The libint-eigen interface

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Contents

1 Terminology

In the LibInt2 basis set context, there is some terminology that should be cleared up. A (non-normalized) Cartesian *primitive Gaussian*, centered on $\mathbf{R}(X, Y, Z)$, is a function of the following form:

$$\varphi(\mathbf{r}; \zeta, \mathbf{n}, \mathbf{R}) = (x - X)^{n_x} (y - Y)^{n_y} (z - Z)^{n_z} \exp\bigl(-\zeta |\mathbf{r} - \mathbf{R}|^2\bigr) \,, \tag{1}$$

in which $\mathbf{n}(n_x, n_y, n_z)$ are called the cartesian angular momenta of the primitive. The sum

$$l = n_x + n_y + n_z \tag{2}$$

of the angular momenta, called the *angular momentum* of a primitive, determines its the type: $l = 0$ refers to an s-type, $l = 1$ to a p-type, etc. In general, there are[1]

$$\binom{l + 3 - 1}{3 - 1} = \frac{(l+1)(l+2)}{2} \tag{3}$$

primitives corresponding to a given angular momentum l. For example, the following primitives all belong to the case $l = 1$ (i.e. for p-type orbitals):

$$\varphi_{p_x}(\zeta) \qquad \varphi_{p_y}(\zeta) \qquad \varphi_{p_z}(\zeta) \,, \tag{4}$$

where we have introduced a short-hand notation for primitives: the exponents are given as arguments, the type is given as subscript, and the center is omitted (and to be deduced from context). For clarity:

$$\varphi_{p_x}(\zeta) \equiv \varphi(\mathbf{r}; \zeta, \mathbf{n} = (1, 0, 0), \mathbf{R}) = (x - X) \exp\bigl(-\zeta |\mathbf{r} - \mathbf{R}|^2\bigr) \,. \tag{5}$$

In the following, we will refer to a set of Gaussian primitives with the same angular momentum l that share the same center as a *shell*.

Often, a predetermined/fixed linear combination (also known as a *contraction*) of primitives is taken, leading to a *contracted GTO* (CGTO):

$$c_1 \varphi_s(\zeta_1) + c_2 \varphi_s(\zeta_2) \,, \tag{6}$$

in which the *contraction coefficients* c have to be specified. CGTOs are the functions that are used as *basis functions* (*atomic orbitals*: AOs). Note that a single primitive can also be used as a basis function, in which case the linear combination is just one times that primitive. A

[1]Number of ways to divide l balls in 3 urns: number of combinations with repetition

graphical explanation of the different concepts of primitives, CGTOs, basis functions and shells is given in Figure 1.

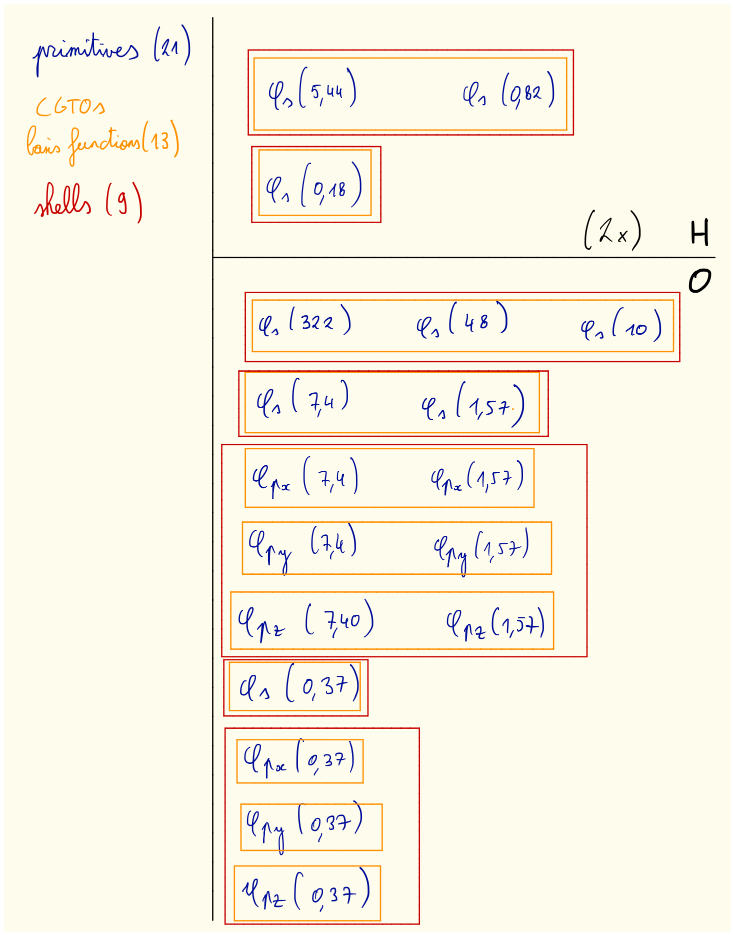


Figure 1: Explanation of the concepts of primitives, CGTOs (basis functions) and shells for water @ 3-21G. φ denotes a Gaussian primitive, its argument being the value of the exponent and its subscript specifying its angular momentum.

Molecular orbitals (MOs) are then written as a linear combination of AOs (which are CGTOs), which in turn serve as a one-electron basis to antisymmetrize into the many-electron basis of the *Slater determinants* (SDs). [1]

Internally, LibInt2 stores (normalized) contraction coefficients and exponents in `libint2::Shell` objects.

2 Are the basis functions (CGTOs) normalized?

When constructing a `libint2::BasisSet` object as in say

```
libint2::BasisSet obs ("STO-3G", atoms);

```

the corresponding file `sto-3g.g94` is read (which is located at your `LIBINT_DATA_PATH` environment variable), in which LibInt2 finds the exponents and contraction coefficients for the given basis for a given element.

In `libint2/basis.h`, we can see the following code (edited for brevity):

```
static ... read_g94_basis_library(...){
    ...
    ref_shells[Z].push_back(
        libint2::Shell{...}
        )
    ...
}

```

which calls a specific constructor of `libint2::Shell`:

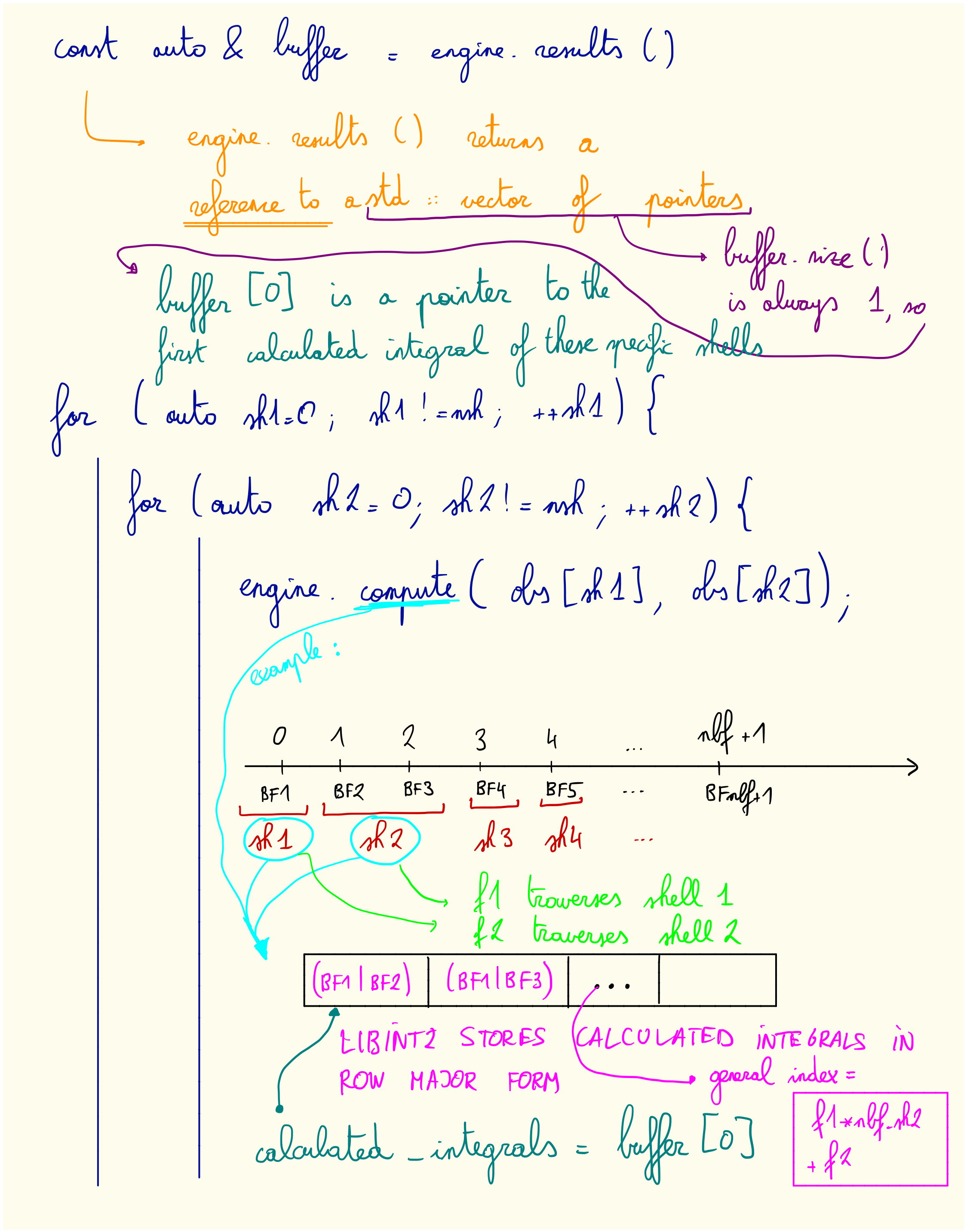
```
Shell(...) {
    // embed normalization factors into contraction
  coefficients
    renorm();
}

```

that makes sure that the CGTO is normalized by including the normalization factor in the contraction coefficients. So, **yes**, LibInt2 internally works with normalized basis functions.

3 Row major storing in `compute_1body()`

Figure 2 features the explanation of the row major storage of the calculated integrals.



```
const auto & buffer = engine.results()
for (auto sh1=0; sh1!=nsh; ++sh1) {
    for (auto sh2=0; sh2!=nsh; ++sh2) {
        engine.compute( obs[sh1], obs[sh2]);
        calculated_integrals = buffer[0]
```

engine.results() returns a reference to a std::vector of pointers

buffer.size() is always 1, so

buffer[0] is a pointer to the first calculated integral of these specific shells

LIBINT2 STORES CALCULATED INTEGRALS IN ROW MAJOR FORM

f1 traverses shell 1
f2 traverses shell 2

general index = $\boxed{f1*nbf\_sh2 + f2}$

Figure 2: Explanation of the function `compute_1body()`, featuring LibInt2's row major storage of the calculated integrals.

References

[1] F. Jensen. *Introduction to Computational Chemistry*. John Wiley & Sons, LTD, second edition, 2007.