Ground State Calculator: Specialized Integration Technique

Adam J. Robinson

December 16, 2019

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1 Problem Statement

The proper calculation of the expectation value of the Hamiltonian requires calculation of the following integral,

$$I_{EN} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\prod_{i=1}^{3} \exp\left[-Y_i x_i^2 + V_i x_i\right]}{\sqrt{\left(R_1 - x_1\right)^2 + \left(R_2 - x_2\right)^2 + \left(R_3 - x_3\right)^2}} dx_1\, dx_2\, dx_3 \tag{1}$$

Here, the subscript EN is short for Electron - Nucleus, because this integral characterizes interactions between the electron and the nucleus. This is actually a simple case of the more complex Electron - Electron integral, which must be calculated for systems with more than one electron.

This integral cannot be comuted analytically. I have tried converting is to polar coordinates and making various substitutions. All attempts to find a complete analytical expression have failed. Furthermore, this integral is very resistant to traditional numeric integration techniques. I've attempted to use the gsl integration functions that are meant to handle integrals with poles and bounds at infinity. When using gsl, the integral took around 5 minutes to compute and suffered from serious instabilities. This document is concerned with the development of a method of integration specific to this integral in particular.

2 Approach

First, note that the numerator is separable with respect to the three variables of integration. The idea behind this integration technique is to write the numerator as a product of three Taylor series of order x^2.

$$\begin{aligned}
f_i\left(x_i\right) &\equiv \exp\left[-Y_i x_i^2 + V_i x_i\right] \\
\mathcal{N} &= \prod_{i=1}^{3} f_i\left(x_i\right) \\
\tilde{\mathcal{N}} &= \prod_{i=1}^{3} a_i + b_i\left(x_i - d_i\right) + \frac{c_i}{2}\left(x_i - d_i\right)^2 \\
&= \prod_{i=1}^{3} a_i - b_i d_i + \frac{c_i d_i^2}{2} + x_i\left(b_i - c_i d_i\right) + \frac{c_i x_i^2}{2} \\
a_i &\equiv f_i\left(d_i\right) \\
b_i &\equiv f_i'\left(d_i\right) \\
c_i &\equiv f_i''\left(d_i\right)
\end{aligned}$$

With this approximation in use, the integrand can be written as $\tilde{\mathcal{N}}$ over the original denominator. This approximation has an error of at most 1 part in 10,000 for in the range given in eq. 2.

$$\mathsf{range} = \left[-0.127 \cdot Y_i^{-1/2},\ 0.127 \cdot Y_i^{-1/2}\right] \tag{2}$$

When the integrand is written as the expression given by eq. 3, it becomes possible to analytically determine the indefinite integral. While the resulting expression is large, it is extremely accurate for the range given by eq. 2. The integral can then be carried out by summing a small number of relatively large intervals given by the indefinite integral of eq. 3.

$$P\left(x_1,\ x_2,\ x_3\right) \equiv \frac{\prod_{i=1}^{3}\left(a_i - b_i d_i + \frac{c_i d_i^2}{2} + x_i\left(b_i - c_i d_i\right) + \frac{c_i x_i^2}{2}\right)}{\sqrt{\left(x_1 - R_1\right)^2 + \left(x_2 - R_2\right)^2 + \left(x_3 - R_3\right)^2}} \tag{3}$$

3 Definition

In this section, I will work out the full definition of the approximation of the integral given by eq. 1. First, I will redefine the constants in eq. 3 to make it more readable.

$$P\left(x_1,\ x_2,\ x_3,\ d_1,\ d_2,\ d_3\right) = \frac{\prod_{i=1}^{3}\left(A_i + B_i x_i + C_i x_i^2\right)}{\sqrt{\left(x_1 - R_1\right)^2 + \left(x_2 - R_2\right)^2 + \left(x_3 - R_3\right)^2}}$$

$$A_i \equiv a_i - b_i d_i + \frac{c_i d_i^2}{2}$$

$$B_i \equiv b_i - c_i d_i$$

$$C_i \equiv \frac{c_i}{2}$$

Next, I will define the procedure for estimating the integral, without explicitely defining all expressions. This serves to motivate the rather complicated indefinite integrals below.

$$\tilde{I}_{EN} \equiv \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} P\left(x_1,\ x_2,\ x_3,\ d_1,\ d_2,\ d_3\right) dx_1\, dx_2\, dx_3 \tag{4}$$

In order to accurately approximate the inner most integral, we need to set our bounds of integration to surround both the pole R_1 and the center of the Gaussian. The range of values that must be encompassed in the range of the integral is given by eqs. 5, 6 and 7.

$$L_i = \min\left\{R_i\ - \epsilon,\ -\frac{V_i}{2Y_i} - \beta\sqrt{\frac{\ln 2}{Y_i}}\right\} \tag{5}$$

$$U_i = \max\left\{R_i\ + \epsilon,\ -\frac{V_i}{2Y_i} + \beta\sqrt{\frac{\ln 2}{Y_i}}\right\} \tag{6}$$

$$\mathcal{R}_i = \left[L_i,\ U_i\right] \tag{7}$$

Here, the factor that is multiplied by β is the full width half max of the Gaussian. β should usually be greater than or equal to 3 in order to ensure that the majority of the Gaussian function has been encompassed by the bounds of integration. ϵ is a small factor that ensures that the pole is encompassed by the bounds of the integral.The sum used to approximate the inner most integral is then,

$$\int_{-\infty}^{+\infty} P\left(x_1,\ x_2,\ x_3,\ d_1,\ d_2,\ d_3\right) dx_1 \approx \sum_{n_1=0}^{N_1-1} P_1^{(-1)}\left(\delta_{n_1} + \Delta x_1,\ \delta_{n_1}\right) - P_1^{(-1)}\left(\delta_{n_1} - \Delta x_1,\ \delta_{n_1}\right)$$

$$P_1\left(a,\ b\right) \equiv P\left(a,\ x_2,\ x_3,\ b,\ d_2,\ d_3\right)$$

$$P_1^{(-1)}\left(a,\ b\right) \equiv \left.\frac{d^{-1}P_1}{dx_1^{-1}}\right|_{(a,\ b)}$$

$$\Delta x_1 \equiv \frac{U_1 - L_1}{N_1}$$

$$\delta_{n_1} \equiv L_1 + \frac{\Delta x_1}{2} + n_1 \Delta x_1$$

Where, N_1 is the number of intervals to divide the integral into. When the integral is centered on the Gaussian, a value of around 20 should suffice. The number of intervals should increase from twenty, proportional to the number of widths of the Gaussian that the center of the Gaussian is away from the pole.

$$N_i = 20 + \gamma\left|\frac{V_i}{2Y_i} + R_i\right|\sqrt{\frac{Y_i}{\ln 2}} \tag{8}$$

Here, γ is an arbitrary factor that can be adjusted. Somewhere between 3 and 8 is probably good. If for example, it was 3, eq. 8 could be interpreted as meaning that three intervals are added for every one full width half max that the center of the Gaussian is away from the pole.

The integral from eq. 4 now reads,

$$\begin{aligned}\tilde{I}_{EN} &\approx \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\sum_{n_1=0}^{N_1-1}\sum_{n_1=0}^{N_1-1} P_1^{(-1)}\left(\delta_{n_1}+\Delta x_1,\ \delta_{n_1}\right) - P_1^{(-1)}\left(\delta_{n_1}-\Delta x_1,\ \delta_{n_1}\right)\,dx_2\,dx_3 \\ &= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\sum_{n_1=0}^{N_1-1} P_1^{(-1)}\left(\delta_{n_1}+\Delta x_1,\ \delta_{n_1}\right)\,dx_2\,dx_3 - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\sum_{n_1=0}^{N_1-1} P_1^{(-1)}\left(\delta_{n_1}-\Delta x_1,\ \delta_{n_1}\right)\,dx_2\,dx_3\end{aligned}$$

The same procedure applied for the inner integral can be applied to the next integral.

$$\int_{-\infty}^{+\infty}\sum_{n_1=0}^{N_1-1} P_1^{(-1)}\left(\delta_{n_1}-\Delta x_1,\ \delta_{n_1}\right)\,dx_2 = \sum_{n_1=0}^{N_1-1}\int_{-\infty}^{+\infty} P_1^{(-1)}\left(\delta_{n_1}-\Delta x_1,\ \delta_{n_1}\right)\,dx_2$$