APPENDIX L

Secular Equation $(H - \varepsilon S)\, c = 0$

A typical approach to solve an eigenvalue problem is its "*algebraization*"; i.e., a 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 (see Chapter 5) $\left(\boldsymbol{H} - \varepsilon \boldsymbol{S}\right) \boldsymbol{c} = \boldsymbol{0}$. Our goal is to reduce this task to the eigenvalue problem of a matrix. If the basis set used were orthonormal, then the goal would be immediately achieved because the secular equation would be reduced to $\left(\boldsymbol{H} - \varepsilon \boldsymbol{1}\right) \boldsymbol{c} = \boldsymbol{0}$ (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 by using the symmetric orthogonalization (see Appendix J available at booksite.elsevier.com/978-0-444-59436-5, p. e99).

Instead of the old basis set (collected in the vector $\boldsymbol{\phi}$), in which the matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ were calculated as $H_{ij} = \left\langle \phi_i | \hat{H} \phi_j \right\rangle$, $S_{ij} = \langle \phi_i | \phi_j \rangle$, we will use the orthogonal basis set $\boldsymbol{\phi}' = \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{\phi}$, where $\boldsymbol{S}^{-\frac{1}{2}}$ is computed as described in Appendix J available at booksite.elsevier.com/978-0-444-59436-5. Then, we multiply the secular equation $\left(\boldsymbol{H} - \varepsilon \boldsymbol{S}\right) \boldsymbol{c} = \boldsymbol{0}$ from the left side by $\boldsymbol{S}^{-\frac{1}{2}}$ and make the following transformations:

$$\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right) \boldsymbol{c} = 0$$
$$\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{1} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right) \boldsymbol{c} = 0$$
$$\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}^{\frac{1}{2}} - \varepsilon \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}\right) \boldsymbol{c} = 0$$
$$\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{S}^{\frac{1}{2}} - \varepsilon \boldsymbol{S}^{\frac{1}{2}}\right) \boldsymbol{c} = 0$$
$$\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{H} \boldsymbol{S}^{-\frac{1}{2}} - \varepsilon \boldsymbol{1}\right) \boldsymbol{S}^{\frac{1}{2}} \boldsymbol{c} = 0$$
$$\left(\tilde{\boldsymbol{H}} - \varepsilon \boldsymbol{1}\right) \tilde{\boldsymbol{c}} = 0$$

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 $\tilde{\boldsymbol{H}}$ (see Appendix K available at booksite.elsevier.com/978-0-444-59436-5, p. e105). Thus,

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

Secular Equation and Normalization

If in the Ritz method we used non-normalized basis functions, then this would not change the eigenvalues obtained from the secular equation. The only thing that would change are eigenvectors. Indeed, imagine that we have solved the secular equation for the normalized basis set functions: $\left(\boldsymbol{H} - \varepsilon \boldsymbol{S}\right)\boldsymbol{c} = \mathbf{0}$. The eigenvalues ε have been obtained from the secular determinant $\det\left(\boldsymbol{H} - \varepsilon \boldsymbol{S}\right) = 0$. Now, one wishes to destroy the normalization and takes new basis functions, which are the old basis set functions multiplied by some numbers, the ith 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 $\det\left(\boldsymbol{H}' - \varepsilon \boldsymbol{S}'\right)$ may be expressed by the old secular determinant times a number.[1] This number is irrelevant since what matters is that the determinant is equal to 0. Thus, whether or not we use the normalized basis set in the secular equation the eigenvalues do not change. The eigenfunctions are also identical, although the eigenvectors $\boldsymbol{c}$ are different–they need to be because they multiply different functions (that are proportional to each other).

If we asked whether the eigenvalues of the matrices $\boldsymbol{H}$ are $\boldsymbol{H}'$ identical, the answer would be no.[2] However, in quantum chemistry, we do not calculate the eigenvalues[3] of $\boldsymbol{H}$, but rather solve the secular equation $\left(\boldsymbol{H}' - \varepsilon \boldsymbol{S}'\right)\boldsymbol{c} = \mathbf{0}$. If $\boldsymbol{H}'$ changes with respect to $\boldsymbol{H}$, then there is a corresponding change of $\boldsymbol{S}'$ when compared to $\boldsymbol{S}$. This guarantees that the εs do not change.

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

2 This is evident–just think of diagonal matrices.

3 Although we often say that way.