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# Introduction to Atomic Units, Normalization and Orthogonalization (Part 2 of a Series)

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# Introduction to Atomic Units, Normalization and Orthogonalization (Part 2 of a Series)

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## I. ABSTRACT

Normalization in physical X, Y, and Z space, where dimensions are measured in centimeters (for instance), leads to different values for normalization constants than when dimensionless spaces such as that employed in atomic units are employed.

## II. INTRODUCTION

The use of atomic units comes with a non-obvious penalty worth mentioning. Where normalizing of orbitals involves choosing forms which force probabilities of finding a particle somewhere in its domain, the values of the normalization constants change according to the nature of the coördinate system being employed. This means that care must be taken to use a consistent "space" when considering quantum chemistry manipulations.

Consider normalization of the 1s orbital,

$$\psi_{1s}(x,y,z) = ce^{-Ar} \tag{1}$$

in atomic units (where A is the atomic number of the nucleus, we often set A = 1 for illustrative purposes). We are interested in evaluating

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{\psi_{1s}^2\right\} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{c^2 e^{-2Ar}\right\} \tag{2}$$

Converting back to "real" units, we have

$$\Psi_{1s}(X,Y,Z) = Ce^{-\frac{Ame^2}{\hbar^2}R} \to Ce^{-\frac{A}{a_0}R}$$

where the mass, "m", is in grams, the electron's charge "e" is in stat-coulomb, and $\hbar$ is in erg-sec, "R" is in cm and $a_0$ is the Bohr radius whose value is $\frac{\hbar^2}{me^2}$ and which has units

$$\frac{erg^2 sec^2}{gram(dyne^{1/2}cm)^2}$$

which works out to be centimeters. The normalization integral for this wavefunction is

$$\int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ \Psi_{1s}^2 \to 1$$

which is

$$\int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ C^2 e^{-2\frac{Ame^2}{\hbar^2}R} \to 1$$

where we are using the "real" form of wavefunctions (and therefore avoiding complex conjugates). This value is chosen to force the probability of finding the electron somewhere we it is known that the electron inhabits this particular orbital, should be certainty. We know that we will choose the normalization constant, C, so that this integral has the value 1.

## III. UNITS

What are the units of C?
The integrand

$$C^2 e^{-2\frac{Ame^2}{\hbar^2}R} dXdYdZ$$

is supposed to be the probability of finding the electron within $dX$ of $X$, i.e., from $X$ to $X + dX$, within $dY$ of $Y$ and within $dZ$ of $Z$. Probabilities are dimensionless, so $C^2$ must have the units $\frac{1}{cm^3}$ to offset the units of dXdYdZ.

## IV. DOING THE INTEGRAL

Oddly enough, in doing the integral, we usually convert back to a form which looks suprisingly enough like the original dimensionless form we started with (but it isn't). We write

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C^2 e^{-2\frac{Zme^2}{\hbar^2}R} dXdYdZ$$

as

$$C^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\gamma R} dXdYdZ$$

Typeset by REVTEX

where $\gamma = 2\frac{Zme^2}{\hbar^2} = 2\frac{A}{a_0}$. Now, we can convert to spherical polar coördinates, and obtain

$$C^2 \int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta d\Theta \int_0^{\infty} dR e^{-\gamma R} R^2$$

which is

$$4\pi C^2 \int_0^{\infty} dR R^2 e^{-\gamma R} \rightarrow 1 \tag{3}$$

### A. Integral Review, trickery

We know that

$$\int dR \left( e^{-\gamma R} \rightarrow \frac{e^{-\gamma R}}{-\gamma} \right)$$

so the definite integral

$$\int_0^{\infty} dR \left( e^{-\gamma R} \right) \rightarrow \left. \frac{e^{-\gamma R}}{-\gamma} \right|_0^{\infty} \rightarrow \frac{1}{\gamma}$$

Further, we can take the derivative of this last equation with respect to $\gamma$ i.e.,

$$\frac{d \left\{ \int_0^{\infty} dR e^{-\gamma R} = \frac{1}{\gamma} \right\}}{d\gamma}$$

which is

$$\int_0^{\infty} dR \left( (-R) e^{-\gamma R} \right) = -\frac{1}{\gamma^2}$$

and we can do this again, i.e.,

$$\frac{d \left\{ \int_0^{\infty} dR \left( (-R) e^{-\gamma R} \right) = -\frac{1}{\gamma^2} \right\}}{d\gamma}$$

which yields

$$\int_0^{\infty} dR \left( (R^2) e^{-\gamma R} \right) = \frac{2}{\gamma^3}$$

which is almost Equation 3.

### B. Alternative Integration using Integration by Parts

Alternatively, we could write

$$\int_0^{\infty} R^2 e^{-\gamma R} dR = \int u dv$$

where $u = R^2$ and $dv = e^{-\gamma R} dR$, employing the standard

$$\frac{d(uv)}{dR} = v\frac{du}{dR} + u\frac{dv}{dR}$$

and multiplying by dR and integrating we would have

$$\int \frac{d(uv)}{dR} dR = \int d(uv) = \int v du + \int u dv$$

We then obtain

$$\int_0^{\infty} R^2 e^{-\gamma R} dR = R^2 \left. \frac{e^{-\gamma R}}{-\gamma} \right|_0^{\infty} - \int_0^{\infty} 2R \frac{e^{-\gamma R}}{-\gamma} dR$$

Since the first term on the r.h.s vanishes, we have

$$\int_0^{\infty} R^2 e^{-\gamma R} dR = \int_0^{\infty} 2R \frac{e^{-\gamma R}}{\gamma} dR$$

which can be integrated again by parts, this time defining u=R, to obtain

$$\int_0^{\infty} R^2 e^{-\gamma R} dR = \int_0^{\infty} 2R \frac{e^{-\gamma R}}{\gamma} dR = \frac{2}{\gamma} \left( R \left. \frac{e^{-\gamma R}}{\gamma} \right|_0^{\infty} + \int_0^{\infty} e^{-\gamma R} dR \right)$$

and again, the first term vanishes, yielding

$$\int_0^{\infty} R^2 e^{-\gamma R} dR = \frac{2}{\gamma^2} \left( \left. \frac{e^{-\gamma R}}{-\gamma} \right|_0^{\infty} \right) = \frac{2}{\gamma^3}$$

again.

## V. CONTINUING

Equation 3 now becomes

$$4\pi C^2 \frac{2}{\gamma^3} = 4\pi C^2 \frac{2}{\left( \frac{2A}{a_0} \right)^3} \rightarrow 1$$

so that, solving for $C^2$ we have

$$C^2 = \frac{\left( \frac{2A}{a_0} \right)^3}{8\pi} \tag{4}$$

so that

$$C = \sqrt{\frac{\left(\frac{2A}{a_0}\right)^3}{8\pi}} = \sqrt{\frac{\left(\frac{A}{a_0}\right)^3}{\pi}}$$

## VI. NORMALIZATION IN ATOMIC UNITS

We now return to the original question, which was, what is the normalization constant (c) when using atomic units? The normalization integral was

$$\int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dY \int_{-\infty}^{\infty} dZ C^2 e^{-2\frac{Ame^2}{\hbar^2}R} = 1 \qquad (5)$$

and we now define the coördinate transformation

$$x = \frac{Ame^2}{\hbar^2} X = \frac{A}{a_0} X$$

with similar equations for Y and Z ($r = \frac{Ame^2}{\hbar^2}R = \frac{A}{a_0}R$). Then

$$dx = \frac{Ame^2}{\hbar^2} dX = \frac{A}{a_0} dX$$

and therfore

$$dX = \frac{dx}{\frac{Ame^2}{\hbar^2}} = \frac{dX}{\frac{A}{a_0}}$$

so, dXdYdZ becomes

$$dXdYdZ = \left(\frac{\hbar^2}{Ame^2}\right)^3 dxdydz = \left(\frac{a_0}{A}\right)^3 dXdYdZ$$

making the integral (Equation 5)

$$\left(\frac{\hbar^2}{Ame^2}\right)^3 \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz C^2 e^{-2r} = 1$$

Then we have employing Equation 4's definition of $C^2$:

$$\left(\frac{a_0}{A}\right)^3 \left(\frac{A}{a_0}\right)^3 \frac{1}{\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz e^{-2r} = 1$$

or, cancelling,

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz e^{-2r} = \pi$$

which would be, in spherical polar coördinates:

$$4\pi \int_0^{\infty} R^2 dR e^{-2r} = \pi$$

(and, where $\gamma = 2$ now)

$$4\frac{2}{2^3} = 1$$

a tautology.

## VII. RETURNING TO THE BEGINNING

Finally, we have from Equation 2

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{\psi_{1s}^2\right\} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \left\{c^2 e^{-2Ar}\right\} \qquad (6)$$

which would be

$$4\pi c^2 \int_0^{\infty} r^2 dr e^{-2Ar}$$

which is

$$4\pi c^2 \frac{2}{(2A)^3}$$

and if we *force* this to be 1, we have

$$4\pi c^2 \frac{1}{4A^3} = 1$$

which says that

$$c = \sqrt{\frac{A^3}{\pi}}$$

which shows that the normalization constant's form depends on the initial choice of coördinate system.