Apendix: Remarks to the Vector Calculus

In physics and physical chemistry (and in this lecture) you can encounter a few conventions and tricks when using vectors. By a vector we usually understand a quantity that has a direction, or it can be a table of three (or more generally, *N*) numbers,

$$\mathbf{v} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}.$$

v_x, v_y, v_z are individual components of the vector **v**. Writing the numbers into a table („matrix") „3 × 1" (number of lines × number of columns) makes it possible to use matrix algebra. The exact form is not important, quite often one can see the „1 × 3" in line notation (v_x v_y v_z), etc. Very often the vector is written using an arrow above the letter, $\vec{v}$, perhaps more comfortable is just using bold letters, **v**.

An important operation is *the scalar product of two vectors* **u** and **v**,

$$\mathbf{u}\cdot\mathbf{v} = \mathbf{u}^t\mathbf{v} = \sum_{\alpha=1}^{3} u_\alpha v_\alpha = u_\alpha v_\alpha = u_x v_x + u_y v_y + u_z v_y = u_1 v_1 + u_2 v_2 + u_3 v_3 .$$

Above, we used five equivalent notations, which one can encounter: using the dot, matrix notation ($\mathbf{u}^t$ is the transpose matrix, in this case the bold print is somewhat redundant), an explicit sum, sum using the Einstein convention (index, occurring in a product just twice is summed over all its possible values) and the explicit list (the coordinates can be written as letters or numbers). Clearly, the scalar product is not vector anymore, but a number, scalar. The commutation gives the same thing, $\mathbf{u}\cdot\mathbf{v} = \mathbf{v}\cdot\mathbf{u}$. We also say that the dots marks *contraction of an index* (α in this case), then one dimension disappears, that is, we obtain the scalar from the vector.

The magnitude, length of a vector is $r = |\mathbf{r}|$ can thus be also written as $r = \sqrt{\mathbf{r}\cdot\mathbf{r}}$, and its square $r^2 = r_x^2 + r_y^2 + r_z^2$ can be written as $\mathbf{r}^2$.

On the other hand, *vector product of vectors* is a vector again, by convention the cross "×" is used for the multiplication:

$$\mathbf{w} = \mathbf{u}\times\mathbf{v}$$

Product components are $w_x = u_y v_z - u_z v_y$, $w_y = u_z v_x - u_x v_z$ a $w_z = u_x v_y - u_y v_x$. Note that $\mathbf{u}\times\mathbf{v} = -\mathbf{v}\times\mathbf{u}$. An alternate notation is $w_\alpha = \varepsilon_{\alpha\beta\gamma} u_\beta v_\gamma$. In the previous formula we again used the Einstein sum convention and the *Levi-Civita antisymmetric tensor* ε_{ijk}. ε_{ijk} is 1 for even and -1 for odd permutations of indices *ijk*, and 0 in case that two or more indices are equal. For example, $\varepsilon_{123} = 1$, $\varepsilon_{132} = \varepsilon_{321} = -1$, $\varepsilon_{133} = \varepsilon_{111} = 0$.

Relatively frequently can also be encountered a vector product again vector-multiplied by a vector. The result is a vector, and can be rewritten using the identity

$$\mathbf{a}\times(\mathbf{b}\times\mathbf{c}) = \mathbf{b}\,\mathbf{a}\cdot\mathbf{c} - \mathbf{c}\,\mathbf{a}\cdot\mathbf{b},$$

which some people remember phonetically as "bac - cab" or "first in the parenthesis scalar-multiplied by the other two minus second in the parenthesis scalar-multiplied by the other two ".

Another expression encountered, for example, when describing molecular electromagnetic properties, is a combined product, $\mathbf{a}\times\mathbf{b}\cdot\mathbf{c}$. We should immediately see that the result is a number, because vector $\mathbf{a}\times\mathbf{b}$ is scalar-multiplied by vector **c**. When developing this expression we can use the rule „cross and dot stay on place, while the vectors are cyclically permuted". That means that

$$\mathbf{a}\times\mathbf{b}\cdot\mathbf{c} = \mathbf{b}\times\mathbf{c}\cdot\mathbf{a} = \mathbf{c}\times\mathbf{a}\cdot\mathbf{b}, \text{ etc.}$$

Two **u** and **v** vectors can be linearly related, such as that $u_\alpha = a_{\alpha\beta} v_\beta$. The ensemble of nine coefficients $\{a_{\alpha\beta}\}$ can be called "3×3" matrix or *tensor of the second order (or rank)*, since it has two indices. Sometimes we can see notation using a double-arrow, $\vec{\vec{a}}$, in analogy to the vectors, but again it might be more practical just to print such objects in bold, as **a**. As for the vectors, we can use matrix notation here, $u = av$ or $\mathbf{u} = \mathbf{av}$, or use the "scalar" dot, $\mathbf{u} = \mathbf{a}\cdot\mathbf{v}$.

We can mention an inconsistency here because the expression $\mathbf{av}$ can be taken as a product of two matrices, but sometimes it may mean that a second rank tensor **a** is just standing in front of vector **v**. In the latter case the results is a third-order tensor containing 27 components, e.g.. $(\mathbf{av})_{\alpha\beta\gamma} = a_{\alpha\beta}v_\gamma$. Similarly, product of two vectors **ab** may be *vector dyad,* that is a second order tensor, $(\mathbf{ab})_{\alpha\beta} = a_\alpha b_\beta$, or somebody may understand it as a matrix multiplication, in this case **ab = a.b**, and we have a scalar product. It the latter case it would be clearer to write $\mathbf{a}^t\mathbf{b}$, but some texts omit these details. When the notation is consistent the meaning is usually clear from the context, nevertheless we mentioned the loopholes of the formalisms for entertainment and better understanding of the vector conventions.

Finally, knowledge of *differential operators* is necessary to understand many quantum chemical and other texts. Quite often, the names came from 19th century and the mechanics of continuum. *Gradient* of a variable dependent on coordinates **r** is increasing dimensionality of the object, for example gradient of a scalar potential $\varphi(\mathbf{r})$ is a vector, **G**:

$$\mathbf{G} = grad\ \varphi = \nabla\varphi \text{, or } G_\alpha = \frac{\partial\varphi}{\partial r_\alpha}.$$

The *Laplace operator* is formally scalar product of two gradients, and thus it is a scalar operator,

$$grad.grad\ \varphi = \nabla\cdot\nabla\varphi = \Delta\varphi = \sum_\alpha \frac{\partial^2\varphi}{\partial r_\alpha^2} = \frac{\partial^2\varphi}{\partial r_\alpha \partial r_\alpha} = \frac{\partial^2\varphi}{\partial r_x^2} + \frac{\partial^2\varphi}{\partial r_y^2} + \frac{\partial^2\varphi}{\partial r_z^2}.$$

The operator of *divergence* is a scalar, too, as it acts as a scalar product of gradient and a vector,

$$div\ \mathbf{a} = \nabla\cdot\mathbf{a} = \sum_\alpha \frac{\partial a_\alpha}{\partial r_\alpha} = \frac{\partial a_\alpha}{\partial r_\alpha} = \frac{\partial a_x}{\partial r_x} + \frac{\partial a_y}{\partial r_y} + \frac{\partial a_z}{\partial r_z}.$$

Note that $\nabla\mathbf{a}$ (without the dot) would be something fundamentally different, that is gradient of a vector, which is a second rank tensor.

Operator of the *rotation* is vector product of gradient and a vector, and the result must then be also a vector

$$rot\ \mathbf{a} = \nabla\times\mathbf{a}$$

of components $(\nabla\times\mathbf{a})_x = \frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z}$, $(\nabla\times\mathbf{a})_y = \frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x}$ a $(\nabla\times\mathbf{a})_z = \frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y}$, which can be abbreviated as $(\nabla\times\mathbf{a})_\alpha = \varepsilon_{\alpha\beta\gamma}\frac{\partial a_\gamma}{\partial r_\beta}$.

Using the differential operators the vector symbolic can be conveniently used, but we must also take into account the differential function of them, acting on a function to the right. A good example of this is the expression $\nabla\times(\mathbf{b}\times\mathbf{c})$. Using the rule „bac-cab“ blindly we get $\mathbf{b}\,\nabla\cdot\mathbf{c} - \mathbf{c}\,\nabla\cdot\mathbf{b}$, which would be correct for the vector transformation alone. However, the gradient still acts on both vectors **b** and **c**, and to get the derivatives right, we must rearrange the result as $\nabla\cdot\mathbf{c}\,\mathbf{b} - \nabla\cdot\mathbf{b}\,\mathbf{c}$.

The notation above can be sometimes extended to more complicated expressions, such as the (scalar) sum $\sum_\alpha\sum_\beta\sum_\gamma T_{\alpha\beta\gamma}a_\alpha b_\beta c_\gamma$ which could be (rarely) written as $\mathbf{T}\cdots\mathbf{abc}$, that is third rank tensor **T** (perhaps we can imagine it with three vector arrows above) is contracted with vectors **a**, **b** and **c**. Summation of each index was indicated by the dot. Of course, this is rather unusual and often a specialist may be lost in such texts. In any case, it belongs to good manners that the used convention and symbols in technical texts are clearly explained.

Exercise: Show that $\nabla\mathbf{r} = \mathbf{1}$, where $\mathbf{1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ is the unit tensor, and that $\nabla \cdot \mathbf{r} = 3$ and that $\nabla \times \mathbf{r} = \mathbf{0}$, where $\mathbf{0} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$. By the way, the units tensor components are $\delta_{\alpha\beta}$, which are known as *Kronecker's delta symbol* ($\delta_{\alpha\beta} = 1$ for $\alpha = \beta$, otherwise $\delta_{\alpha\beta} = 0$).

Exercise: Constant magnetic field is described by a field vector $\mathbf{B}_0$. Show that the corresponding vector potential is $\mathbf{A} = -\frac{1}{2}\mathbf{r} \times \mathbf{B}_0$ (remember that $\mathbf{B} = \nabla \times \mathbf{A}$).