{l_{b}}\left(U_{a} r_{b}\right) R_{l_{b}}\left(r_{b}\right) r_{b}^{2}}{U_{a}^{l_{b}+1}} \\
& \times \int_{\left|K_{c}-K\right|}^{K_{c}+K} \frac{d U_{c}}{4} \frac{\int_{0}^{\infty} d r_{d} J_{l_{b}}\left(U_{c} r_{d}\right) R_{l_{d}}\left(r_{d}\right) r_{d}^{2}}{U_{c}^{l_{d}+1}} \tag{24}
\end{align*}
$$

This is our main result as it presents the Coulomb four center integrals in a nearly factorable form.

## III. CONCLUSIONS

In this work we have presented some formulas for four center integrals associated with the Coulomb interaction.

These results are in a nearly factorable form and depend on the Fourier Bessel transforms of the radial wave function given in Eq. (3), as well as auxiliary integrals see Eq. (24). In the future it would be of interest to combine the new basis sets introduced in Ref. [6] where all basis wave functions are of the form considered in Eq. (11) to study the electronic structures of small molecules through either HF or DFT methods.
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