Lecture 15: Slater Determinants

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Hartree Product

- Configuration State Functions (CSF): (Simple) symmetry adapted basis state for N-electron systems
- Early attempt: Hartree product

$$\Phi_H(x_1, \ldots, x_N) = \phi_1(x_1) \cdots \phi_N(x_N),$$

  where the orbitals $\{\phi_p\}$ are orthonormal
- Resulting N electron probability amplitude is simple product of (statistically independent) single-electron orbital probabilities,

$$|\Phi_H(x_1, \ldots, x_N)|^2 = |\phi_1(x_1)|^2 \cdots |\phi_N(x_N)|^2.$$

- Unsuitable because electrons are indistinguishable, violates spin-statistics theorem

Determinants

$f : \mathbf{A} \in \mathbf{C}^{n\times n} \to f(\mathbf{A}) \in \mathbf{C}$ is called *determinant* of $\mathbf{A} = (\mathbf{a}_1 \cdots \mathbf{a}_n)$, i.e., $f(\mathbf{A}) = \det(\mathbf{A}) = |\mathbf{A}|$, if and only if

(i) f is linear in each column, i.e.,

$$f\begin{pmatrix}\cdots & c\mathbf{a}_k + \mathbf{b} & \cdots\end{pmatrix} = cf\begin{pmatrix}\cdots & \mathbf{a}_k & \cdots\end{pmatrix} + f\begin{pmatrix}\cdots & \mathbf{b} & \cdots\end{pmatrix}$$

$\forall k, 1 \leq k \leq n, c \in \mathbf{C}, \mathbf{b} \in \mathbf{C}^n$.

(ii) f is antisymmetric under column exchange, i.e.,

$$f\begin{pmatrix}\cdots & \mathbf{a}_k & \cdots a_l & \cdots\end{pmatrix} = -f\begin{pmatrix}\cdots & \mathbf{a}_l & \cdots & \mathbf{a}_k & \cdots\end{pmatrix}$$

(iii) $f(\mathbf{1}) = 1$

Leibniz Formula

- Alternative definition using $S(N)$:

$$f(\mathbf{A}) = n!\,\hat{\mathcal{A}}\,a_{11}\cdots a_{nn},$$

- Projection operator on the totally antisymmetric IRREP of $S(N)$ ("antisymmetrizer"):

$$\hat{\mathcal{A}} = \frac{1}{n!}\sum_{P\in \mathsf{S}_n} \mathrm{sgn}(P)\hat{P}$$

- $\hat{P}$: permutations of n columns, $\mathrm{sgn}(P)$: Antisymmetric IRREP characters, $+1$ for even and -1 for odd permutations

Slater Determinant

- Antisymmetrized (and renormalized) Hartree product:

$$\Phi(x_1, \ldots, x_N) = \sqrt{N!}\,\hat{\mathcal{A}}\,\Phi_H = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \ldots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \ldots & \phi_2(x_N) \\ \ldots & \ldots & \vdots & \ldots \\ \phi_N(x_1) & \phi_N(x_2) & \ldots & \phi_N(x_N) \end{vmatrix}$$

- Satisfies antisymmetry requirement
- Can be CSF for closed-shell singlet and high-spin open shell states
- The simplest admissible many-electron wavefunction
- Describes N “noninteracting” electrons subject to Pauli principle: Only “Fermi”, no “Coulomb” correlation

Example: Two Electrons in Two Orbitals

- Slater determinant:

$$\Phi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) \\ \phi_2(x_1) & \phi_2(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1) \right]$$

- Triplet ($M_s = 1$) case: Both orbitals have α spin, but different spatial parts:

$$\phi_1(x_1) = \phi_1(\mathbf{r}_1)\delta_{\sigma_1\alpha}, \quad \phi_2(x_2) = \phi_2(\mathbf{r}_2)\delta_{\sigma_2\alpha}$$

- Triplet Slater determinant:

$$\Phi_t(x_1, x_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) \right] \delta_{\sigma_1\alpha}\delta_{\sigma_2\alpha}$$

  Separates into antisymmetric spacial and symmetric spin parts
- The two electrons must occupy spatially different orbitals
- Spatial triplet wavefunction has nodes for $\mathbf{r}_1 = \mathbf{r}_2$ ("Fermi hole")
- This is a CSF with $\hat{S}^2$ eigenvalue 1

Example: Two Electrons in Two Orbitals

- Closed-shell singlet ($M_s = 0$) case: Both orbitals have identical spatial parts:

$$\phi_1(x_1) = \phi(\mathbf{r}_1)\delta_{\sigma_1\alpha}, \quad \phi_2(x_2) = \phi(\mathbf{r}_2)\delta_{\sigma_2\beta}$$

- Closed-shell singlet Slater determinant:

$$\Phi_s(x_1, x_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$

- No Fermi hole
- This is a CSF with $\hat{S}^2$ eigenvalue 0

Example: Two Electrons in Two Orbitals

- Closed-shell singlet ($M_s = 0$) case: Both orbitals have identical spatial parts:

$$\phi_1(x_1) = \phi(\mathbf{r}_1)\delta_{\sigma_1\alpha}, \quad \phi_2(x_2) = \phi(\mathbf{r}_2)\delta_{\sigma_2\beta}$$

- Closed-shell singlet Slater determinant:

$$\Phi_s(x_1, x_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\frac{1}{\sqrt{2}}\left[\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$

- No Fermi hole
- This is a CSF with $\hat{S}^2$ eigenvalue 0

Example: Two Electrons in Two Orbitals

- Open-shell singlet ($M_s = 0$) case: Both orbitals have different spatial parts:

$$\phi_1(x_1) = \phi_1(\mathbf{r}_1)\delta_{\sigma_1\alpha}, \quad \phi_2(x_2) = \phi_2(\mathbf{r}_2)\delta_{\sigma_2\beta}$$

- Open-shell singlet Slater determinant (one of two):

$$\Phi_{\text{oss}}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$

- This is *not* a CSF, because it is not an $\hat{S}^2$ eigenstate!
- OSS singlet CSF requires linear combination of (at least) 2 determinants:

$$\Psi_{\text{oss}}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\right] \times \frac{1}{\sqrt{2}}\left[\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$

Example: Two Electrons in Two Orbitals

- Triplet ($M_s = 0$) case: Both orbitals have different spatial parts:

$$\phi_1(x_1) = \phi_1(\mathbf{r}_1)\delta_{\sigma_1\alpha}, \quad \phi_2(x_2) = \phi_2(\mathbf{r}_2)\delta_{\sigma_2\beta}$$

- Open-shell singlet Slater determinant (one of two):

$$\Phi_{\text{oss}}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} + \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$

- This is *not* a CSF, because it is not an $\hat{S}^2$ eigenstate!
- $M_S = 0$ triplet CSF requires linear combination of (at least) 2 determinants:

$$\Psi_{\text{t},0}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\right] \times \frac{1}{\sqrt{2}}\left[\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} + \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right]$$