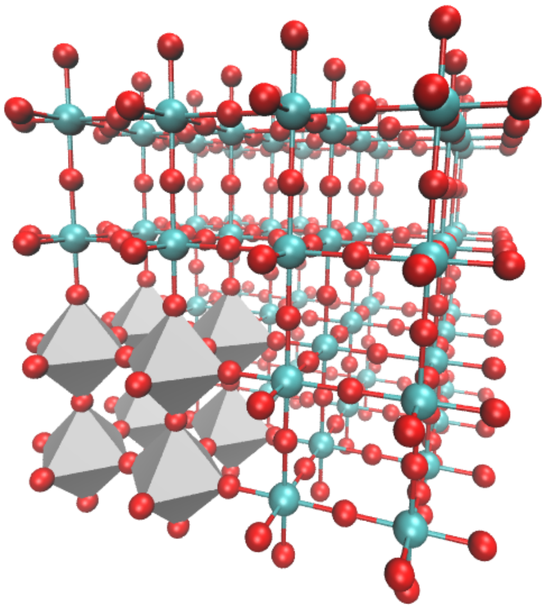
Slater Determinant Energy



Prof. Lee M. Thompson

Slater Determinants

Electronic energy of Slater determinant

- Represent wavefunction as a Slater determinant and compute expectation value

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x)\hat{x}\Psi(x)dx}{\int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx} \rightarrow E = \frac{\langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle}$$

- Assuming we know the form of the molecular orbitals (which generally we don't)

- Useful relation for the upcoming derivation:

$$\int\int f(x)g(y)dxdy = \int f(x)dx \int g(y)dy$$

Slater Determinants

Overlap of Slater determinants

- $\langle \Psi_{SD} | \Psi_{SD} \rangle$ is the overlap of two Slater determinants (inner product)

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = \left(\left\langle \prod_{i=1}^{N_{\text{elec}}} \chi_i \right| \hat{A}^{\dagger} \sqrt{N_{\text{elec}}!} \right) \left(\sqrt{N_{\text{elec}}!} \hat{A} \left| \prod_{j=1}^{N_{\text{elec}}} \chi_j \right\rangle \right)$$

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = N_{\text{elec}}! \left\langle \prod_{i=1}^{N_{\text{elec}}} \chi_i \middle| \hat{A} \prod_{j=1}^{N_{\text{elec}}} \chi_j \right\rangle = \sum_{\pi \in S_N} \epsilon_{\pi} \left\langle \prod_{i=1}^{N_{\text{elec}}} \chi_i \middle| \hat{\pi} \prod_{j=1}^{N_{\text{elec}}} \chi_j \right\rangle$$

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = \langle \chi_1 \chi_2 \ldots \chi_{N_{\text{elec}}} | \chi_1 \chi_2 \ldots \chi_{N_{\text{elec}}} \rangle + \epsilon \langle \chi_1 \chi_2 \ldots \chi_{N_{\text{elec}}} | \chi_2 \chi_1 \ldots \chi_{N_{\text{elec}}} \rangle + \ldots$$

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = \langle \chi_1 | \chi_1 \rangle \langle \chi_2 | \chi_2 \rangle \ldots \langle \chi_{N_{\text{elec}}} | \chi_{N_{\text{elec}}} \rangle + \epsilon_{12} \langle \chi_1 | \chi_2 \rangle \langle \chi_2 | \chi_1 \rangle \ldots \langle \chi_{N_{\text{elec}}} | \chi_{N_{\text{elec}}} \rangle + \ldots$$

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = \delta_{11} \delta_{22} \ldots \delta_{N_{\text{elec}} N_{\text{elec}}} + \epsilon_{12} \delta_{12} \delta_{21} \ldots \delta_{N_{\text{elec}} N_{\text{elec}}} + \ldots$$

$$\langle \Psi_{SD} | \Psi_{SD} \rangle = 1 + 0 + \ldots = 1$$

Only one term survives **if** ket and bra equal

Slater Determinants

Hamiltonian matrix element of Slater determinants

$$E = \frac{\langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle} = \langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle$$

$$\hat{H}_{\text{elec}} = -\sum_{i=1}^{N_{\text{elec}}} \frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_{I}^{N_{\text{atoms}}} \sum_{i=1}^{N_{\text{elec}}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=i+1}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H}_{\text{elec}} = \sum_{i=1}^{N_{\text{elec}}} \hat{h}_i + \sum_{i=1}^{N_{\text{elec}}} \sum_{j=1}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$E_{\text{elec}} = \left\langle \Psi_{SD} \middle| \sum_{i} \hat{h}_i \middle| \Psi_{SD} \right\rangle + \left\langle \Psi_{SD} \middle| \sum_{i<j} \frac{1}{\mathbf{r}_{ij}} \middle| \Psi_{SD} \right\rangle$$

$$E_{\text{elec}} = E_{\text{k}} + E_{\text{ne}} + E_{\text{ee}} = E_0 + E_1$$

Slater Determinants

1) One-electron Energy

$$E_0 = \left\langle \Psi_{SD} \middle| \sum_i \hat{h}_i \middle| \Psi_{SD} \right\rangle = \sum_i \left(\left\langle \prod_k \chi_k \middle| \hat{A}^\dagger \sqrt{N_{\text{elec}}!} \right) \hat{h}_i \left(\sqrt{N_{\text{elec}}!} \middle| \hat{A} \prod_j \chi_j \right\rangle \right)$$

$$E_0 = \sum_i N_{\text{elec}}! \left\langle \prod_k \chi_k \middle| \hat{h}_i \middle| \hat{A} \prod_j \chi_j \right\rangle = \sum_i \left\langle \prod_k \chi_k \middle| \hat{h}_i \middle| \sum_{\pi \in S_N} \epsilon_\pi \hat{\pi} \prod_j \chi_j \right\rangle$$

$$E_0 = \sum_i \sum_{\pi \in S_N} \epsilon_\pi \left\langle \prod_k \chi_k \middle| \hat{h}_i \middle| \hat{\pi} \prod_j \chi_j \right\rangle$$

$$E_0 = \langle \chi_1 \chi_2 \ldots | \hat{h}_1 | \chi_1 \chi_2 \ldots \rangle - \langle \chi_1 \chi_2 \ldots | \hat{h}_1 | \chi_2 \chi_1 \ldots \rangle + \ldots$$

$$E_0 = \langle \chi_1 | \hat{h}_1 | \chi_1 \rangle \langle \chi_2 | \chi_2 \rangle \ldots - \langle \chi_1 | \hat{h}_1 | \chi_2 \rangle \langle \chi_2 | \chi_1 \rangle \ldots + \ldots$$

$$E_0 = \langle \chi_1 | \hat{h}_1 | \chi_1 \rangle + \langle \chi_2 | \hat{h}_2 | \chi_2 \rangle + \ldots = \sum_i \langle \chi_i | \hat{h}_i | \chi_i \rangle$$

Slater Determinants

2) Two-electron Energy

$$E_1 = \left\langle \Psi_{SD} \middle| \sum_{i<j} r_{ij}^{-1} \middle| \Psi_{SD} \right\rangle = \sum_{i<j} \left(\left(\left\langle \prod_k \chi_k \middle| \hat{A}^\dagger \sqrt{N_{\text{elec}}!} \right) r_{ij}^{-1} \left(\sqrt{N_{\text{elec}}!} \middle| \hat{A} \prod_l \chi_l \right\rangle \right) \right)$$

$$E_1 = \sum_{i<j} N_{\text{elec}}! \left\langle \prod_k \chi_k \middle| r_{ij}^{-1} \middle| \hat{A} \prod_l \chi_l \right\rangle = \sum_{i<j} \left\langle \prod_k \chi_k \middle| r_{ij}^{-1} \middle| \sum_{\pi \in S_N} \epsilon_\pi \hat{\pi} \prod_l \chi_l \right\rangle$$

$$E_1 = \sum_{i<j} \sum_{\pi \in S_N} \epsilon_\pi \left\langle \prod_k \chi_k \middle| r_{ij}^{-1} \middle| \hat{\pi} \prod_l \chi_l \right\rangle$$

$$E_1 = \langle \chi_1 \chi_2 \ldots | r_{12}^{-1} | \chi_1 \chi_2 \ldots \rangle - \langle \chi_1 \chi_2 \ldots | r_{12}^{-1} | \chi_2 \chi_1 \ldots \rangle + \ldots$$

$$E_1 = \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_1 \chi_2 \rangle \langle \chi_3 | \chi_3 \rangle \ldots - \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_2 \chi_1 \rangle \langle \chi_3 | \chi_3 \rangle \ldots + \ldots$$

$$E_1 = \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | r_{12}^{-1} | \chi_2 \chi_1 \rangle + \ldots$$

$$E_1 = \sum_{i<j} \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_j \chi_i \rangle$$

Coulomb integral

Exchange integral

Slater Determinants

2) Two-electron Energy

$$E_1 = \sum_{i<j} \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_j \chi_i \rangle$$

$$= \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{ij}^{-1} | \chi_j \chi_i \rangle$$

$$= \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j | r_{ij}^{-1} (1 - \hat{\pi}_{12}) | \chi_i \chi_j \rangle$$

Electronic energy of Slater determinant

$$E = \langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle = \sum_{i} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j | r_{ij}^{-1} (1 - \hat{\pi}_{12}) | \chi_i \chi_j \rangle$$

Spin Independent Eqns.

Integrate out spin

$$E = \langle \Psi_{SD} | \hat{H} | \Psi_{SD} \rangle = \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j | r_{ij}^{-1} (1 - \hat{\pi}_{12}) | \chi_i \chi_j \rangle$$

$$\int\int f(x) g(y) dx dy = \int f(x) dx \int g(y) dy$$

$$|\chi_i(\mathbf{x})\rangle = |\psi_i(\mathbf{r}) \sigma_i(\omega)\rangle$$
$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$
$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$

1) One-electron integral

$$\begin{aligned}
\langle \chi_1(\mathbf{x}_1) | \hat{h}_1(\mathbf{r}_1) | \chi_1(\mathbf{x}_1) \rangle &= \langle \psi_1(\mathbf{r}_1) \sigma_1(\omega_1) | \hat{h}(\mathbf{r}_1) | \psi_1(\mathbf{r}_1) \sigma_1(\omega_1) \rangle \\
&= \langle \psi_1(\mathbf{r}_1) | \hat{h}_1(\mathbf{r}_1) | \psi_1(\mathbf{r}_1) \rangle \langle \sigma_1(\omega_1) | \sigma_1(\omega_1) \rangle \\
&= \langle \psi_1(\mathbf{r}_1) | \hat{h}_1(\mathbf{r}_1) | \psi_1(\mathbf{r}_1) \rangle
\end{aligned}$$

Spin Independent Eqns.

2) Coulomb integral

$$\left\langle \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1,\mathbf{r}_2) \middle| \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \right\rangle =$$

$$\left\langle \psi_1(\mathbf{r}_1)\sigma_1(\omega_1)\psi_2(\mathbf{r}_2)\sigma_2(\omega_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1,\mathbf{r}_2) \middle| \psi_1(\mathbf{r}_1)\sigma_1(\omega_1)\psi_2(\mathbf{r}_2)\sigma_2(\omega_2) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1,\mathbf{r}_2) \middle| \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \right\rangle \left\langle \sigma_1(\omega_1)\sigma_2(\omega_2) \middle| \sigma_1(\omega_1)\sigma_2(\omega_2) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1,\mathbf{r}_2) \middle| \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \right\rangle \left\langle \sigma_1(\omega_1) \middle| \sigma_1(\omega_1) \right\rangle \left\langle \sigma_2(\omega_2) \middle| \sigma_2(\omega_2) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1,\mathbf{r}_2) \middle| \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \right\rangle$$

Spin Independent Eqns.

3) Exchange integral

$$\left\langle \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2)\hat{\pi}_{12} \middle| \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \right\rangle$$

Note the change of indices in ket functions

$$= \left\langle \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) \middle| \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\sigma_1(\omega_1)\psi_2(\mathbf{r}_2)\sigma_2(\omega_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) \middle| \psi_1(\mathbf{r}_2)\sigma_1(\omega_2)\psi_2(\mathbf{r}_1)\sigma_2(\omega_1) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) \middle| \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \right\rangle \left\langle \sigma_1(\omega_1)\sigma_2(\omega_2) \middle| \sigma_1(\omega_2)\sigma_2(\omega_1) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) \middle| \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \right\rangle \left\langle \sigma_1(\omega_1) \middle| \sigma_2(\omega_1) \right\rangle \left\langle \sigma_2(\omega_2) \middle| \sigma_1(\omega_2) \right\rangle$$

$$= \left\langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \middle| \frac{1}{r_{12}}(\mathbf{r}_1, \mathbf{r}_2) \middle| \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1) \right\rangle \delta_{\sigma_1\sigma_2}\delta_{\sigma_2\sigma_1}$$

Exchange is zero between electrons of different spins!

Integral Notation

Physicist's notation

$$\langle i|\hat{h}|j\rangle = \int \chi_i^*(\mathbf{x}_1)\hat{h}\chi_j(\mathbf{x}_1)d\mathbf{x}_1$$

$$\langle ij|r_{ij}^{-1}|kl\rangle = \langle ij|kl\rangle = \int\int \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)r_{12}^{-1}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)d\mathbf{x}_1\mathbf{x}_2$$

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

Core: $h_{ii} = \langle i|\hat{h}|i\rangle$

Coulomb: $J_{ij} = \langle ij|ij\rangle$

Exchange: $K_{ij} = \langle ij|ji\rangle$

Integral Notation

Chemist's notation

- Spin orbitals

$$[i|\hat{h}|j] = \int \chi_i^*(\mathbf{x}_1)\hat{h}\chi_j(\mathbf{x}_1)d\mathbf{x}_1$$

$$[ij|kl] = \int\int \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)r_{12}^{-1}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2)d\mathbf{x}_1\mathbf{x}_2 = \langle ik|jl\rangle$$

- Spatial orbitals

$$(i|\hat{h}|j) = \int \psi_i^*(\mathbf{r}_1)\hat{h}\psi_j(\mathbf{r}_1)d\mathbf{r}_1$$

$$(ij|kl) = \int\int \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)r_{12}^{-1}\psi_k^*(\mathbf{r}_2)\psi_l(\mathbf{r}_2)d\mathbf{r}_1\mathbf{r}_2$$

$$\langle ij||kl\rangle = (ij|kl) - (il|kj)$$

Core: $h_{ii} = (i|\hat{h}|i)$

Coulomb: $J_{ij} = (ii|jj)$

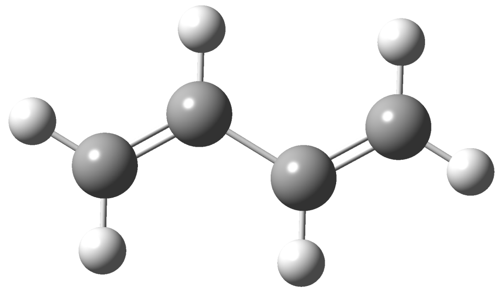
Exchange: $K_{ij} = (ij|ji)$

Physical Interpretation

Interpretation of terms in SD energy

- In the chemists spin orbital notation the energy is

$$E_{SD} = \sum_{i}^{N_{\text{elec}}} h_{ii} + \sum_{i>j}^{N_{\text{elec}}} [ii\,|\,jj] - [ij\,|\,ji]$$



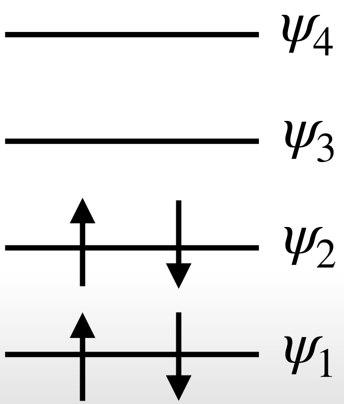
- Not all these terms survive spin integration

$$E_{SD} = h_{11} + h_{\bar{1}\bar{1}} + h_{22} + h_{\bar{2}\bar{2}} + J_{1\bar{1}} + J_{12} + J_{1\bar{2}} + J_{\bar{1}2} + J_{\bar{1}\bar{2}} + J_{2\bar{2}} - K_{12} - K_{\bar{1}\bar{2}}$$

- If spatial parts of each MO are equal for α and β and $N_\alpha = N_\beta$ - **Restricted** wavefunction

$$E_{SD} = 2(h_{11} + h_{22}) + J_{11} + 4J_{12} + J_{22} - 2K_{12}$$

$$E_{SD} = 2\sum_{i}^{N_{\text{elec}}/2} h_{ii} + \sum_{ij}^{N_{\text{elec}}/2} 2J_{ij} - K_{ij}$$

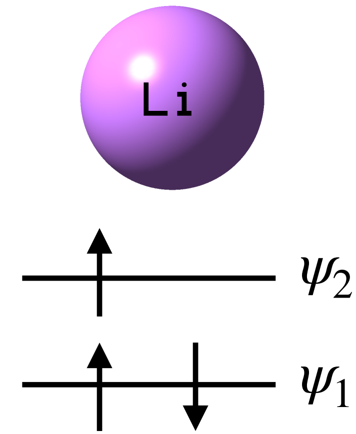


Physical Interpretation

Interpretation of terms in SD energy

- If $N_\alpha \neq N_\beta$ but spatial parts of each MO are equal for α and β - **Restricted open-shell** wavefunction

$$E_{SD} = 2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$$



- If spatial parts of any MO are different for α and β (possibly $N_\alpha \neq N_\beta$) - **Unrestricted** wavefunction

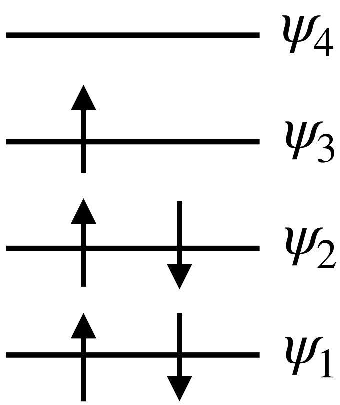
$$E_{SD} = h_{11} + h_{\bar{1}\bar{1}} + h_{22} + J_{1\bar{1}} + J_{12} + J_{\bar{1}2} - K_{12}$$

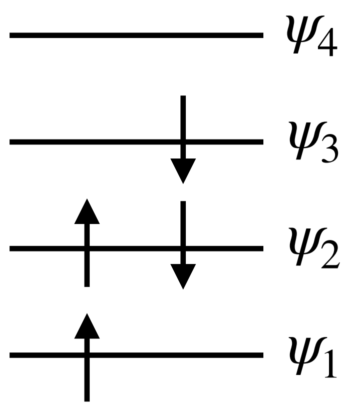
- Origin of Hund's rules (predict high spin)

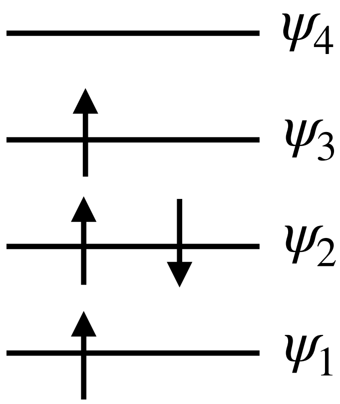
$$E_{SD} = h_{11} + h_{22} + J_{12} - K_{12}$$

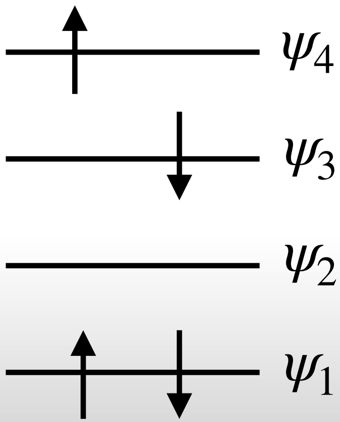
$$E_{SD} = h_{11} + h_{\bar{2}\bar{2}} + J_{1\bar{2}}$$

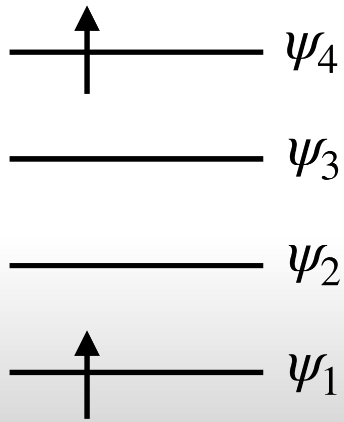
Physical Interpretation

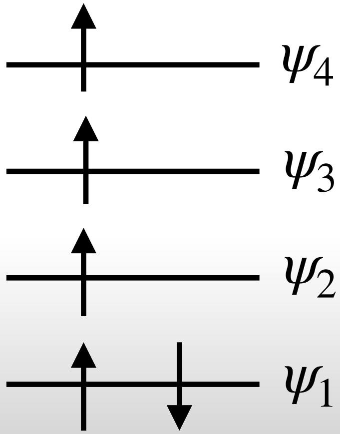












Summary

- Need to build in wavefunction antisymmetry manually - Slater Determinant
- Can derive energy of Slater determinant wavefunction given set of known spatial orbitals
- **The problem is, we still don’t know the actual form of the orbitals**