The High-Speed, High-Precision Evaluation of Four- Electron Integrals

Adam Malone | Ryan Foster | Faculty Mentor Dr. Frederick King - Dept. of Chemistry, UWEC

Introduction

In quantum mechanics, an atom is represented by it's wave function. Through the manipulation of an atom's wave function, observable quantities such as position, momentum, and energy may be calculated.

These calculations are difficult to perform. Computational strategies must be developed which take speed, accuracy, and loss-of-precision in to account.

Wave Functions

For multi-electron atoms, the inclusion of explicit electron-electron separation distances in the wave function leads to accurate results.[1] For Helium, which has 2 electrons, the wave function looks like

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\mu=1}^{N} c_\mu \; r_1^{i_\mu} \; r_2^{j_\mu} \; r_{12}^{m_\mu} \; e^{-\alpha_\mu r_1-\beta_\mu r_1} \tag{1}$$

r_1, r_2	electron-nuclear separation
r_{12}	electron-electron separation
$c_\mu, \alpha_\mu, \beta_\mu$	parameters, > 0 determined by linear algebra
i_μ, j_μ, m_μ	integers ≥ 0

The bigger the atom, the more complicated the wave function becomes. Each Beryllium wave function, for example has 4 radial and exponential components, and 6 inter-electron components.

Energy

To calculate the expectation value of the energy of an atomic system, one applies the Hamiltonian operator to the wave function, multiplies by the complex conjugate, and integrates over all space.

$$\langle\psi|\hat{H}|\psi\rangle \quad \text{or,} \quad \int \psi^* \hat{H} \psi \; d\mathbf{v}$$

The complexity of this integral depends on the powers the correlation terms are raised to (m for the Helium example above). For example, odd and even powers must be handled differently. For the 4-electron system, the energy integral reduces to an 6-fold infinite summation over the correlation factor indicies:

$$\sum_{m',n',p',q',s',t'}^{\infty} I_\Omega(m',n',p',q',s',t') I_R(m,n,p,q,s,t,m',n',p',q',s',t',\alpha,\beta,\gamma,\delta)$$

Where I_Ω is the angular part of the integral, which does not present any computational difficulty. The radial part, I_R *does* unfortunately.

The radial integral, I_R can be expressed as *another* infinite sum over six variables of the auxiliary integral,

$$W_4=\int_0^\infty x^I e^{-ax}dx\int_x^\infty y^J e^{-by}dy\int_y^\infty z^K e^{-cz}dz\int_z^\infty w^L e^{-dw}dw \tag{2}$$

Approximation

The W_4 integral can be broken up into a sum of another auxiliary function, W_3. The W_3 can in turn be broken up into a sum of

$$W_2\left(i,j,a,b\right)=\int_0^\infty x^i e^{-ax}dx\int_x^\infty y^j e^{-by}dy \tag{3}$$

Depending on the signs of the J, K, L from (2), these sums either terminate or are infinite. This W_2 integral is the innermost computation in the nested sums, so an increase in efficiency at this point counts for a lot.

The integral converges for $a, b > 0$, $i \geq 0$, and $i+j \geq -1$. The problem cases arise when $j < 0$. There is a closed-form solution to the integral in this case, but it is not acceptable for use in practical calculation because of a major loss of precision. The following infinite series expansion of W_2 does not have this problem

$$W_2\left(i,j,a,b\right)=\frac{i!}{a(a+b)^{i+j+1}}\sum_{m=1}^{\infty}\frac{(i+j+m)!}{(m+i)!}\left(\frac{a}{a+b}\right)^m \tag{4}$$

Convergence Acceleration

There exist methods to speed up the convergence of an infinite series.[2] An alternating series is preferred, because attempting to convergence-accelerate a series with strictly positive terms can actually have a negative effect on the convergence.

Equation (4) can be written as a hypergeometric series:

$$W_2\left(i,j,a,b\right)=\frac{i!}{a(a+b)^{i+j+1}}\;{}_2F_1\left(i+j+2,1;i+2,\frac{a}{a+b}\right)$$

This hypergeometric series can be transormed to [3]

$${}_2F_1\left(\alpha,\beta;\gamma,z\right)=(1-z)^{-\beta}{}_2F_1\left(\beta,\gamma-\alpha;\gamma,\frac{z}{z-1}\right)$$

This changes the variable $\frac{a}{a+b}$ to

$$\frac{\frac{a}{a+b}}{\frac{a}{a+b}-1}=\frac{a}{a+b}\frac{a+b}{-b}=-\frac{a}{b}$$

Now we have an alternating series, and convergence acceleration may be applied as long as $a < b$.

Conclusion

The convergence acceleration described above was successful in reducing the number of terms needed to approximate W_2 (for $a < b$). The case $a > b$ has yet to be dealt with. This method could possibly be extended to the more complicated W_3 and W_4 integrals.

Acknowledgements

Funding provided by:

- Petroleum Research Fund, The American Chemical Society.
- ORSP, UWEC.

REFERENCES

1. King, Frederick W. "Analysis of Some Integrals Arising in the Atomic Four-Electron Problem." J. Chem. Phys 99 (1993): 3622-3628.
2. Wimp, Jet. Sequence Transformations and Their Applications. Academic P, 1981.
3. Abramowitz, and Stegun. Handbook of Mathematical Functions. Dover Publications, 1965. 599.