K. DIAGONALIZATION OF A MATRIX

In quantum chemistry we often encounter the following mathematical problem.

We have a Hermitian[1] matrix $\boldsymbol{A}$ (of dimension n), i.e. $\boldsymbol{A}^\dagger = \boldsymbol{A}$, and are interested in all numbers λ (called "eigenvalues"[2]) and the corresponding column vectors ("eigenvectors" of dimension n) $\boldsymbol{L}$, that satisfy the following equation

$$(\boldsymbol{A} - \lambda \mathbf{1})\boldsymbol{L} = \mathbf{0}, \tag{K.1}$$

where $\mathbf{1}$ is the unit matrix (of dimension n). There are n solutions to the last equation: n eigenvalues of λ and also n eigenvectors $\boldsymbol{L}$. Some eigenvalues λ may be equal (degeneracy), i.e. two or more linearly independent eigenvectors $\boldsymbol{L}$ correspond to a single eigenvalue λ. From (K.1) it is shown that any vector $\boldsymbol{L}$ is determined only to the accuracy of a multiplicative factor.[3] This is why, in future, there will be justification for normalizing them to unity.

In quantum chemistry the eigenvalue problem is solved in two ways: one is easy for $n \leqslant 2$, but more and more difficult for larger n, the second (using computers) treats all cases uniformly.

- The first way sees the eigenvalue equation as a set of linear homogeneous equations for the unknown components of vector $\boldsymbol{L}$. Then the condition for the nontrivial solution[4] to exist is: $\det(\boldsymbol{A} - \lambda \mathbf{1}) = 0$. This condition can be fulfilled only for some particular values of λ, which are to be found by expanding the determinant and solving the resulting n-th degree polynomial equation for λ. Then each solution λ is inserted into eq. (K.1) and the components of the corresponding vector $\boldsymbol{L}$ are found using any method applicable to linear equations. Thus, we end up with λ_k and $\boldsymbol{L}_k$ for $k = 1, 2, 3, \ldots, n$.
- The second way is based on diagonalization of $\boldsymbol{A}$.

First, let us show that *the same* λ's satisfy the eigenvalue equation (K.1), but with a much simpler matrix. To this end let us multiply (K.1) by (at the moment)

[1] In practice, matrix $\boldsymbol{A}$ is usually real, and therefore satisfies $(\boldsymbol{A}^T)^* = \boldsymbol{A}^T = \boldsymbol{A}$, i.e. $\boldsymbol{A}$ is symmetric.

[2] They are real.

[3] In other words, a unnormalized wave function still satisfies the Schrödinger equation, or an arbitrary amplitude can be assigned to any normal mode.

[4] The trivial one is obviously $\boldsymbol{L} = \mathbf{0}$, which is however unacceptable, since the wave function cannot vanish everywhere, or atoms have to vibrate, etc.

the *arbitrary* non-singular[5] square matrix[6] $\boldsymbol{B}$. We obtain the following chain of transformations $\boldsymbol{B}^{-1}(\boldsymbol{A}-\lambda\mathbf{1})\boldsymbol{L}=\boldsymbol{B}^{-1}(\boldsymbol{A}\boldsymbol{B}\boldsymbol{B}^{-1}-\lambda\mathbf{1})\boldsymbol{L}=(\boldsymbol{B}^{-1}\boldsymbol{A}\boldsymbol{B}-\lambda\mathbf{1})\boldsymbol{B}^{-1}\boldsymbol{L}=(\tilde{\boldsymbol{A}}-\lambda\mathbf{1})\tilde{\boldsymbol{L}}=\mathbf{0}$, where[7] $\tilde{\boldsymbol{A}}=\boldsymbol{B}^{-1}\boldsymbol{A}\boldsymbol{B}$, and $\tilde{\boldsymbol{L}}=\boldsymbol{B}^{-1}\boldsymbol{L}$. Thus, another matrix and other eigenvectors, but *the same* λ's! Now, let us choose such a special $\boldsymbol{B}$ so as to have the resulting equation as simple as possible, i.e. with a diagonal $\tilde{\boldsymbol{A}}$. Then we will know,[8] what the λ values have to be in order to satisfy the equation $(\tilde{\boldsymbol{A}}-\lambda\mathbf{1})\tilde{\boldsymbol{L}}=\mathbf{0}$.

Indeed, if $\tilde{\boldsymbol{A}}$ were diagonal, then

$$\det(\tilde{\boldsymbol{A}}-\lambda\mathbf{1})=\prod_{k=1}^{n}(\tilde{A}_{kk}-\lambda)=0,$$

which gives the solution $\lambda_k=\tilde{A}_{kk}$. Then, it is easy to find the corresponding vector $\tilde{\boldsymbol{L}}_k$. For example, $\tilde{\boldsymbol{L}}_1$ we find from equation $(\tilde{\boldsymbol{A}}-\lambda_1\mathbf{1})\tilde{\boldsymbol{L}}_1=\mathbf{0}$ in the following way:[9]

$$\begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & \tilde{A}_{22}-\lambda_1 & 0 & \dots & 0 \\ 0 & 0 & \tilde{A}_{33}-\lambda_1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \tilde{A}_{nn}-\lambda_1 \end{pmatrix} \begin{pmatrix} \tilde{L}_{1,1} \\ \tilde{L}_{1,2} \\ \tilde{L}_{1,3} \\ \dots \\ \tilde{L}_{1,n} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix},$$

which means that to get $\mathbf{0}$ on the right side, we have to have an *arbitrary* $\tilde{L}_{1,1}$, while the other $\tilde{L}_{1,j}=0$ for $j=2,3,\dots,n$.

To have the length of $\tilde{\boldsymbol{L}}_1$ equal to 1, it is sufficient to put $\tilde{L}_{1,1}=1$. Similarly, we easily find that the vectors $\tilde{\boldsymbol{L}}_k$ corresponding to λ_k simply represent the column vectors with all components equal to 0 except component k, which equals 1. We are interested in vectors $\boldsymbol{L}$, rather than $\tilde{\boldsymbol{L}}$. We get these vectors from $\boldsymbol{L}=\boldsymbol{B}\tilde{\boldsymbol{L}}$, and taking into account the form of $\tilde{\boldsymbol{L}}$, this means that $\boldsymbol{L}_k$ is nothing else but the k-th column of matrix $\boldsymbol{B}$. Since $\boldsymbol{B}$ is known, because this is precisely the matrix which led to the diagonalization, there is therefore no problem with $\boldsymbol{L}$:

> the columns of $\boldsymbol{B}$ represent the eigenvectors $\boldsymbol{L}$ of the equation $(\boldsymbol{A}-\lambda\mathbf{1})\boldsymbol{L}=\mathbf{0}$.

This is it.

[5] That is, its inverse matrix exists.

[6] To be found.

[7] Such a *unitary matrix* $\boldsymbol{B}$ (i.e. satisfying $(\boldsymbol{B}^T)^*=\boldsymbol{B}^{-1}$) can be found, that $\boldsymbol{B}^{-1}\boldsymbol{A}\boldsymbol{B}$ is *real and diagonal*. When (as is the case in most applications) we have to do with real matrices, then instead of unitary and Hermitian matrices, we have to do with orthogonal and symmetric matrices, respectively.

[8] Just by looking.

[9] The λ has been replaced by λ_1, because we are interested in getting $\tilde{\boldsymbol{L}}_1$.