

Chem237: Lecture 14

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WORK IN PROGRESS We have talked about linear transformations that consist of taking some general matrix $\mathbf{A} \in \mathbb{C}$ and having it act on a vector \vec{x} to create a new vector \vec{b} , i.e.

$$\mathbf{A}\vec{x} = \vec{b}. \quad (1)$$

In situations where the matrix multiplication results in the same vector multiplied by a scalar, we call it an eigenvalue problem,

$$\mathbf{A}\vec{x} = \lambda\vec{x}. \quad (2)$$

In this case, we call \vec{x} an eigenvector of \mathbf{A} , and λ is an eigenvalue of \mathbf{A} . The scalar λ is only an eigenvalue of \mathbf{A} if $\mathbf{A} - \lambda\mathbf{I}$ is singular. This idea can be seen more clearly by manipulating equation (2).

$$\mathbf{A}\vec{x} = \lambda\vec{x} \implies \mathbf{A}\vec{x} - \lambda\vec{x} = \mathbf{0} \implies (\mathbf{A} - \lambda\mathbf{I})\vec{x} = \mathbf{0} \quad (3)$$

Notice how we multiplied λ by the identity matrix because we cannot subtract a scalar from a matrix. If we were to multiply both sides by $(\mathbf{A} - \lambda\mathbf{I})^{-1}$, then we would be left with the trivial solution that $x_i = 0$ for all i . So what we'll do is impose the idea that $(\mathbf{A} - \lambda\mathbf{I})$ does not have an inverse. This means that the determinant of $(\mathbf{A} - \lambda\mathbf{I})$ must be equal to 0. Recall that noninvertible or **singular** matrices must have a determinant equal to 0. This allows us to write

$$\det(\mathbf{A} - \lambda\mathbf{I}) = 0 \quad (4)$$

and it has two names: the **characteristic equation** and the **secular equation**. Since we already used "characteristic polynomial" in Lecture 1 for solving homogenous ODEs, we will call the above equation the secular equation. The secular equation is a polynomial of degree N where N is the dimensionality of \mathbf{A} . How do we know there will always be N eigenvalues? Let's consider a matrix $\mathbf{A} \in \mathbb{R}^3$, and write out the determinant explicitly

$$\det \begin{bmatrix} A_{11} - \lambda & A_{12} & A_{13} \\ A_{21} & A_{22} - \lambda & A_{23} \\ A_{31} & A_{32} & A_{33} - \lambda \end{bmatrix} \quad (5)$$

so we can make use of the technique called **determinant expansion by minors**. We can pick any row or column for this technique and we'll choose to go along the first row for no particular reason. Therefore, the expansion becomes,

$$\det(\mathbf{A} - \lambda\mathbf{I}) = (A_{11} - \lambda)\det \begin{bmatrix} A_{22} - \lambda & A_{23} \\ A_{32} & A_{33} - \lambda \end{bmatrix} - (A_{12})\det \begin{bmatrix} A_{21} & A_{23} \\ A_{31} & A_{33} - \lambda \end{bmatrix} + (A_{13})\det \begin{bmatrix} A_{21} & A_{22} - \lambda \\ A_{31} & A_{32} \end{bmatrix} \quad (6)$$

When we write out the remaining three determinants,

$$\begin{aligned} \det(\mathbf{A} - \lambda\mathbf{I}) &= (A_{11} - \lambda) \left[(A_{22} - \lambda)(A_{33} - \lambda) - (A_{32})(A_{23}) \right] - (A_{12}) \left[(A_{21})(A_{33} - \lambda) - (A_{31})(A_{23}) \right] \\ &\quad + (A_{13}) \left[(A_{21})(A_{32}) - (A_{31})(A_{22} - \lambda) \right] = 0 \end{aligned} \quad (7)$$

we can see that the result is a polynomial of degree 3 in λ since each matrix element is a scalar. This same technique can be used to show that an $N \times N$ matrix can yield a secular equation with N roots and thus N complex eigenvalues, assuming that the matrix itself is complex. The technique for finding the i th eigenvector corresponding to the i th eigenvalue is to solve equation 3 by plugging in λ_i and solving for \vec{x} . Once we have found the eigenvalues and eigenvectors of \mathbf{A} , we can write the eigendecomposition of \mathbf{A} ; a very useful technique that is used a lot in chemistry and physics.

$$\mathbf{A} = \mathbf{X}\mathbf{\Lambda}\mathbf{X}^{-1} \quad (8)$$

Here, \mathbf{X} is an $N \times N$ matrix where each column is an eigenvector of \mathbf{A} ,

$$\mathbf{X} = [\vec{x}_1 \quad \vec{x}_2 \quad \cdots \quad \vec{x}_N] \quad (9)$$

and Λ is a diagonal matrix where the i th diagonal element corresponds to the eigenvalue in the i th column of \mathbf{X} .

$$\Lambda = \begin{bmatrix} \lambda_1 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & \lambda_N \end{bmatrix} \quad (10)$$

You will often find people in literature introducing eigendecomposition as finding a matrix \mathbf{X} that diagonalizes \mathbf{A} . This is because any matrix written in the basis of its eigenvectors results in a diagonal matrix of its eigenvalues. To see this, we can left multiply equation (8) by \mathbf{X}^{-1} and right multiply by \mathbf{X} to get Λ in the basis of its eigenvectors.

$$\Lambda = \mathbf{X}^{-1} \mathbf{A} \mathbf{X} \quad (11)$$

A special case to consider is when our matrix \mathbf{A} is hermitian. In this case, $\mathbf{A} = \mathbf{A}^\dagger$ where \dagger denotes the conjugate transpose. One property of hermitian matrices is that the eigenvalues are all real. To prove this, consider equation (2) for a hermitian matrix \mathbf{A} .

$$\mathbf{A} \vec{x} = \lambda \vec{x} \quad (12)$$

Left multiplying by \vec{x}^\dagger gives

$$\begin{aligned} \vec{x}^\dagger \mathbf{A} \vec{x} &= \vec{x}^\dagger \lambda \vec{x} \\ &= \lambda \vec{x}^\dagger \vec{x} \\ &= \lambda |\vec{x}|^2 \end{aligned} \quad (13)$$

where $|\vec{x}|$ denotes the modulus of \vec{x} . Then we take the conjugate transpose of both sides

$$\begin{aligned} (\vec{x}^\dagger \mathbf{A} \vec{x})^\dagger &= (\lambda |\vec{x}|^2)^\dagger \\ \vec{x}^\dagger \mathbf{A}^\dagger (\vec{x}^\dagger)^\dagger &= (|\vec{x}|^2)^\dagger \lambda^\dagger \end{aligned} \quad (14)$$

Since \mathbf{A} is hermitian, then $\mathbf{A}^\dagger = \mathbf{A}$. Also, $(|\vec{x}|^2)^\dagger = |\vec{x}|^2$ because the square modulus of any complex number is a real number. So,

$$\begin{aligned} \vec{x}^\dagger \mathbf{A}^\dagger (\vec{x}^\dagger)^\dagger &= (|\vec{x}|^2)^\dagger \lambda^\dagger \\ \vec{x}^\dagger \mathbf{A} \vec{x} &= |\vec{x}|^2 \lambda^\dagger \\ \vec{x}^\dagger \lambda \vec{x} &= |\vec{x}|^2 \lambda^\dagger \\ \lambda |\vec{x}|^2 &= \lambda^\dagger |\vec{x}|^2 \\ \lambda &= \lambda^\dagger \\ \lambda &= \lambda^* \end{aligned} \quad (15)$$

The last line follows from the fact that the transpose of any scalar is the scalar itself.

Another important property of hermitian matrices is that each of the eigenvectors are orthogonal. To prove this, consider two distinct eigenvectors and eigenvalues of a hermitian matrix \mathbf{A} such that

$$\mathbf{A} \vec{x}_1 = \lambda_1 \vec{x}_1 \quad \mathbf{A} \vec{x}_2 = \lambda_2 \vec{x}_2 \quad (16)$$

If we multiply the first equation by \vec{x}_2^\dagger and take the conjugate transpose of both sides then

$$\begin{aligned} \vec{x}_2^\dagger \mathbf{A} \vec{x}_1 &= \vec{x}_2^\dagger \lambda_1 \vec{x}_1 \\ (\vec{x}_2^\dagger \mathbf{A} \vec{x}_1)^\dagger &= (\vec{x}_2^\dagger \lambda_1 \vec{x}_1)^\dagger \\ \vec{x}_1^\dagger \mathbf{A}^\dagger \vec{x}_2 &= \vec{x}_1^\dagger \lambda_1^\dagger \vec{x}_2 \\ \vec{x}_1^\dagger \mathbf{A} \vec{x}_2 &= \vec{x}_1^\dagger \lambda_1 \vec{x}_2 \\ \vec{x}_1^\dagger \lambda_2 \vec{x}_2 &= \vec{x}_1^\dagger \lambda_1 \vec{x}_2 \\ \lambda_2 \vec{x}_1^\dagger \vec{x}_2 &= \lambda_1 \vec{x}_1^\dagger \vec{x}_2 \end{aligned} \quad (17)$$

which is only possible if the eigenvectors are orthogonal, i.e. $\vec{x}_1^\dagger \vec{x}_2 = 0$ because $\lambda_1 \neq \lambda_2$.

If we refer back to the eigendecomposition of a hermitian matrix \mathbf{A} , we can say then that $\Lambda^\dagger = \Lambda$ because the eigenvalue matrix is diagonal and each of the eigenvalues are real. We can also say that \mathbf{X} is unitary, i.e. $\mathbf{X}^{-1} = \mathbf{X}^\dagger$, because \mathbf{X} is made up of the eigenvectors of \mathbf{A} , which are all orthogonal.

The fact that the eigenvectors of a hermitian matrix are orthogonal allows us to write the eigenvalue problem as equation (2), which is the form that we are all used to seeing. For any general matrix \mathbf{A} , we can write the generalized eigenvalue problem as

$$(\mathbf{A} - \lambda \mathbf{S})\vec{x} = \vec{0} \tag{18}$$

where \mathbf{S} is the overlap matrix whose off-diagonal elements are non-zero.