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Consider the case where $n = 1$. Even without any assumptions, a 1×1 matrix always has $\begin{bmatrix}1\end{bmatrix}$ as its eigenvector. Hence the statement holds.

Now consider the case where $n = 2$. Assume that A and B are Hermitian matrices such that $AB - BA$ is singular. Then $AB - BA$ has a 0 as one of its eigenvalues. However, note that

$$\mathrm{tr}(AB - BA) = \mathrm{tr}(AB - BA) = \mathrm{tr}(AB) - \mathrm{tr}(BA) = 0$$

where $\mathrm{tr}(AB - BA)$ should be the sum of the two eigenvalues of $AB - BA$. Therefore the only eigenvalue of $AB - BA$ is 0, with algebraic multiplicity 2. It follows that $AB - BA = O$, that is, $AB = BA$ always. Now let λ be a eigenvalue of A, and let W_λ be the eigenspace of A corresponding to λ. Then for any $v_\lambda \in W_\lambda$, we have

$$A(Bv_\lambda) = B(Av_\lambda) = B(\lambda v_\lambda) = \lambda(Bv_\lambda)$$

so W_λ is a B-invariant subspace of $\mathbb{C}^2$. Thus considering $B|_{W_\lambda} : W_\lambda \to W_\lambda$, there must exist an eigenvector $w \in W_\lambda$ of $B|_{W_\lambda}$, which also becomes an eigenvector of B. Here, from $w \in W_\lambda$, w is also an eigenvector of A with eigenvalue λ. Therefore A and B have a common eigenvector, namely w. Hence the statement holds.

On the other hand, suppose $n \geqslant 3$. Let A and B to be

$$A = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 2 & 0 & \cdots & 0 \\ 0 & 0 & 3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & n \end{bmatrix}, \quad B = \begin{bmatrix} 1 & 1 & 1 & \cdots & 1 \\ 1 & 1 & 0 & \cdots & 0 \\ 1 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & 0 & 0 & \cdots & 1 \end{bmatrix}$$

then by simple calculation we have

$$AB - BA = \begin{bmatrix} 0 & -1 & -2 & \cdots & -(n-1) \\ 1 & 0 & 0 & \cdots & 0 \\ 2 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ n-1 & 0 & 0 & \cdots & 0 \end{bmatrix}$$

so $AB - BA$ is clearly singular. However the eigenvectors of A are the standard basis vectors $\{e_1, e_2, \cdots, e_n\}$ while for any $i = 1, 2, \cdots, n$ we can see by some simple calculation that Be_i is never a multiple of e_i. This shows that an eigenvector of A cannot also be an eigenvector of B, that is, A and B cannot have a common eigenvector.

Therefore the only positive integers such that the statement

$$AB - BA \text{ singular} \Rightarrow \ A \text{ and } B \text{ have a common eigenvector}$$

for $n \times n$ Hermitian matrices A and B holds are 1 and 2.