L. SECULAR EQUATION $(H - \varepsilon S)c = 0$

A typical ε approach for solving an eigenvalue problem is its "algebraization", i.e. representation of the wave function as a linear combination of the known basis functions with the unknown coefficients. Then instead of searching for a function, we try to find the expansion coefficients $\boldsymbol{c}$ from the secular equation[1] $(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = 0$. Our goal is to reduce this task to the eigenvalue problem of a matrix. If the basis set used is orthonormal, the goal would be immediately achieved, because the secular equation would be reduced to $(\boldsymbol{H} - \varepsilon \mathbf{1})\boldsymbol{c} = 0$, i.e. the eigenvalue problem. However, in most cases the basis set used is not orthonormal. We may, however, orthonormalize the basis. We will achieve this using symmetric orthogonalization (see Appendix J, p. 977).

Instead of the old basis set (collected in the vector $\boldsymbol{\phi}$), in which the matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ were calculated: $H_{ij} = \langle \phi_i | \hat{H} \phi_j \rangle$, $S_{ij} = \langle \phi_i | \phi_j \rangle$ we will use the orthogonal basis set $\boldsymbol{\phi}' = \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{\phi}$, where $\boldsymbol{S}^{-\frac{1}{2}}$ is calculated as described in Appendix J. Then we multiply the secular equation $(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = \mathbf{0}$ from the left by $\boldsymbol{S}^{-\frac{1}{2}}$ and make the following transformations

$$
\begin{aligned}
\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right)\boldsymbol{c} &= 0, \\
\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \mathbf{1} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right)\boldsymbol{c} &= 0, \\
\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}^{\frac{1}{2}} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right)\boldsymbol{c} &= 0, \\
\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}^{\frac{1}{2}} - \varepsilon \boldsymbol{S}^{\frac{1}{2}}\right)\boldsymbol{c} &= 0, \\
\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} - \varepsilon \mathbf{1}\right)\boldsymbol{S}^{\frac{1}{2}} \boldsymbol{c} &= 0, \\
\left(\tilde{\boldsymbol{H}} - \varepsilon \mathbf{1}\right)\tilde{\boldsymbol{c}} &= 0
\end{aligned}
$$

with $\tilde{\boldsymbol{H}} = \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}}$ and $\tilde{\boldsymbol{c}} = \boldsymbol{S}^{\frac{1}{2}} \boldsymbol{c}$.

The new equation represents the eigenvalue problem, which we solve by diagonalization of $\tilde{\boldsymbol{H}}$ (Appendix K, p. 982). Thus,

> the equation $(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = \mathbf{0}$ is equivalent to the eigenvalue problem $(\tilde{\boldsymbol{H}} - \varepsilon \mathbf{1})\tilde{\boldsymbol{c}} = \mathbf{0}$. To obtain $\tilde{\boldsymbol{H}}$, we have to diagonalize $\boldsymbol{S}$ to calculate $\boldsymbol{S}^{\frac{1}{2}}$ and $\boldsymbol{S}^{-\frac{1}{2}}$.

[1] See Chapter 5.

Secular equation and normalization

If we used non-normalized basis functions in the Ritz method, this would not change the eigenvalues obtained from the secular equation. The only thing that would change are the eigenvectors. Indeed, imagine we have solved the secular equation for the normalized basis set functions: $(\boldsymbol{H} - \varepsilon \boldsymbol{S})\boldsymbol{c} = \boldsymbol{0}$. The eigenvalues ε have been obtained from the secular determinant $\det(\boldsymbol{H} - \varepsilon \boldsymbol{S}) = 0$. Now we wish to destroy the normalization and take new basis functions, which are the old basis set functions multiplied by some numbers, the i-th function by a_i. Then a new overlap integral and the corresponding matrix element of the Hamiltonian $\hat{H}$ would be $S'_{ij} = a_i a_j S_{ij}$, $H'_{ij} = a_i a_j H_{ij}$. The new secular determinant $\det(\boldsymbol{H}' - \varepsilon \boldsymbol{S}')$ may be expressed by the old secular determinant times a number.[2] This number is irrelevant, since what matters is that the determinant is equal to 0. Thus, whether in the secular equation we use the normalized basis set or not, the eigenvalues do not change. The eigenfunctions are also identical, although the eigenvectors $\boldsymbol{c}$ are different – they have to be, because they multiply different functions (which are proportional to each other).

If we ask whether the eigenvalues of the matrices $\boldsymbol{H}$ are $\boldsymbol{H}'$ identical, the answer would be: no.[3] However, in quantum chemistry we do not calculate the eigenvalues[4] of $\boldsymbol{H}$, but solve the secular equation $(\boldsymbol{H}' - \varepsilon \boldsymbol{S}')\boldsymbol{c} = \boldsymbol{0}$. If $\boldsymbol{H}'$ changes with respect to $\boldsymbol{H}$, there is a corresponding change of $\boldsymbol{S}'$ when compared to $\boldsymbol{S}$. This guarantees that the ε's do not change.

[2] We divide the new determinant by a_1, which means dividing the elements of the first row by a_1 and in this way removing from them a_1, both in $\boldsymbol{H}'$ and in $\boldsymbol{S}'$. Doing the same with a_2 and the second row, etc., and then repeating the procedure for columns (instead of rows), we finally get the old determinant times a number.

[3] This is evident, just think of diagonal matrices.

[4] Although we often say it this way.