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$1s_A$ $1s_B$ Overlap Integrals, Analytic and Maple Approches

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$1s_A - 1s_B$ overlap computation

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I. SYNOPSIS

The calculation of overlap between adjacent orbitals (not on the same center) requires a slight facility with calculus which is quite instructive. That calculation is presented here.

II. INTRODUCTION

Avoiding the blind use of Maple and/or Mathematica is important for many who need to know that they have sufficient learning to ascertain the validity and veracity of symbolic calculus programs **before** committing to their usage in real problems whose size renders them daunting in a paper and pencil environment.

Here, we consider the integral

$$\int_{\text{all space}} d\tau \psi_{1s_A}^* \psi_{1s_B}$$

where ψ_{1s_A} means a $1s$ orbital located (centered) on nucleus A, and another similar orbital centered on nucleus B.

The text book form

$$\psi_{1s} = e^{-r}$$

for hydrogen atoms doesn't suffice once we deal with more than one center, as in the case of a diatomic molecule of hydrogen (H_2), as an example. Thus we must confront the two (or more) center *molecular* orbitals, whether constructed from atomic orbitals or not, and search how to actually do the calculus we need to do in order to perform quantum chemical calculations.

III. IN CARTESIAN COÖRDINATES

Traditionally, diatomic molecules have been treated in a vertical arrangement, with one nucleus located on the $+z$ axis and the other on the $-z$ axis (the reason being that the molecule has symmetry then about the z axis, and in the transition from Cartesian to Cylindrical Polar coordinates it is the z axis which is chosen as the cylinder axis). Thus, nucleus "A" is usually located at $z = R/2$ while nucleus "B" is located at $z = -R/2$. Using $R/2$ as the displacement allows us to use R as the internuclear distance.

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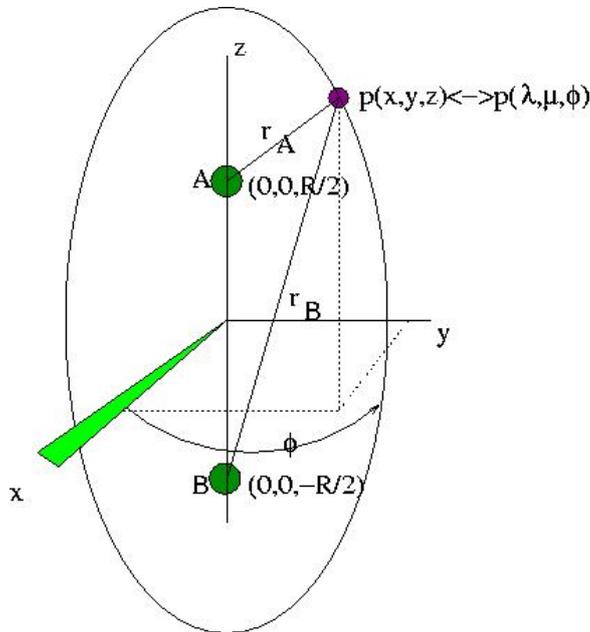


FIG. 1: The traditional orientation of a diatomic molecule.

So, we make the transition to "proper" coordinates [1] in stages, starting with

$$\psi_{1s_A} = e^{-r_A}$$

and

$$\psi_{1s_B} = e^{-r_B}$$

With these choices, which are obvious, we have for the LCAO

$$\psi_{LCAO-MO} = c_A e^{-r_A} + c_B e^{-r_B}$$

and, for clarity in this presentation, we let the constants be equal to each other and equal to one, i.e.,

$$c_A = c_B = 1$$

so that

$$\psi_{LCAO-MO} = e^{-r_A} + e^{-r_B}$$

Now, by elementary geometric considerations we have

$$r_A = \sqrt{x^2 + y^2 + (z - R/2)^2}$$

and

$$r_B = \sqrt{x^2 + y^2 + (z + R/2)^2}$$

so, substituting, we obtain

$$\psi_{LCAO-MO} = e^{-\sqrt{x^2+y^2+(z-R/2)^2}} + e^{-\sqrt{x^2+y^2+(z+R/2)^2}}$$

which means that our LCAO-MO is a function of x , y , and z as it should be.

The overlap calculation we've been asked to do (at the outset) is related to normalizing this wave function, since of the three integrals required in the normalization, one of them is the overlap integral:

$$\int_{\text{all space}} dx dy dz \left(e^{-\sqrt{x^2+y^2+(z-R/2)^2}} e^{-\sqrt{x^2+y^2+(z+R/2)^2}} \right)$$

$$\int_{-\infty}^{\infty} dx \left(\int_{-\infty}^{\infty} dy \left\{ \int_{-\infty}^{\infty} dz \left(e^{-\sqrt{x^2+y^2+(z-R/2)^2}} e^{-\sqrt{x^2+y^2+(z+R/2)^2}} \right) \right\} \right)$$

we see that we can not write this as the product of independent integrals over dx , dy and dz . The variables are hopelessly intermixed, and unsusceptible to simplification!

Ah, what to do?

IV. SWITCH TO ELLIPTICAL COÖRDINATES

In several separate pieces addressing H_2^+ wave functions, I've addressed the question [2]. of elliptical coördinates. These consist of a three coördinates, λ , μ , and φ . The latter corresponds to the polar angle in both cylindrical coördinates and spherical polar coördinates. The first two, which lie in the (to be replaced) $x - y$ plane, correspond to ellipses and hyperbolas

$$\lambda = \frac{r_A + r_B}{R}$$

and

$$\mu = \frac{r_A - r_B}{R}$$

These definitions, which happen to be based on the same radii as are used in this two nucleus problem, can be inverted to

$$r_A = \frac{R}{2}(\lambda + \mu)$$

with the concomitant definition

$$r_B = \frac{R}{2}(\lambda - \mu)$$

where we have explicitly converted to Cartesian coördinates in both the integrand and the differential volume element ($d\tau = dx dy dz$). We note in passing that since these wave functions are real, we've dropped the complex conjugates.

Now all the expertise we have from 2 years of calculus will not help us do this integral by brute force. Re-writing it:

This last form is perfect for allowing us to re-write the integrals and wave functions!

We write

$$\psi_{1s_A} = e^{-\frac{R}{2}(\lambda + \mu)}$$

while

$$\psi_{1s_B} = e^{-\frac{R}{2}(\lambda - \mu)}$$

so

$$\int_{\text{all space}} d\tau \psi_{1s_A}^* \psi_{1s_B} = \int d\tau e^{-\frac{R}{2}(\lambda + \mu)} e^{-\frac{R}{2}(\lambda - \mu)}$$

The μ 's cancel in the exponentials, and the two λ terms add together, i.e.,

$$\int d\tau e^{-\frac{R}{2}(\lambda - \frac{R}{2}\lambda)} e^{-\frac{R}{2}\mu} e^{-\frac{R}{2}(-\mu)}$$

so

$$\int d\tau e^{-\frac{R}{2}(2\lambda)} e^{-\frac{R}{2}\mu} e^{-\frac{R}{2}(-\mu)}$$

The only question left is, what is $d\tau$? In Cartesian coördinates, we know it's $dx dy dz$ while in spherical polar coördinates it's $r^2 \sin \vartheta \cos \varphi dr d\vartheta d\varphi$ but in elliptical coördinates it's $\frac{R^2}{8} d\varphi (\lambda^2 - \mu^2) d\lambda d\mu$. Finally, the limits $\varphi = 0 \rightarrow 2\pi$, $\lambda = 1 \rightarrow \infty$, and $\mu = -1 \rightarrow +1$. Knowing this, the rest is elementary.

V. MAPLE

In the following Maple code, the actual wave functions have included a variational parameter α in the exponents,

to allow optimization (another topic not covered here). Further, $d\tau$ has been evaluated (as derived in the Elliptical Coördinate paper cited earlier). Other than that, the rest is straightforward.

And by the way, Maple really isn't required for such trivial integrals.

Parenthetically, it's interesting to note that the overlap, often written S_{AB} , is truly a function of R , as can be seen explicitly in the Maple result (last line of output).

VI. MAPLE CODE

```
> #1s1soverlap.mws 1s orbitals in var11
> assume (alpha > 0, R > 0);
> SAB := (Pi*(R^3)/4)*(lambda^2-mu^2)*
> exp(-alpha*R*lambda);
> SAB1 := int(SAB,mu);
> SAB11 := subs(mu=1,SAB1);
> SABm1 := subs(mu=-1,SAB1);
> SAB1direct := collect(expand(SAB11 -
SABm1),exp(-alpha*R*lambda));
> SAB1 := int(SAB,mu=-1..1);
> SAB2 := int(SAB1,lambda=1..infinity);
```

$$SAB := \frac{1}{4} \pi R^{-3} (\lambda^2 - \mu^2) e^{(-\alpha R \lambda)}$$

$$SAB1 := \frac{1}{4} \pi R^{-3} e^{(-\alpha R \lambda)} (\lambda^2 \mu - \frac{1}{3} \mu^3)$$

$$SAB11 := \frac{1}{4} \pi R^{-3} e^{(-\alpha R \lambda)} (\lambda^2 - \frac{1}{3})$$

$$SABm1 := \frac{1}{4} \pi R^{-3} e^{(-\alpha R \lambda)} (-\lambda^2 + \frac{1}{3})$$

$$SAB1direct := \frac{1}{2} \frac{\pi R^{-3} \lambda^2}{e^{(\alpha R \lambda)}} - \frac{1}{6} \frac{\pi R^{-3}}{e^{(\alpha R \lambda)}}$$

$$SAB1 := \frac{1}{6} \pi R^{-3} (3\lambda^2 - 1) e^{(-\alpha R \lambda)}$$

$$SAB2 := \frac{(\frac{1}{3} \alpha^{-2} R^{-2} + \alpha^{-1} R^{-1} + 1) \pi e^{(-\alpha R)}}{\alpha^{-3}}$$

It is worth noting that the explicit R dependence of what is commonly called S_{AB} , i.e., the last Maple expression (above) has been demonstrated.

[1] We need to be clear here that there are going to be only 3 coördinates, and the nuclei have to be located in terms of these three coördinates and, at the same time, the electron's position. There will be three "numbers", three triples, $(0, 0, R/2)$, $(0, 0, -R/2)$ and (x_e, y_e, z_e) where the

first two are for the two nuclei and the third is for the electron.

[2] C. W. David, <http://digitalcommons.uconn.edu/chem.educ/5>