

Lecture 24 Supplement: General Eigenvalue Problem for LCAO-MO Expressed in Matrix Notation[‡]

In order to solve for the R_{AB} -dependent LCAO-MO electronic energy and electronic wavefunctions we must solve a “Generalized Eigenvalue Equation” (see page 8 of Lecture Notes #24). For a 2-AO LCAO-MO problem, we must solve

$$\begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{\text{avg}} \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

This corresponds to two linear homogeneous equations in two unknowns, c_1 and c_2 . (Note that, for this 2 AO variational function, the Hamiltonian matrix is

$$\mathbf{H} = \begin{pmatrix} \varepsilon & V_{12} \\ V_{12} & \varepsilon \end{pmatrix}$$

and the overlap matrix is

$$\mathbf{S} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix}.)$$

This type of equation is more widely applicable. You can use $N \gg 2$ AO's in the variational determination of the lowest E_{avg} . The condition for a non-trivial (“trivial” means all $c_i = 0$) solution is that the numerical value of the determinant of the coefficients of the $\{c_i\}$ must be zero. In other words, the determinant of $\mathbf{H} - E_{\text{avg}}\mathbf{S}$ is zero. This condition is satisfied by varying E_{avg} . For an N -state variational basis set, there are N values of E_{avg} that satisfy this $\det(\mathbf{H} - E_{\text{avg}}\mathbf{S}) = 0$ condition, because \mathbf{H} and \mathbf{S} are $N \times N$ matrices when we are working with N AOs in the basis set. We actually want to know all N of these values of E_{avg} (not merely the smallest one) and the set of $\{c_i\}$ that is generated for *each value* of E_{avg} . Each value of E_{avg} corresponds to the variational best energy of a particular MO (and the corresponding set of $\{c_i\}$ represents this MO in the AO basis set), thus we see that we recover N MOs from N AOs, a result that you might remember from 5.111/2.

[‡]The acronyms employed here are widely used: AO = Atomic Orbitals, LCAO = Linear Combination of Atomic Orbitals, MO = Molecular Orbitals.

The **Generalized Eigenvalue Equation** may be expressed in matrix form

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c}.$$

You know how to construct both \mathbf{H} and \mathbf{S} from AO's centered at R_A and R_B . You need the atomic orbital energies along the diagonal of \mathbf{H} and the values of the atom-A, atom-B 1-electron interaction energies in the off-diagonal position:

$$\begin{array}{ll} \text{Diagonal} & H_{nl_A, nl_A} = \varepsilon_{nl}(R) = \varepsilon_{nl}^{(0)} + \varepsilon'_{nl}(R) \\ \text{Off-Diagonal} & H_{nl_A, nl_B} = V_{nl_A, nl_B}. \end{array}$$

Non-Lecture

$$\begin{aligned} H_{nl_A, nl_A} &= \varepsilon_{nl}^{(0)} + \varepsilon'_{nl}(R) \\ \varepsilon'_{nl} &\equiv \int nl_A(r) \frac{1}{|\mathbf{R}_B - \hat{\mathbf{r}}|} nl_A(r) dr \end{aligned}$$

where $\varepsilon_{nl}^{(0)}$ is the eigen-energy of an electron in the nl orbital centered on nucleus A . This orbital is an eigenfunction of the hydrogen atom one-electron Hamiltonian

$$\mathbf{h}_A = \frac{-\nabla_r^2}{2} - \frac{1}{|\mathbf{R}_A - \hat{\mathbf{r}}|}.$$

$\varepsilon'_{nl}(R)$ is the energy associated with an electron in the nl orbital centered on nucleus A interacting with nucleus B at a distance R from nucleus A . Also included in $\varepsilon'_{nl}(R)$ is the energy of repulsion between nuclei A and B . Note that $\varepsilon'_{nl} \rightarrow 0$ as $R \rightarrow \infty$ and $\varepsilon'_{nl} \rightarrow \infty$ as $R \rightarrow 0$.

Rigorously, you should include interaction terms off-diagonal in nl , but these are often neglected (especially for homonuclear diatomic molecules) as a convenient approximation. However, same-atom off-diagonal terms like $H_{nl_A, n'l'_A}$ are *rigorously* zero because the nl_A and $n'l'_A$ AO's are eigenfunctions of their respective 1- e^- Hamiltonian. You also know how to construct the \mathbf{S} matrix

$$\begin{array}{ll} S_{nl_A, nl_A} = 1 & \text{(independent of } R) \\ S_{nl_A, n'l'_A} = 0 & \text{(independent of } R) \\ S_{nl_A, nl_B} \neq 0 & \text{(} R\text{-dependent)} \end{array}$$

Note that the atom A and atom B basis functions are respectively two sets of orthonormal AO's. So how do we solve

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0$$

when \mathbf{S} is *not* the identity matrix?

\mathbf{S} is a real, symmetric matrix. There must exist a unitary transformation that diagonalizes \mathbf{S}

$$\mathbf{U}\mathbf{S}\mathbf{U}^\dagger = \begin{pmatrix} S_1 & 0 & 0 & 0 \\ 0 & S_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & S_N \end{pmatrix} = \tilde{\mathbf{S}}$$

where the S_i along the diagonal of $\tilde{\mathbf{S}}$ are the eigenvalues of \mathbf{S} . This diagonal matrix, $\tilde{\mathbf{S}}$, can be converted into the identity matrix (all 1's along the diagonal) by the following transformation:

$$(\tilde{\mathbf{S}})^{-1/2}\mathbf{U}\mathbf{S}\mathbf{U}^\dagger(\tilde{\mathbf{S}})^{-1/2} = \mathbf{1}.$$

This transforms all of the basis functions into an *orthonormal* set of functions.

You might find it strange to think about a mathematical function of a matrix. For $\tilde{\mathbf{S}}$, which is a diagonal matrix, it is trivial to compute $\tilde{\mathbf{S}}^{1/2}$ by taking the square root of the only non-zero elements of $\tilde{\mathbf{S}}$, which all lie along the diagonal of $\tilde{\mathbf{S}}$. For a non-diagonal symmetric or Hermitian matrix, \mathbf{A} , it is possible to compute any $\mathbf{f}(\mathbf{A})$ as follows:

1. Diagonalize \mathbf{A} : $\mathbf{T}\mathbf{A}\mathbf{T}^\dagger = \tilde{\mathbf{A}}$.

2. Compute $\mathbf{f}(\tilde{\mathbf{A}})$ as

$$\mathbf{f}(\tilde{\mathbf{A}}) = \begin{pmatrix} f(A_1) & 0 & 0 & 0 \\ 0 & f(A_2) & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & f(A_N) \end{pmatrix}.$$

3. Transform $\mathbf{f}(\tilde{\mathbf{A}})$ back to the original basis set

$$\mathbf{T}^\dagger\mathbf{f}(\tilde{\mathbf{A}})\mathbf{T} = \mathbf{T}^\dagger\mathbf{f}(\mathbf{A})\mathbf{T}.$$

By definition, for a unitary matrix

$$\mathbf{U}^\dagger = \mathbf{U}^{-1}$$

so

$$\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}.$$

Also

$$\tilde{\mathbf{S}}^{-1/2} \tilde{\mathbf{S}}^{1/2} = \mathbf{1}.$$

Thus

$$\mathbf{U}^\dagger \tilde{\mathbf{S}}^{-1/2} \tilde{\mathbf{S}}^{1/2} \mathbf{U} = \mathbf{1}.$$

We now insert this very useful combination of matrices between the matrix $(\mathbf{H} - E\mathbf{S})$ and the vector \mathbf{c} and then multiply on the left by $\tilde{\mathbf{S}}^{-1/2} \mathbf{U}$

$$\tilde{\mathbf{S}}^{-1/2} \mathbf{U} (\mathbf{H} - E\mathbf{S}) \mathbf{U}^\dagger \tilde{\mathbf{S}}^{-1/2} \tilde{\mathbf{S}}^{1/2} \mathbf{U} \mathbf{c} = 0.$$

Now define $\tilde{\mathbf{H}}$ as

$$\tilde{\mathbf{H}} = \tilde{\mathbf{S}}^{-1/2} \mathbf{U} \mathbf{H} \mathbf{U}^\dagger \tilde{\mathbf{S}}^{-1/2}$$

and define $\tilde{\mathbf{c}}$ as

$$\tilde{\mathbf{c}} = \tilde{\mathbf{S}}^{1/2} \mathbf{U} \mathbf{c}.$$

Now put it all together and call $|\tilde{\mathbf{H}} - E\mathbf{1}|$ the “*secular determinant*”

$$(\tilde{\mathbf{H}} - E\mathbf{1})\tilde{\mathbf{c}} = 0.$$

Now we must solve for the zeroes of the secular determinant. This is the usual form of the secular equation. This procedure is equivalent to diagonalizing $\tilde{\mathbf{H}}$ to find the eigenvalues of $\tilde{\mathbf{H}}$. $\tilde{\mathbf{H}}$ is merely the original LCAO-MO Hamiltonian transformed into an orthonormal basis set. Let \mathbf{T} be a unitary matrix that diagonalizes $\tilde{\mathbf{H}}$

$$\mathbf{T} \tilde{\mathbf{H}} \mathbf{T}^\dagger = \tilde{\tilde{\mathbf{H}}} = \begin{pmatrix} E_1 & 0 & 0 & 0 \\ 0 & E_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & E_N \end{pmatrix}.$$

Now insert $\mathbf{T}^\dagger \mathbf{T} = \mathbf{1}$ between $(\tilde{\mathbf{H}} - E\mathbf{1})$ and $\tilde{\mathbf{c}}$ and multiply on the left by \mathbf{T} and we have the desired final result

$$\begin{aligned} \mathbf{T}(\tilde{\mathbf{H}} - E\mathbf{1})\mathbf{T}^\dagger \mathbf{T} \tilde{\mathbf{c}} &= \\ (\tilde{\tilde{\mathbf{H}}} - E\mathbf{1})\tilde{\tilde{\mathbf{c}}} &= 0 \end{aligned}$$

where

$$\begin{aligned}\tilde{\mathbf{c}} &= \mathbf{T}\mathbf{c} = \mathbf{T}\tilde{\mathbf{S}}^{1/2}\mathbf{U}\mathbf{c} \\ \tilde{c}_i &= \sum_j \sum_k \sum_\ell T_{ij} \tilde{S}_{jj}^{1/2} U_{jk} c_k \\ c_k &= \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ j \end{pmatrix} \leftarrow k\text{-th position}\end{aligned}$$

Let

$$\begin{aligned}\mathbf{R} &= \mathbf{T}\tilde{\mathbf{S}}^{1/2}\mathbf{U} \\ \tilde{c}_i &= \sum_j R_{ij} c_j\end{aligned}$$

which means that the i -th eigenvector, expressed in the original LCAO-MO basis set, is the i -th row of \mathbf{R} . \tilde{c}_i is the eigenvector that corresponds to the i -th eigenvalue of $\tilde{\mathbf{H}}$.

MIT OpenCourseWare
<https://ocw.mit.edu/>

5.61 Physical Chemistry
Fall 2017

For information about citing these materials or our Terms of Use, visit: <https://ocw.mit.edu/terms>.