Exact formulas for multipole moments using Slater-type molecular orbitals

Herbert W. Jones
Department of Physics, Florida A&M University, Tallahassee, Florida 32307
(Received 3 September 1985)

A triple infinite sum of formulas expressed as an expansion in Legendre polynomials is generated by use of computer algebra to represent the potential from the midpoint of two Slater-type orbitals; the charge density that determines the potential is given as the product of the two orbitals. An example using 1*s* orbitals shows that only a few terms are needed to obtain four-figure accuracy. Exact formulas are obtained for multipole moments by means of a careful study of expanded formulas, allowing an "extrapolation to infinity." This Löwdin alpha-function approach augmented by using a *C* matrix to characterize Slater-type orbitals can be readily generalized to all cases.

I. INTRODUCTION

In a recent article[1] the author expanded the electrostatic potential due to the product of two separated 1*s* Slater-type orbitals (STO's) in a series of Legendre polynomials. By use of a computer algebra implementation of the Löwdin alpha-function method with a "*C* matrix" to characterize an orbital, exact formulas were generated for each radial function associated with the Legendre polynomials. However, in that paper the origin of the coordinate system was placed on one of the nuclei. For problems of electron scattering[2–4] and molecular interactions the coordinate system should be placed at the center of mass. Here this case will be considered for 1*s* orbitals and furthermore, exact formulas for multiple moments will be generated.

II. DERIVATION OF THE POTENTIAL

A STO is represented in its local coordinate system by

$$\chi = AR^{N-1}e^{-\zeta R}Y_L^M(\Theta,\phi) \ , \tag{1}$$

where $A=(2\zeta)^{N+1/2}[(2N)!]^{-1/2}$ is the normalization factor, N,L,M are the quantum numbers of the orbital, and ζ is the screening constant. If this orbital is centered at the (x,y,z) point $(0,0,a)$ in the reference coordinate system (r,θ,ϕ), then in this system an expansion in spherical harmonics is as follows:[1,5]

$$\chi = \frac{A}{\zeta^{N-1}}\left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!}\right]^{1/2}\sum_{l=M}^{\infty}\left[\frac{4\pi(l+M)!}{(2l+1)(l-M)!}\right]^{1/2}(-1)^M\alpha_l^{NLM}(\zeta a,\zeta r)\,Y_l^M(\theta,\phi) \ , \tag{2}$$

where

$$\alpha_l^{NLM}(\zeta a,\zeta r)=\frac{(2l+1)[(l-M)!]}{2[(l+M)!]}\sum_{i=0}^{N+L+l}\sum_{j=0}^{N+l}C_l^{NLM}(i,j)H_{ij}(\zeta a,\zeta r)(\zeta a)^{i-L-l-1}(\zeta r)^{j-l-1} \ ,$$

and

$$H_{ij}(\zeta a,\zeta r)=\begin{cases}e^{-\zeta a}[(-1)^j e^{\zeta r}-e^{-\zeta r}], & r<a,\\ e^{-\zeta r}[(-1)^i e^{\zeta a}-e^{-\zeta a}], & r>a.\end{cases}$$

Let us immediately specialize to the case of 1*s* orbitals with screening constants of 1. Take χ_a to be centered along the z axis at a distance of $-a$ from the origin and χ_b to be centered along the z axis at a distance of a from the origin. We seek the potential at an arbitrary point (r_2,θ_2,ϕ_2) due to the charge distribution $\chi_a(1)\chi_b(1)$. Thus

$$V(r_2)=\int(\chi_a\chi_b/r_{12})\,dv_1 \text{ or } \int dv_1\frac{\chi_a\chi_b}{r_{12}} \ . \tag{3}$$

Now we may write

$$\chi_a=\sum_{m=0}^{\infty}\frac{2}{2m+1}(-1)^m\alpha_m Y_m^0(\theta,\phi) \ , \tag{4}$$

where

$$\alpha_m=\frac{2m+1}{2}\sum_{i=0}^{m+1}\sum_{j=0}^{m+1}C_m(i,j)H_{ij}a^{i-m-1}r_1^{j-m-1} \ ,$$

and

$$H_{ij}=\begin{cases}e^{-a}[(-1)^j e^{r_1}-e^{-r_1}], & r_1<a,\\ e^{-r_1}[(-1)^i e^{a}-e^{-a}], & r_1>a.\end{cases}$$

Note that the multiplication by $(-1)^m$ moves the orbital to the negative z axis. Also, we have

$$\chi_b=\sum_{n=0}^{\infty}\frac{2}{2n+1}\alpha_n Y_n^0(\theta,\phi), \tag{5}$$

where

$$\alpha_n=\frac{2n+1}{2}\sum_{p=0}^{n+1}\sum_{q=0}^{n+1}C_n(p,q)H_{pq}a^{p-n-1}r_1^{q-n-1} \ ,$$

and

$$H_{pq}=\begin{cases}e^{-a}[(-1)^q e^{r_1}-e^{-r_1}], & r_1<a,\\ e^{-r_1}[(-1)^p e^{a}-e^{-a}], & r_1>a.\end{cases}$$

The Laplace expansion for $1/r_{12}$ is

$$\frac{1}{r_{12}}=4\pi\sum_{\lambda=0}^{\infty}\sum_{\nu=-\lambda}^{\lambda}(2\lambda+1)^{-1}\frac{r_<^\lambda}{r_>^{\lambda+1}}[Y_\lambda^\nu(\theta_1,\phi_1)]^*Y_\lambda^\nu(\theta_2,\phi_2)\ , \tag{6}$$

where $r_>$ is the larger of r_2 and r_1, and $r_<$ is the smaller of r_1 and r_2.

Substituting in the equation for potential and using the orthogonality rules for spherical harmonics, we get

$$V(\mathbf{r}_2)=4\pi\sum_{\lambda}\sum_{m}\sum_{n}Y_\lambda^0(\theta_2,\phi_2)(2\lambda+1)^{-1}\frac{2}{(2m+1)^{1/2}}\frac{2(-1)^m}{(2n+1)^{1/2}}$$
$$\times\int dr_1\,r_1^2\,\alpha_m\alpha_n\frac{r_<^\lambda}{r_>^{\lambda+1}}\int d\phi_1\,d\theta_1\sin\theta_1\,Y_\lambda^0(\theta_1,\phi_1)^*Y_m(\theta_1,\phi_1)\,Y_n^0(\theta_1,\phi_1)\ . \tag{7}$$

It is more convenient to work with Legendre polynomials obtained by using the identity

$$Y_l^0(\theta,\phi)=\left[\frac{2l+1}{4\pi}\right]^{1/2}P_l(\cos\theta)\ . \tag{8}$$

After the ϕ integration we get

$$V(\mathbf{r}_2)=\sum_{\lambda}P_\lambda(\cos\theta_2)\sum_{m}\sum_{n}V_{\lambda mn}(r_2)\ , \tag{9}$$

with

$$V_{\lambda mn}(r_2)=2\int d\theta\sin\theta P_\lambda P_m P_n\int dr_1\,r_1^2(-1)^m\alpha_m\alpha_n\frac{r_<^\lambda}{r_>^{\lambda+1}}\ . \tag{10}$$

In this paper we only consider the case $r_2>a$.

The radial integration naturally divides into three regions. We consider in detail the inner region. To be explicit, we write the expression for that part of the potential $V_{\lambda mn}^{(I)}$ due to the charges enclosed in a sphere of radius a:

$$V_{\lambda mn}^{(I)}=2\int d\theta\sin\theta P_\lambda P_m P_n\frac{2m+1}{2}\frac{2n+1}{2}\sum_{i,j,p,q}(-1)^m C_m(i,j)C_n(p,q)a^{i-m+p-n-2}\frac{e^{-2a}}{r_2^{\lambda+1}}$$
$$\times\int_0^a dr_1\,r_1^{-m+q-n+\lambda}[(-1)^{j+q}e^{2r_1}-(-1)^j-(-1)^q+e^{-2r_1}]\ . \tag{11}$$

Our computer algebra simply keeps track of the powers of r_2 and a which form polynomials that are to be multiplied by obvious functions of r_2 and a that are added to represent $V_{\lambda mn}$. For instance, we find that, dropping subscript 2,

$$V_{000}=2.5a^{-2}+e^{-2a}(-2.5a^{-2}-5.0a^{-1}-4.0a^0-4a/3)+[a^{-2}(-1.25/r-0.25)+a^{-1}(1.5/r)+a^0(-0.5/r)]e^{2a}e^{-2r}$$
$$+[a^{-2}(2.5/r+0.5)+a^0(-1/r)]e^{-2r}+[a^{-2}(-1.25/r-0.25)+a^{-1}(-1.2/r)+a^0(-0.5/r)]e^{-2a}e^{-2r}$$
$$+(-a^{-2}+2a^{-1}-a^0)e^{2a}\mathrm{Ei}(-2r)+(2a^{-2}-2a^0)\mathrm{Ei}(-2r)+(-a^{-2}-2a^{-1}-a^0)e^{-2a}\mathrm{Ei}(-2r). \tag{12}$$

Similar formulas result for various values of λ,m,n. For a numerical comparison we take the case $a=1$, $r_2=1.5$, and $\theta_2=0°$. Letting m and n range from 0 to 8 such that $m+n<8$ in the summations, we obtain $\lambda=0$, 0.326 974; $\lambda=1$, 0.0; $\lambda=2$, 0.012 494; $\lambda=3$, 0.0; $\lambda=4$, 0.001 357; $\lambda=5$, 0.0; $\lambda=6$, 0.000 207; $\lambda=7$, 0.0; $\lambda=8$, 0.000 073. The sum of these values is 0.341 107. This compares well with the exact value[1,6] of 0.341 021.

III. EXACT FORMULAS FOR MULTIPOLE MOMENTS

For values of r_2 essentially beyond the charge distribution, an expansion of the potential in multipoles is appropriate. In this case the r_2 limit on the integrals may be replaced by infinity. The monopole ($\lambda=0$) is composed of an infinite number of terms as m and n take on all values. We write a few terms, dropping the subscript 2, as follows:

$$V_{000}=\frac{1}{r}[2.5/a^2+e^{-2a}(-2.5/a^2-5.0/a-4a^0-4a/3)]\ ,$$

$$V_{011}=0.0\ ,$$

$$V_{022}=\frac{1}{r}[52.5/a^4-7.5/a^2+e^{-2a}(-52.5/a^4-105/a^3-97.5/a^2-20a^0-4a)]\ ,$$

$$V_{033}=0.0\ ,$$

$$V_{044}=\frac{1}{r}[2362.5/a^6-262.5/a^4+12.5/a^2+e^{-2a}(-262.5/a^6-4725/a^5-4462.5/a^4-2625/a^3-1062.5/a^2$$
$$-305/a-60a^0+20a/3)]\ .$$

We may factor out e^{-2a} from the first part of the terms by multiplying by e^{2a}, using computer algebra. Then we obtain

$$V_{000}=\frac{e^{-2a}}{r}(1.000+2.000a+1.666a^2+0.666a^3+0.222a^4+0.063a^5+\cdots),$$

$$V_{022}=\frac{e^{-2a}}{r}(0.000+0.000a-0.333a^2-0.666a^3-0.333a^4-0.116a^5+\cdots),$$

$$V_{044}=\frac{e^{-2a}}{r}(0.000+0.000a+0.000a^2+0.000a^3+0.111a^4+0.068a^5+\cdots).$$

Addition gives us

$$V_{000}+V_{022}+V_{044}=\frac{e^{-2r}}{r}(1.000+2.000a+1.333a^2+0.000a^3+0.000a^4+0.0154a^5+\cdots).$$

The addition of more and more m,n values simply pushes the line of zeros further and further out, but leaves the formulas intact (the overlap integral). Hence we may "extrapolate to infinity"[7] and obtain exact formulas for the multipole moments. We have thus obtained the following multipole expansion:

$$V(r,\theta)=e^{-2a}(1+2a+4a^2/3)\frac{P_0(\cos\theta)}{r}+e^{-2a}(a^2/5+2a^3/5+4a^4/15)\frac{P_2(\cos\theta)}{r^3}$$
$$+e^{-2a}(3a^4/35+6a^5/35+4a^6/35)\frac{P_4(\cos\theta)}{r^5}+e^{-2a}(a^6/21+2a^7/21+4a^8/63)\frac{P_6(\cos\theta)}{r^7}+\cdots. \quad (13)$$

As a confirmation of this formula, we calculated the potential for $r=9$ and $\theta=0°$ to be 0.065 323; this is identical to the value found by using the Hirschfelder and Weygandt table.[8]

IV. CONCLUSION

The methods shown here are readily generalizable to orbitals with higher quantum numbers because only the C-matrix elements and dimensions of the C matrix need be changed. Because the C-matrix elements are integers, all formulas may be made exact. The technique of "extrapolating to infinity" should be generally useful when dealing with partial wave expansions by means of computer algebra.

ACKNOWLEDGMENTS

The author wishes to acknowledge many useful discussions with Dr. Charles A. Weatherford and the encouragement of Dr. Aaron Temkin. Partial support for this work was provided by the U.S. National Aeronautical and Space Administration under Grant No. NSG-5307.

[1]H. W. Jones, Phys. Rev. A **30**, 1 (1984).
[2]F. H. M. Faisal, J. Phys. B **3**, 636 (1970).
[3]M. A. Morrison, Comput. Phys. Commun. **21**, 63 (1980).
[4]G. B. Schmid and D. W. Norcross, Comput. Phys. Commun. **21**, 79 (1980).
[5]H. W. Jones and C. A. Weatherford, Int. J. Quantum Chem., Quantum Chem. Symp. **12**, 483 (1978).
[6]H. P. Trivedi and E. O. Steinborn, Phys. Rev. A **27**, 670 (1983).
[7]H. W. Jones, *ETO Multicenter Molecular Integrals,* edited by C. A. Weatherford and H. W. Jones (Reidel, Dordrecht, 1982), p. 53; Int. J. Quantum Chem., Quantum Chem. Symp. (to be published).
[8]J. O. Hirschfelder and C. N. Weygandt, J. Chem. Phys. **6**, 806 (1938).