We prove that the single-particle wavefunctions in the Slater determinant must be linearly independent.

Let $\{\phi_i(\vec{x})\}_{i=1}^{N}$ be single-particle wavefunctions. Then, the Slater determinant is given by

$$\Psi(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \vdots & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix}$$

Suppose that $\{\phi_i(\vec{x})\}$ are linearly dependent. Then, there exists coefficients $a_1, \dots, a_N$, not all zero, such that

$$a_1 \phi_1(\vec{x}) + \cdots + a_N \phi_N(\vec{x}) \neq 0.$$

Let a_j be the first such non-zero coefficient. Then,

$$\phi_j(\vec{x}) = -\frac{a_1}{a_j}\phi_1(\vec{x}) - \cdots - \frac{a_{j-1}}{a_j}\phi_{j-1}(\vec{x}) -$$

$$-\frac{a_{j+1}}{a_j}\phi_{j+1}(\vec{x}) - \cdots - \frac{a_N}{a_j}\phi_N(\vec{x}).$$

For compact shorthand, let $b_i \equiv \frac{-a_i}{a_j}$, $b_j = 0$. Then,

$$\phi_j(\vec{x}) = \sum_i b_i \phi_i(\vec{x}).$$

Substituting into our Slater determinant, we have

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & \sum_i b_i \phi_i(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \vdots & & \ddots & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & \sum_i b_i \phi_i(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix}$$

Next, we use the following lemma.

Lemma:

The determinant of a matrix is unchanged when a scalar multiple of one column is added to another.

Proof

We consider a matrix $A = (\vec{a}_1 \cdots \vec{a}_j \cdots \vec{a}_k \cdots \vec{a}_N)$.

The determinant is multilinear in its columns, meaning

$$|\vec{a}_1 \cdots \vec{a}_j + \lambda \vec{a}_k \cdots \vec{a}_k \cdots \vec{a}_N| = |\vec{a}_1 \cdots \vec{a}_j \cdots \vec{a}_k \cdots \vec{a}_N| +$$

$$\lambda |\vec{a}_1 \cdots \vec{a}_k \cdots \vec{a}_k \cdots \vec{a}_N| = |\vec{a}_1 \cdots \vec{a}_j \cdots \vec{a}_k \cdots \vec{a}_N|.$$

The final equality follows from the fact that the determinant is also antisymmetric upon interchange of any two columns, implying that

$$\left|\vec{a}_1 \cdots \vec{a}_k \cdots \vec{a}_k \cdots \vec{a}_N\right| = -\left|\vec{a}_1 \cdots \vec{a}_k \cdots \vec{a}_k \cdots \vec{a}_N\right| = 0 \qquad \boxed{}$$

From this lemma, it follows that

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & \sum_i b_i \phi_i(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \vdots & \ddots & & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & \sum_i b_i \phi_i(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix} =$$

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & \sum_i b_i \phi_i(\vec{x}_1) - \sum_i b_i \phi_i(\vec{x}_1) & \cdots & \phi_N(\vec{x}_1) \\ \vdots & \ddots & & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & \sum_i b_i \phi_i(\vec{x}_N) - \sum_i b_i \phi_i(\vec{x}_N) & \cdots & \phi_N(\vec{x}_N) \end{vmatrix} =$$

$$\frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(\vec{x}_1) & \cdots & 0 & \cdots & \phi_N(\vec{x}_1) \\ \vdots & & \vdots & & \vdots \\ \phi_1(\vec{x}_N) & \cdots & 0 & \cdots & \phi_N(\vec{x}_N) \end{vmatrix} = 0,$$

where the final equality comes from the cofactor expansion of the determinant, summing down the j^{th} column.

Therefore, we have shown that if the single-particle wavefunctions are linearly dependent, $\Psi = 0$. Clearly, this is not normalizable, and hence not a physical state, and we conclude that the single-particle wavefunctions must be linearly independent.

$\boxtimes$

(As a simple corollary, the linear independence of the $\phi_i(\vec{x})$ implies that we can choose them to be orthonormal using the Gram-Schmidt process.)