We start with the Schrödinger equation in the differential form:

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

If we substitute $\Psi = \sum_k a_k |\phi_k\rangle$, i.e.

$$H\left(\sum_k a_k|\phi_k\rangle\right) = i\hbar \sum_k \dot{a}_k |\phi_k\rangle$$

(note that ϕ_k does not depend on time)

Now we multiply by $\langle\phi_m|$ and get

$$\sum_k a_k \underbrace{\langle\phi_m|H|\phi_k\rangle}_{H_{mk}} = i\hbar \sum_k \dot{a}_k \underbrace{\langle\phi_m|\phi_k\rangle}_{S_{mk}}$$

or in the matrix form

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = i\hbar \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} \dot{a}_1 \\ \dot{a}_2 \end{pmatrix}.$$

i.e.

$$H\vec{a} = i\hbar S\dot{\vec{a}}$$